Kinetic Studies on *Pisum sativum* Waste (Pea pod) Hydrolysis to Furfural

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To obtain a higher furfural yield from *Pisum sativum* (pea pod) waste, the effects of the process variables phosphoric acid concentration (wt.%), reaction temperature, and liquid solid ratio (LSR) were investigated. A new reaction scheme was proposed consisting of series and parallel reactions for the formation of furfural. Kinetic models were developed to describe changes in the concentration of furfural with time. A modified Arrhenius equation was used to find out correlations between kinetic coefficients and reaction parameters. A maximum furfural concentration of 5.27 g/L (40.6% yield based on total conversion of pentosans) was obtained using 6% (wt.%) H_3PO_4 and liquid-to-solid ratio of 1:10 at 160 °C. Reaction parameters such as acid concentration, reaction temperature, and liquid solid ratio had a strong effect on the yield of furfural.

Keywords: Pisum sativum; Acid hydrolysis; Phosphoric acid; Xylose; Furfural

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INTRODUCTION

Lignocellulosic biomass is the most abundant feed-stock available on the earth, and it can be used as an alternative feed-stock for production of value-added chemicals and biofuels (Dawson and Boopathy 2007). The development of effective and profitable technologies that utilize waste lignocellulosic materials is a common objective for many researchers (Abad *et al.* 1997), and the formation of furfural from waste biomass has drawn much attraction worldwide. Furfural (2-furfuraldehyde) contains a heterocyclic ring with an aldehyde group, which is mainly responsible for the synthesis of new compounds from furfural. Furfural is very important because of its industrial uses and applications, and it is a very satisfactory solvent for most natural gums and resins. The largest individual commercial use of furfural is in the production of chemical intermediates such as hexamethylene diamine and adipic acid, which are the two main ingredients required in nylon manufacturing. Furfural alcohol, another important derivative of furfural, is produced by the high-pressure hydrogenation of furfural in liquid phase (Merlo *et al.* 2009). Catalytic hydrogenation of furfural produces methylfuran, which is used for synthesis of crysanthemate pesticides and perfume intermediates (Panagiotopoulou and Vlachos 2014). Therefore, furfural is an important chemical material. Since there is no synthetic route for production of furfural is present, it is exclusively produced from hydrolysis of lignocellulosic biomass. World market for production of furfural is currently estimated at about 200,000 to 210,000 tpa, of which 60 to 62% is consumed for the production of furfuryl alcohol (Mamman *et al.* 2008).

Furfural can be produced from the acid hydrolysis of pentosans, which are contained in most agricultural residues, such as eucalyptus (Abad *et al.*1997), rice hull (Hector *et al.* 1998), rice straw (Keikhosro *et al.* 2006), corn stover (Qiang *et al.* 2011), wheat straw (Guerra *et al.* 2012), and sorghum straw (Tellez-Luis *et al.* 2002). H_2SO_4 (Hector *et al.* 1998; Tellez-Luis *et al.* 2002; Keikhosro *et al.* 2006; Guerra *et al.* 2012), CH_3COOH (Abad *et al.* 1997), HCl (Herrera *et al.* 2003), and HNO_3 (Rodriguez-Chong *et al.* 2004) are the commonly used acids for biomass hydrolysis. Biomass type, reaction temperature, and reaction time play a crucial role on the final yield of furfural.

The hydrolysis of biomass produces pentose sugars (xylose and arabinose), which generate furfural when dehydrated. During hydrolysis, acid releases protons, which combine with polymeric chain of sugar monomers to break ether bonds and produce monomeric sugars. Higher furfural yield can be obtained at higher acid concentrations and elevated reaction temperatures. The maximum furfural yield at 5% acid concentration (4 g/L) is significantly higher than at 1% acid concentration (1.2 g/L) during the hydrolysis of wheat straw (Guerra *et al.* 2012). The actual maximum yield of furfural is in between 23 and 30% based on the maximum conversion of pentosans (xylan and araban) in the raw material and different reaction conditions (Abad *et al.* 1997; Aguilar *et al.* 2002; Tellez-Luis *et al.* 2002; Rodriguez-Chong *et al.* 2004; Guerra *et al.* 2012).

Biomass acid hydrolysis reactions are complex heterogeneous solid-liquid reactions involving diffusion mass transfer and chemical reaction steps. Due to complexities involved in modeling of this type of reaction system, these reactions are often modeled as pseudo-homogenous first order irreversible reactions. Satisfactory results have been obtained using these assumptions for modeling biomass hydrolysis reactions. There are various kinetic models and mechanisms describing the acid catalyzed hydrolysis of lignocellulosic biomass (Abad *et al.* 1997; Aguilar *et al.* 2002; Tellez-Luis *et al.* 2002; Rodriguez-Chong *et al.* 2004; Keikhosro *et al.* 2006; Guerra *et al.* 2012). During dilute acid hydrolysis of biomass, hemicellulose is easily hydrolyzed due to its amorphous branched structure. Cellulose hydrolysis is difficult to hydrolyze due to its crystalline structure (Guerra *et al.* 2012).

