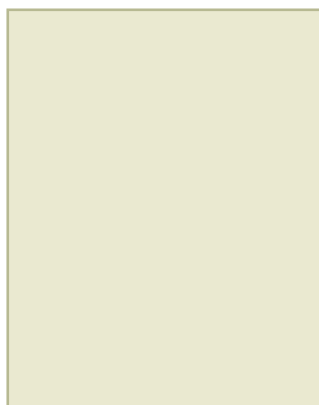


# Kinetic Study of Wheat straw acid hydrolysis using Phosphoric acid to Produce Furfural

**Abstract:** *Acid hydrolysis of cheap and renewable lignocellulosic biomass can produce a number of value added products, principally xylose, arabinose and finally their degradation product, furfural. Using biomass from agricultural residues to produce chemicals by different technologies, has many consequences such as elimination of waste, reduction of dependence on chemicals produced by petrochemical industry and production of value-added products. In this study, agricultural wastes, wheat straw was hydrolyzed using phosphoric acid at variable acid concentrations (1%, 2%) and reaction time (0-210 min) at 140°C. Kinetic models were developed to describe the variation of remaining quantity of xylan, arabinan in raw material, concentration of xylose, arabinose, furfural and acetic acid in liquid solution with time. Optimal conditions for maximum furfural concentration were an acid mass fraction of 2% at 140°C with reaction time 210 min. At these reaction conditions hydrolyzate yielded concentration of xylose, arabinose and furfural 9.5(g/L), 2.76 (g/L) and 3.94(g/L) respectively. It has been shown that similar to sulphuric and hydrochloric acids, phosphoric acid can also be used for hydrolysis of the wheat straw to produce value added chemicals..*

**Key Words:** *Wheat straw, Acid hydrolysis, Modeling, xylose, arabinose, furfural, acetic acid.*



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## Introduction

Wheat straw is an agricultural based renewable and lignocellulosic waste which is found abundantly worldwide. Apart from animal feeding, wheat straw is mostly used for production of pulp, paper and paper board in countries like many Asian countries India and China. Though it is a valuable raw material in Indian pulp and

paper mill, it can also be utilized in more economic way such as its utilization for production of value added chemicals similar to other lignocellulosic biomass wastes. Wheat straw is a complex polymer substance which mainly consists of structural components of high molecular weight (cellulose, hemicellulose and lignin) and non structural component of low molecular weight (extractives and inorganic compounds). Cellulose is a glucon polymer made-up of linear chains of 1, 4- $\beta$ -anhydroglucose units. Cellulose is a straight chain crystalline structure while hemicellulose is a branched chain and amorphous. Lignin is a complex polymer of phenolic type of compounds. Hemicellulose is easily hydrolysable compared to cellulose and Lignin due to its amorphous structure. On hydrolysis of hemicelluloses, mainly xylose and arabinose are obtained which on degradation give furfural. Therefore acid hydrolysis of wheat straw can be a good method to produce furfural [11]. Due to high content of acid hydrolysable components in wheat straw, it is also a better alternative for the production of biochemicals and fuels.

Furfural is used as a solvent for chemical refining and resin synthesis in the petrochemical and automobile industries [3, 8, 13]. In petrochemical industries, it is used as a selective solvent for separating saturated and unsaturated compounds [15]. The hydrolysis of wheat straw on industrial scale is environmentally as well as economically feasible process as it eliminates environmental waste and produces chemicals and biofuels from a very cheap raw material [17].

Different acids can be used for the dilute acid hydrolysis of the biomass for breaking down the structure of lignocellulosic and to produce xylose, arabinose, glucose, acetic acid and furfural. In dilute acid hydrolysis, mostly hydrolysis of the hemicellulosic fraction takes place. Hydrolysis of cellulosic fraction takes place only up to very small extent. Acid catalyzed hydrolysis mainly uses sulphuric acid [16], hydrochloric acid [4,3], nitric acid [12], acetic acid [1] or hydrofluoric acid [7]. Previous studies shows that sulphuric acid is the most used catalyst in hydrolysis process of lignocellulosic waste materials.

Hydrogen ions released by acids break the heterocyclic ether bonds between the sugar monomers in the polymeric chains formed by the hemicellulose and cellulose. On hydrolysis of hemicellulose and cellulose, monomeric sugars such as xylose, arabinose, glucose and acetic acid produce. In same reaction conditions, monomers dehydrate to form furfural and HMF (5-hydroxymethyl-2-furaldehyde). Acetic acid produces on hydrolysis of acetyl groups. During dilute acid hydrolysis, hydrolysis of cellulose takes place to very less extent due to its crystalline structure. After dilute acid hydrolysis of biomass, the remaining solid residue contains mostly cellulose and lignin. This solid residue can be further utilized for production of bioethanol by fermentation of this residue. Some studies exist in literature dealing with dilute acid hydrolysis of wheat straw [6, 12]. Sulphuric acid was used for prehydrolysis of wheat straw in these studies. In some literature studies [16], combined severity factor including reaction time, reaction temperature and acid concentration was used to analyze the extent of xylan hydrolysis. It was shown that at higher combined severity factor (31.6) and reaction conditions (acid concentration 2.5% (w/w), reaction temperature 170°C, reaction time 15 min.) almost 93% of initial hemicellulose could be removed. It has also shown that as combined severity factor increases solubilization of xylan also increases. In previous studies [2], hydrolyzates obtained after hydrolysis, neutralized and used for further fermentation to produce ethanol. Sulphuric acid was used for the hydrolysis of wheat straw at 130°C [6] and hydrolysis process was optimized to obtain maximum xylose solution with low concentration of degradation products.

In this study, phosphoric acid hydrolysis of wheat straw was carried out at 140°C. Reaction kinetic models were developed to explain concentration of different products varying with time and acid concentrations. The hydrolysis process was optimized for maximum furfural concentration with low pentose sugars.

## Materials and methods

### Raw material preparation

Wheat straw (*Triticum aestivum*) was collected from an agricultural farm in Saharanpur (India) at the geo-coordinates 29.96710N, 77.55100E after harvesting of wheat crop. Wheat straw was thoroughly washed, cleaned, air dried and milled in a dry defibrator grinding machine. It was grounded to pass a minimum (0.4 mm) 40 mesh screen. Homogenous samples were collected for further analysis. Seal packed samples were stored in cold condition to inhibit the growth of bacteria till it was utilized.

### Raw material characterization

Extractives and moisture content of wheat straw was analysed by ASTM procedures (ASTM D-1107/1106). Extractives were removed because these are not considered as part of biomass and it may interfere with further analysis. All experimental runs have been carried out by extractive free biomass. Acid soluble lignin, acetyl content, xylan, glucan, arabinan and ash were determined by different standard methods of ASTM. The composition of wheat straw used in this study is shown in Table 1.

### Hydrolysis of Raw Material

Hydrolysis of raw material was carried out in stainless steel cylindrical batch reactors each of 1 liter capacity. Batch reactors were kept in a rotary digester filled with water as heating media. Digester was furnished with two heating coils each of 1.2 kW capacity. Heating coils heated up water and due to heat up of water, reaction mixture inside reactors became heated. Rotational speed of digester was 2.5 rotations per minute. Due to this rotation, reaction mixture inside batch reactors is mixed properly and hydrolysis reaction took place. Whole reaction system was arranged with temperature and pressure gauges which showed temperature and pressure of reaction media and heating medium. At starting of each experiment, batch reactors were loaded with required amount of solid biomass, acid and water, sealed with stainless steel cap and put in rotary digester. Electrical heating of heating media and rotation of digester started. Within time of 15 min., temperature of heating media reached upto 140°C. When the temperature of heating media was 143°C, the temperature inside batch reactors was

Table 1- Chemical composition of wheat straw used in this study

Components	Method	Mass percentage(based on oven dry material)
Glucan	ASTM E 1758-01	37.80
Xylan	ASTM E 1758-01	19.58
Arabinan	ASTM E 1758-01	2.12
Moisture	ASTM D-1106	9.48
Lignin(Klason lignin+Acid soluble lignin)	ASTM E 1758-01	16.45
Ethanol-benzene solubility	ASTM D-1107	6.84
Acetyl	ASTM E 1758-01	2.15
Ash	ASTM D-1102-84	8.70

140°C. Negligible reaction has been assumed in time period of heating up of reaction mixture. After lapse of reaction time, lid of digester was opened and batch reactors were taken out from rotary digester for analysis of the reaction products. Digester was equipped with feedback temperature control mechanism such that it kept the reaction temperature fixed at its desired temperature. Experimental runs were performed at two different acid percentages (1% and 2% (w/w)), liquid and solid ratio at 1:10 and taking 10 gm. of raw material. Solid residues and hydrolyzed samples were analyzed during different time intervals between 0-210 min. Hydrolyzed samples were neutralized with calcium carbonate to maintain pH of samples about 7. Neutralized samples diluted with

distilled water 1:100(v/v), centrifuged to separate the water insoluble phenolic fractions and filtered with filter paper(0.2µm).Liquid samples were preserved in cold condition such that no degradation should take place during storage. Liquid hydrolyzed samples were analyzed by SHIMADZU SIL-20AHI HPLC for xylose,arabinose,furfural and acetic acid. HPLC conditions used in these analyses were such that: column C-18, detector-Photo Diode Array, elution mode-Isocratic , flow-1.0 ml/min, mobile phase- Sulphuric acid 0.005 M, sampling speed -15µL/sec., column temperature- 45°C, purge time-25.0min, injection volume-10 µL. Detection of compounds was based on comparing of retention time with retention time of compounds in standard pure solutions. Concentrations of different compounds were measured by peak area in chromatograms. All runs were carried out in duplicate and means of all these were used for analysis purpose. Non-linear regression analysis was carried out by commercial optimization routine using Newton's method (Solver, Microsoft excel 2007) using minimization of differences between experimental and calculated values.

## Results and discussion

### Composition of raw material and potential concentrations

The composition of wheat straw (based on oven dry material) used in this study is shown in Table 1. The composition of glucon, xylan, arabinan, acetyl and lignin were in the same range as for other lignocellulosic wastes, such as wheat straw [16], rice straw [9] and corn stover [14]. For example, the xylan mass percentage in wheat straw used in this study was 19.58 % (w/w). It shows very well similarity with other results such as 20.20% shown in other studies [6]. High quantity of xylan in this waste makes it suitable for production of monomeric sugars and its decomposition products.

Maximum potential concentration of each sugar was calculated using following equation described in literature [6]:

$$P_0 = I \frac{CX_{no} / 100}{LSR} \rho \dots\dots\dots(1)$$

Where  $P_0$  is the maximum (potential) concentration of each sugar assuming a total conversion of corresponding polysaccharides into sugar (g/L) without degradation,  $I$  is the ratio of the stoichiometric coefficients (  $I_{pentose} = 150/132$ ,  $I_{pentose} = 180/162$ ,  $I_{pentose} = 96/132$ ,  $I_{pentose} = 126/162$ ,  $I_{pentose} = 60/41$ ), is the % composition of raw material for the

polysaccharide(g of polysaccharide per 100 g of raw material, on dry basis), LSR is the liquid to solid ratio used while experiments(10 g/g) and  $\rho$  is the density of hydrolysates after hydrolysis reaction(1020 kg/m<sup>3</sup>). Applying Eq. (1), Maximum potential concentration of different compounds ( xylose 22.69 g/L; arabinose, 4.16 g/L; acetic acid , 5.9 g/L; Furfural ,16.10 g/L) was obtained. Acid hydrolysis of biomass with dilute acids affects mainly hemicellulosic part of biomass, cellulose and lignin almost remain unreacted.

### Compositional analysis of hydrolysates

Hydrolysates were collected after completion of hydrolysis reaction. Fig.2 shows the variation of concentration of xylan on time and acid percentage. Residual xylan decreases in substrate biomass as hydrolysis reaction proceeds. Xylose concentration was reached upto 21.9 g/L on biomass reaction with 2% acid after 75 min. Xylose concentration was increased upto a maximum limit and after that it was decreased with further increase of reaction time and acid concentration. Increase in acid concentration, favors the decomposition of xylose into furfural. During the acid hydrolysis of wheat straw, cellulose also hydrolyzes to glucose. Arabinose releases from hemicellulosic portion of biomass. Maximum concentration obtained of arabinose was 3.5 g/L at 120 min. of reaction time and 2% acid concentration. Reaching at it's maximum,concentration of arabinose



decreases during further reaction. Increase of acid concentration decreases the arabinose concentration which shows degradation of arabinose to furfural. Fig. 3 shows concentration variation of xylose on time and acid concentration. Furfural produces from degradation reactions of xylose and arabinose. Furfural concentration increased with the increase of acid concentration and reaction time. The highest concentration of furfural was obtained 3.94g/L with 2% H<sub>3</sub>PO<sub>4</sub> at 140°C for 210 min. Acetyl groups present in biomass was also hydrolysed during acid hydrolysis. Due to hydrolysis of acetyl groups, acetic acid was produced during reaction. In this study maximum obtained concentration of acetic acid was 2.82 g/L while reaction conditions were 2% H<sub>3</sub>PO<sub>4</sub> at 140°C for 210 min.

**Kinetic Models**

In different literatures, the hydrolysis of biomass is usually consists pseudo-homogenous first order irreversible series and parallel reactions. Development of actual mechanism for hydrolysis process of biomass is very difficult due to complexity of reactions which contains mass transfer and reaction steps. Due to all these complexities, it is common practice to use simplified model. The proposed kinetics in this study for formation of furfural is given by as following (Fig.1).

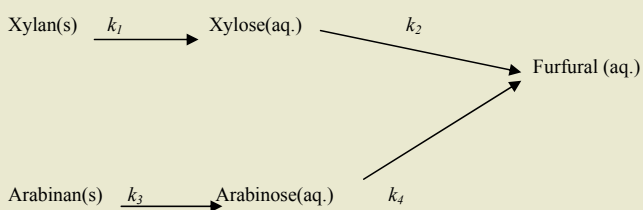


Fig. 1-Proposed kinetics for furfural formation from decomposition of pentosans

**Kinetic modeling of xylan concentration in solid:**

The differential Eq. (1) describing the quantity of xylan in raw material can be written as follows:

$$\frac{dA}{dt} = -k_1[A - (1 - \alpha)A_0] \dots\dots\dots(1)$$

Where A is the xylan concentration (g/L) in raw material at any time t, k<sub>1</sub> is the initial potential concentration (g/L) of xylan in raw material, k<sub>1</sub> is the rate constant for decomposition of solid xylan into xylose (min<sup>-1</sup>); α is the ratio of soluble xylan to total xylan (g/g). On solving differential Eq. (1) using boundary conditions (at t = 0, A=A<sub>0</sub>), the xylan concentration can be expressed by Eq.(2) as following:

$$A = A_0[(1 - \alpha) + \alpha e^{-k_1 t}] \dots\dots\dots(2)$$

To determine the remaining quantity of xylan in solid material, first it was found out that what quantity had been dissolved in reaction media and using correction factor (0.88) and mass balance, remaining quantity of xylan in solid material was converted in terms of liquid concentration (g/L). Experimental data were fitted by Eq. (2) and Fig.2 shows the experimental and predicted values for xylan concentration. Separate curve fitting was performed for data for each set of acid concentration. Kinetic and statistical values of these fittings have been shown in Table 2.

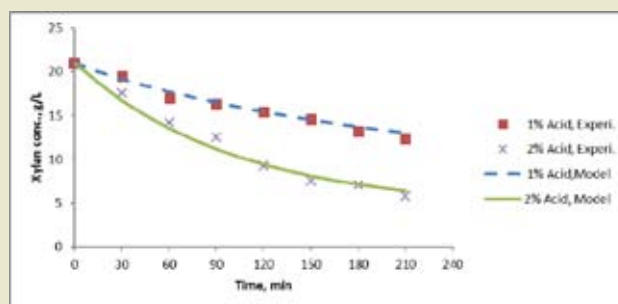


Fig.2 –Experimental and predicted dependence of concentration of xylan on time in extracted raw material at different acid mass fractions %(w/w).

Table 2. Kinetics and statistical parameters of xylan hydrolysis with H<sub>3</sub>PO<sub>4</sub> at 140°C

Experimental condition	α	K <sub>1</sub>	R <sup>2</sup>	R <sup>2</sup> adj.	F-test prob.	t-test prob.
1% H <sub>3</sub> PO <sub>4</sub>	0.625	0.0583	0.9867	0.9814	0.8695	0.8932
2% H <sub>3</sub> PO <sub>4</sub>	0.813	0.0826	0.9939	0.9915	0.8750	0.9391

The statistical parameters ( $R^2$ ,  $R^2_{adj.}$ , F-test and t-test) show that Eq. (2) fits very well with experimental results. The values of kinetic coefficients increase on increase of acid concentration. The value of  $\alpha$  was found in the range of 0.625-0.813, which is in accordance with other studies related to acid hydrolysis of biomass [6, 10, 18]. The value of  $\alpha$  varies with operational conditions of reaction, as acid concentration increases, the ratio of hydrolysis susceptibility also increases. This range of  $\alpha$  is similar for other lignocellulosic materials such as sugar cane bagasse [18] and corn cob [5]. The value of  $\alpha$  depends upon operational condition of reaction and usually increases on increasing of catalyst concentration. In literature [6], the value of  $\alpha$  varied from 0.55-0.85 depending on different acid concentrations.

Kinetic parameter  $k_1$  was correlated with the phosphoric acid concentration by a generalized empirical Eq. (3) as given below :

$$k_1 = a_{10} C^{n_1} \dots\dots\dots(3)$$

Where  $a_{10}$  and  $n_1$  are regression parameters to show dependence of acid concentration on kinetic coefficient, is acid concentration % (w/w). Using non-linear regression to Eq.(3),  $k_1$  was correlated with phosphoric acid concentration as follows:

$$k_1 = 0.04986 C^{0.71} \dots\dots\dots(4)$$

The Eq. (4) is considered well fitted ( $R^2=0.9657$ , F-test probability=0.9616). Value of regression parameter  $n_1$  was similar (0.86) to reported for other biomass materials [5]. Knowing above kinetic parameters, it is possible to predict xylan concentration (in term of g/L) in raw material at any time and acid concentration in the range of study (0-210 min. and 1-2%  $H_3PO_4$ ).

**Kinetic modeling of xylose concentration**

Xylose is the main hydrolysis product of xylan. Concentration of xylose at any time  $t$  can be expressed by following differential Eq. (5).

$$\frac{dX}{dt} = k_1 A - k_2 X \dots\dots\dots(5)$$

On solving Eq. (5) using boundary conditions (at  $t = 0$ ,  $x = 0$ ), concentration profile for xylose appears as shown in the following Eq.(6) :

$$X = \frac{k_1 A_0 (1 - \alpha)}{k_2} [1 - e^{-k_2 t}] + \frac{k_1 \alpha A_0}{(k_2 - k_1)} [e^{-k_1 t} - e^{-k_2 t}] \dots\dots(6)$$

Where  $X$  is the xylose concentration (g/L),  $A_0$  is the initial potential concentration of xylan corresponding with the quantitative conversion to xylose,  $\alpha$  is the mass ratio of hydrolysable mass fraction of xylan to total xylan,  $k_1$  is the reaction constant of generation reaction from xylan to xylose(min-1),  $k_2$  is the reaction constant of degradation reaction from xylose to furfural (min-1). Experimental data obtained from experiments were fitted to Eq. (6) and Fig. 3 shows the experimental and predicted dependence of xylose concentration as functions of time and acid concentration. Statistical and kinetic parameters obtained by non-linear regression, are shown in Table 3.

The statistical parameters ( $R^2$ ,  $R^2_{adj.}$ , F-test and t-test) shows that above model fits well with experimental results.

Kinetic coefficient ( $k_1$ ) for xylose generation reaction is approximately 70 times higher than kinetic coefficient of xylose degradation reaction ( $k_2$ ). Dependence of  $k_2$  on phosphoric acid concentration is modeled by a generalized empirical Eq. (7) as given in the following equation.

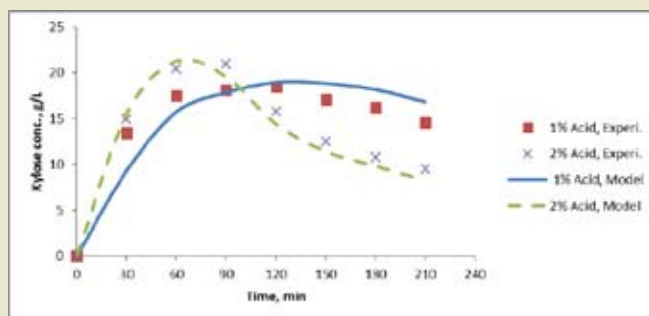


Fig. 3- Experimental and predicted concentration dependence of the xylose on time at different acid mass fractions % (w/w).

Table 3. Kinetics and statistical parameters of generation and degradation of xylose while hydrolysis of wheat straw using H<sub>3</sub>PO<sub>4</sub> at 140°C.

Experimental condition	k <sub>1</sub>	k <sub>2</sub>	R <sup>2</sup>	R <sup>2</sup> adj.	F-test prob.	t-test prob.
1% H <sub>3</sub> PO <sub>4</sub>	0.0583	0.00076	0.998	0.937	0.873	0.935
2% H <sub>3</sub> PO <sub>4</sub>	0.0826	0.00468	0.983	0.941	0.982	0.961

$$k_2 = a_{20}C^{n_2} \dots\dots\dots(7)$$

Where α<sub>20</sub> and n<sub>2</sub> are regression parameters to show dependence of acid concentration on kinetic coefficient and C is % acid concentration by weight. Applying non-linear regression to Eq. (7), k<sub>2</sub> is correlated with H<sub>3</sub>PO<sub>4</sub> concentration by Eq.(8) as given below:

$$k_2 = 0.00029C^{1.34} \dots\dots\dots(8)$$

The regression parameter α<sub>10</sub> for k<sub>1</sub> was more than 15 times than that for k<sub>2</sub> and n<sub>1</sub> was smaller than 1.63 times than that for k<sub>2</sub>. α<sub>20</sub> and n<sub>2</sub> are in the same range as reported in other studies [10].

**Kinetic modeling of arabinan concentration**

The differential equation describing concentration of arabinan at any time t in raw material may be written in the following Eq.(9).

$$\frac{dD}{dt} = -k_3[D - (1 - \beta)D_0] \dots\dots\dots(9)$$

where D is the quantity of arabinan in raw material ( in terms of g/L) at any time t during reaction, k<sub>3</sub> is the kinetic coefficient for hydrolysis of arabinan, D<sub>0</sub> is the initial potential arabinan in raw material (g/L) and β is the mass ratio of hydrolysable arabinan to total arabinan in raw material (g/g). On solving above differential equation using boundary conditions (at t = 0, D = D<sub>0</sub> ), concentration variation of arabinan in raw material ( in term of g/L) is described by the following Eq.(10).

$$D = D_0[(1 - \beta) + \beta \exp(-k_3t)] \dots\dots\dots(10)$$

Experimental data was fitted using non-linear regression by model Eq. [10]. Experimental and predicted dependence of arabinan concentration is shown in Fig.4. In Table 4, kinetic and statistical parameters are given which were obtained on non-linear regression of model Eq. (10) for different set of reaction conditions. Different statistical parameters (R<sup>2</sup>, R<sup>2</sup>adj., F-test prob., t-test prob. ) show that this model fits very well to experimental results. Based on values of hydrolysis reaction constant of arabinan, it has been shown that as acid concentration increases, the values of kinetic coefficient also increase. The value of β was in the range 0.38-0.65, which was higher than previously reported values 0.22-0.32 [6]. Effect of phosphoric acid concentration on k<sub>3</sub> can be modeled as follows by Eq.[11].

$$k_3 = a_{30}C^{n_3} \dots\dots\dots(11)$$

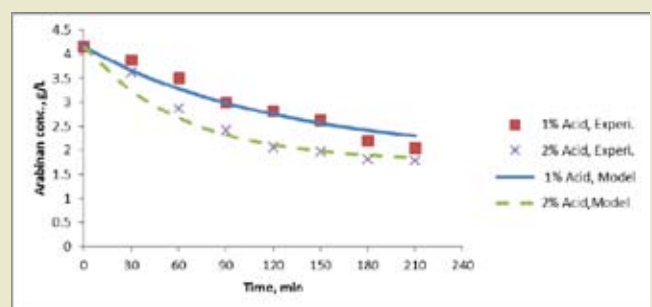


Fig. 4-Experimental and predicted concentration dependence of Arabinan concentration on time at different acid mass fractions % (w/w).

Table 4. Kinetics and statistical parameters of hydrolysis of arabinan using H<sub>3</sub>PO<sub>4</sub> at 140°C.

Experimental condition	β	k <sub>3</sub>	R <sup>2</sup>	R <sup>2</sup> adj.	F-test prob.	t-test prob.
1% H <sub>3</sub> PO <sub>4</sub>	0.38	0.0608	0.951	0.94	0.8936	0.8753
2% H <sub>3</sub> PO <sub>4</sub>	0.65	0.0764	0.982	0.96	0.9261	0.9263

Where  $\alpha_{30}$  and  $n_3$  are regression parameters and  $C$  is the mass fraction of acid in % (w/w). Using non-linear regression, correlation of  $k_3$  and  $H_3PO_4$  is shown in the following Eq.(12).

$$k_3 = 0.05763C^{0.68} \dots\dots\dots(12)$$

The value of regression parameters is in the same range as reported in other literature [18].

### 3.3.4 Kinetic modeling of arabinose concentration

Arabinose is released from arabinan , a hemicellulosic heteropolymer, during hydrolysis of arabinan. The formation and degradation of arabinose in reaction media can be described by Eq.(13) as follows:

$$\frac{dE}{dt} = k_3D - k_4E \dots\dots\dots(13)$$

Where  $E$  is the concentration (g/L) of arabinose in liquid solution,  $k_3$  is reaction coefficient for generation of arabinose( $\text{min}^{-1}$ ) and  $k_4$  is the reaction coefficient for degradation reaction of arabinose to furfural ( $\text{min}^{-1}$ ). On solving Eq.(13) using boundary condition (at  $t=0 E=0$ ), following concentration profile appears for arabinose concentration as shown in Eq.(14).

$$E = \frac{D_o k_3 (1 - \beta)}{k_4} (1 - e^{-k_4 t}) + \frac{k_3 D_o \beta}{(k_4 - k_3)} (e^{-k_3 t} - e^{-k_4 t}) \dots\dots\dots(14)$$

Experimental results of arabinose concentration were fitted using non-linear regression to Eq. (14). Fig.5 shows the experimental and predicted dependence of arabinose concentration on acid % and reaction time. Table 5 shows the kinetic and statistical parameters

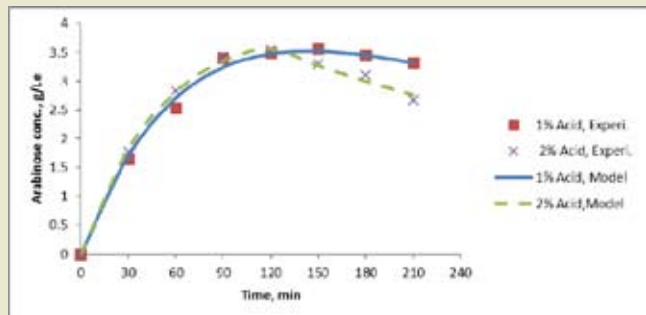


Fig. 5- Experimental and predicted concentration dependence of arabinose concentration on time at different acid mass fractions % (w/w).

for fitting of model Eq. (14). Decrease in arabinose concentration was observed after reaction time of 120 min., showing degradation of arabinose into furfural at high acid concentration and at higher reaction time. Kinetic coefficients show that arabinose decomposition is much slower than arabinose generation. Modeling of  $k_4$  with phosphoric acid concentration % (w/w) is done as follows , shown in Eq. [15].

$$k_4 = k_{40}C^{n_4} \dots\dots\dots(15)$$

Where  $k_{40}$  and  $n_4$  are regression parameters and  $C$  is mass fraction of acid % (w/w). Non-linear regression of model Eq.(12)  $k_4$  correlated with acid concentration (%w/w) as shown in following Eq.(16).

$$k_4 = 0.0159C^{1.16} \dots\dots\dots(16)$$

### Kinetic modeling of Furfural concentration

In hydrolysis of wheat straw, furfural is generated as decomposition product of monomeric pentose sugars (xylose and arabinose). The generation of furfural can be described by the following Eq.(17).

$$\frac{dF}{dt} = k_2X + k_4E \dots\dots\dots(17)$$

Table 5. Kinetics and statistical parameters of arabinose degradation using  $H_3PO_4$  at 1400C.

Experimental condition	$k_4$	$R^2$	$R^2$ adj.	F-test prob.	t-test prob.
1% $H_3PO_4$	0.0179	0.972	0.926	0.959	0.9883
2% $H_3PO_4$	0.0273	0.981	0.942	0.969	0.9974



Where  $F$  is the concentration of furfural (g/L) at any time  $t$ ,  $X$  and  $E$  are the concentrations of xylose and arabinose (g/L) respectively. On solving differential Eq. (17) with boundary conditions (at  $t=0, F=0$ ), concentration profile for furfural appears as shown in the following Eq.(18).

$$F = k_1 A_0 (1-\alpha) \left[ t + \frac{e^{-k_2 t} - 1}{k_2} \right] + \frac{k_1 k_2 \alpha A_0}{(k_2 - k_1)} \left[ \frac{1 - e^{-k_1 t}}{k_1} - \frac{1 - e^{-k_2 t}}{k_2} \right] + k_3 D_0 (1-\beta) \left[ t + \frac{e^{-k_4 t} - 1}{k_4} \right] + \frac{k_3 k_4 \beta D_0}{(k_4 - k_3)} \left[ \frac{1 - e^{-k_3 t}}{k_3} - \frac{1 - e^{-k_4 t}}{k_4} \right] \dots\dots\dots(18)$$

Model Eq. (18), describes the concentration of furfural depending upon xylose and arabinose concentrations with time and susceptibility ratios for xylan and arabinan. Table 6 shows the kinetics and statistical parameters obtained on non-linear regression of Eq.(18) with experimental results using Levenberg Markquardt algorithm. Fig.6 shows the concentration of furfural as function of reaction time and acid percentage % (w/w). It is shown that susceptible ratios and kinetic parameters were affected by acid concentration. The values of  $\alpha$ ,  $\beta$ ,  $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$  increased on increasing acid concentration. Maximum furfural concentration achieved was 3.94 g/L using 2%  $H_3PO_4$  while in similar other study [6], it was 2.93 g/L using reaction conditions 130°C, 180 min. reaction time and 2% (w/w)  $H_2SO_4$ .

**Kinetic modeling of acetyl concentration:**

During acid hydrolysis of lignocellulosic materials, acetic acid is generated due to hydrolysis of acetyl groups present in the acetylated hemicellulosic portion. The proposed kinetic model for acetic acid formation could be described by model Eqn.(19).as follows:

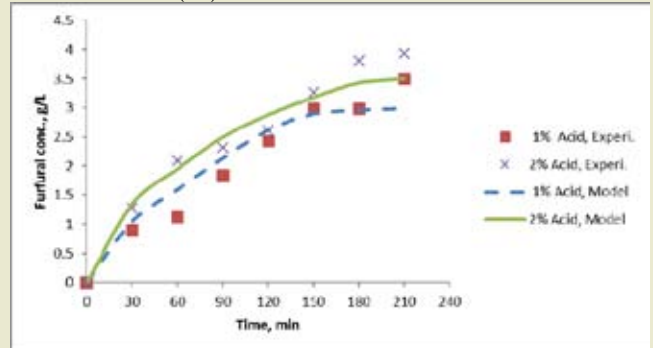


Fig.6- Experimental and predicted concentration dependence of furfural on time at different acid mass fractions % (w/w).

The following differential Eq. (20) is obtained on the basis of above kinetic model:

$$\frac{dG}{dt} = -k_5 A_c \dots\dots\dots(20)$$

Where  $G$  is the acetic acid concentration (g/L) at any time  $t$ ,  $A_c$  is the acetyl concentration in raw material (in terms of g/L),  $k_5$  is the kinetic coefficient of generation reaction for acetic acid from acetyl group. Solving Eq.(20), using boundary conditions (at  $t=0, A_c=A_{c0}$ ), concentration of acetyl content in raw material follows the following Eq.(20).

$$A_c = A_{c0} [(1-\gamma) + \gamma \exp(-k_5 t)] \dots\dots\dots(21)$$

Where  $\gamma$  is the susceptibility ratio of acetyl group. As acid concentration increases, acetyl content in biomass decreases. Fig. 7 shows the dependence

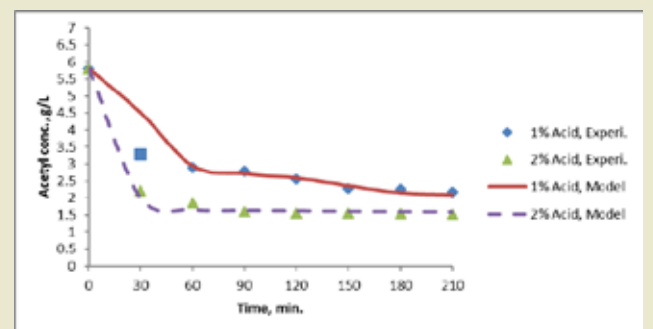


Fig.7- Experimental and predicted concentration dependence of acetyl in raw material on time at different acid mass fractions % (w/w).

Table 6. Kinetics and statistical parameters of furfural formation for  $H_3PO_4$  hydrolysis of wheat straw at 140°C

Experimental condition	$\alpha$	$\beta$	$k_1$	$k_2$	$k_3$	$k_4$	$R^2$	$R^2$ adj.	F-test prob.	t-test prob.
1% $H_3PO_4$	0.625	0.38	0.0583	0.00076	0.0583	0.0179	0.985	0.942	0.910	0.918
2% $H_3PO_4$	0.813	0.65	0.0826	0.00468	0.0719	0.0273	0.974	0.920	0.864	0.915

of acetyl concentration as functions of time and acid concentration. At 2% H<sub>3</sub>PO<sub>4</sub>, almost all removable acetyl group releases within 90 min. of reaction time.

The differential equation describing the concentration of acetic acid at any time *t* is expressed by Eq.(22) as follows.

$$\frac{dG}{dt} = k_5 A_C \dots\dots\dots(22)$$

Where *G* the concentration of acetic acid (g/L), *k*<sub>5</sub> is the kinetic coefficient of acetic acid generation.

Solving differential equation Eq.(22) using boundary condition (at *t*=0, *G*=0), concentration of acetic acid can be expressed by Eq.(23) as follows :

$$G = A_{C0} [k_5(1 - \gamma)t + \gamma(1 - \exp(-k_5 t))] \dots\dots\dots(23)$$

Experimental data of acetic acid concentration was fitted applying Eq.(23). Kinetic and statistical parameters of acetic acid concentration are shown in Table 7. Fig. 8 shows the experimental and predicted dependence of acetic acid concentration as functions of reaction time and H<sub>3</sub>PO<sub>4</sub> concentration.

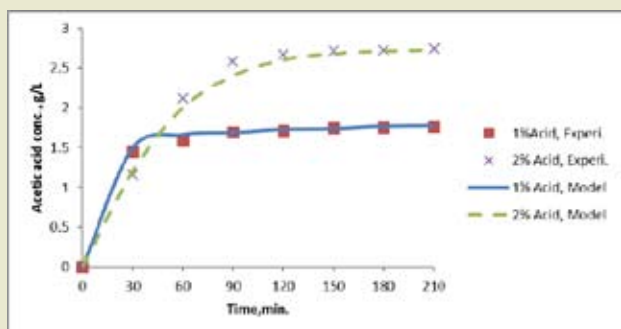


Fig.8 -Experimental and predicted concentration dependence of acetic acid on time and different acid mass fraction %(w/w).

The kinetic parameter (*k*<sub>5</sub>) decreases with the increase of the acid concentration. The parameter *γ* was also affected by acid concentration. Kinetic parameter *k*<sub>5</sub> was correlated with the phosphoric acid concentration %( w/w) by a generalized empirical Eq.(24).

$$k_5 = k_{50} C^{n_5} \dots\dots\dots(24)$$

Where *k*<sub>50</sub> and *n*<sub>5</sub> are the regression parameters and *C* is the acid %(w/w). Applying a non-linear regression analysis to the Eq.(21), *k*<sub>5</sub> correlated with H<sub>3</sub>PO<sub>4</sub> concentration as shown in Eq.(25).

$$k_5 = 0.0685 C^{-0.26} \dots\dots\dots(25)$$

This equation is well fitted as shown by statistical parameters (*R*<sup>2</sup> = 0.94, *F*-test probability=0.956).

#### 4.0 Overall Optimization

The objective of this study was to develop kinetic models that could be used to determine optimal conditions for the hydrolysis of wheat straw using phosphoric acid to obtain solutions of furfural with it's maximum concentration. Using kinetic model equations of xylose, arabinose, furfural and values of kinetic parameters of these model equations, operational conditions for furfural were optimized. Hydrolysis with phosphoric acid at 140°C resulted to obtain xylose concentrations varied between 13.45 g/L (1% acid, 30 min.) and 20.5 g/L (2% acid, 60 min.), arabinose concentration between 1.70 g/L (1% acid, 30 min.) and 3.50 g/L (2% acid, 120 min.), furfural concentration between 0.9 g/L (1% acid, 30 min.) and 3.94 g/L (2% acid, 210 min.) and that of acetic acid between 1.2 g/L (2% acid, 30 min.) and 2.75 g/L (2% acid, 210 min.). As acid concentration and reaction time increase, furfural concentration steadily increases. For maximum furfural concentration, overall optimum conditions were considered to be those ( 140°C, 2% acid and 210 min.) able to allow obtaining furfural 3.94 g/L and monomeric sugars at their low level of concentration (9.5 g/L xylose, 2.76 g/L arabinose). Hydrolyzate samples with similar composition during

Table 7. Kinetics and statistical parameters of acetic acid formation for H<sub>3</sub>PO<sub>4</sub> hydrolysis of wheat straw at 140°C.

Experimental condition	<i>γ</i>	<i>A</i> <sub>C0</sub>	<i>k</i> <sub>5</sub>	<i>R</i> <sup>2</sup>	<i>R</i> <sup>2</sup> adj.	<i>F</i> -test prob.	<i>t</i> -test prob.
1% H <sub>3</sub> PO <sub>4</sub>	0.49	5.9	0.074	0.974	0.915	0.9742	0.9657
2% H <sub>3</sub> PO <sub>4</sub>	0.61	5.9	0.057	0.991	0.941	0.8824	0.9162

similar reaction conditions were also obtained from dilute acid hydrolysis of sugar cane bagasse [18], sorghum straw [19] and wheat straw [6].

### Conclusion

Experimental data on the xylan and arabinan degradation, xylose, arabinose, furfural and acetic acid generation were obtained under different acid mass fractions and reaction times. The results were

modeled using multiple reaction model. The kinetic reaction model consisted series and parallel reactions and every reaction was assumed to be pseudo-homogenous first order and irreversible. The developed kinetic models can be used to find out concentration of different sugars and degradation products at any time during the reaction (0-210 min.). Chosen optimized condition (140°C, 2% acid and 210 min.) for furfural production allows about 90.35% hemicelluloses hydrolysis.

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