Agricultural residues can be exploited to form potential sources for a large number of chemicals and other industrial products in a very economical and feasible manner due to their large availability, low cast, need for their proper disposal, and their ability to yield value-added chemicals at very low cost (Romero *et al.* 2010). *Pisum sativum* (pea pod) waste is produced after removing spherical pea seeds from pea pods. *P. sativum* is a kind of pulse which is cultivated in India abundantly producing more than 2.1 million tons per annum (Department of Agriculture, Cooperation and Farmers Welfare; agricoop.nic.in). The annual *P. sativum* waste produced in India is about 1.5 million tons. This waste can be used as fodder for cattle or it is disposed of by burning in an open environment, causing harm to the atmosphere. Developing technologies to use this abundant natural waste in economically profitable ways are very attractive in the present scenario of the energy crisis.

To date, there are no published reports on the acid hydrolysis of *P. sativum* waste. The objective of this work was to study the production of furfural from *P. sativum* waste using a phosphoric acid catalyzed process. The effects of reaction parameters such as acid concentration, reaction time, reaction temperature, and liquid-to-solid ratio on the yield of furfural were investigated. Kinetic models were developed for the concentration of furfural over reaction time. The kinetic parameters of mathematical models were used to optimize the concentration of furfural.

EXPERIMENTAL

Materials and Methods

Raw material preparation

P. sativum waste used in this study was collected from a local farm (Saharanpur, India) after removing the spherical pea seeds from the pods. The material was air-dried and milled in a defibrator grinding machine. Ground material was passed through a stack of sieves. The material first passed through a 60-mesh sieve, and the portion retained on an 80-mesh sieve was collected for further experimentation. The average particle size of material collected for experimentation was 0.20 mm. Extractives in the raw material were removed using ethanol-benzene and hot water mixtures, as described in standard procedures ASTM D1105-96(2013) and ASTM D1110-84(2013). Samples of extractive-free material were used to determine the structural carbohydrate, ash, and moisture contents.

Hydrolysis reaction

The hydrolysis experiments were carried out in a 1.0 L stainless steel (316 L) batch reactor, which was immersed in a rotatory digester. A thermocouple was fitted inside the reactor to show the reaction temperature. Each experiment was initiated by the addition of the required amount of raw material, deionized water, and phosphoric acid and then heating the reaction mixture to the reaction temperature. The digester was rotated at 2.5 rotations per minute to ensure proper mixing. Experimental runs were carried out at three different acid concentrations of 3, 6, and 9 (wt.%) three different solid-to-liquid ratios of 1:5, 1:10 and 1:15 and three different reaction temperatures of 100, 130 and 160 °C. Samples of the hydrolysis reactions were taken after certain reaction periods.

Analysis of reaction product

Liquid samples obtained after hydrolysis were centrifuged, diluted with deionized water (1:50 v/v), neutralized using calcium carbonate to pH 5 to 6, and filtered through a 0.20 µm filter for analysis by a HPLC (High performance liquid chromatography) instrument (Shimadzu SIL-20 AHI, Kyoto, Japan). The HPLC analysis was carried out using a C-18 column with isocratic elution (flow rate of 1.00 mL/min; mobile phase: 0.005 MH_2SO_4). A photo diode array detector was used for all compounds. The sampling speed was 15 µL/s, and the injection volume was 10 µL. Detection of compounds was based on comparing the retention time of compounds in each hydrolysis sample, using a chromatograph, with the retention time of compounds in pure solutions. The concentration of compounds in each hydrolysis sample was found using the peak area.

The yield of furfural was calculated using Eq. 1:

$$Yield\ (\%) = \frac{Actual\ concentration\ of\ furfural\ \left({}^{g}/_{L}\right)}{Maximum\ theoretical\ concentration\ of\ furfural\ \left({}^{g}/_{L}\right)} \times\ 100 \qquad (1)$$

The maximum theoretical concentration of furfural was calculated using Eq. 2,

$$F_0 = \frac{96}{132}\frac{\%P}{LSR}\rho \qquad (2)$$

where F_0 is the maximum theoretical concentration of furfural (g/L), 96/132 is the stoichiometric factor for furfural, % P is the pentosan mass percent in raw material, LSR is the liquid to solid ratio, and ρ is the density of hydrolysates (g/L).

Kinetic Models

Due to the complexities in kinetic modeling of the biomass hydrolysis process, common kinetic models used to describe these reactions are pseudo-homogenous irreversible first order (Abad *et al.* 1997; Aguilar *et al.* 2002; Tellez-Luis *et al.* 2002; Rodriguez-Chong *et al.* 2004; Keikhosro *et al.* 2006; Guerra *et al.* 2012). In the present study, the kinetic modeling of reactions was performed with this assumption, and further introducing the susceptible fraction of xylan (α) and arabnan (β) into monomeric sugars. The susceptible fraction is defined as the mass ratio of hydrolysable pentosan (xylan and arabinan) to total pentosan. Based on these assumptions, a kinetic model consisting of series and parallel reactions for furfural formation is proposed in Fig. 1.

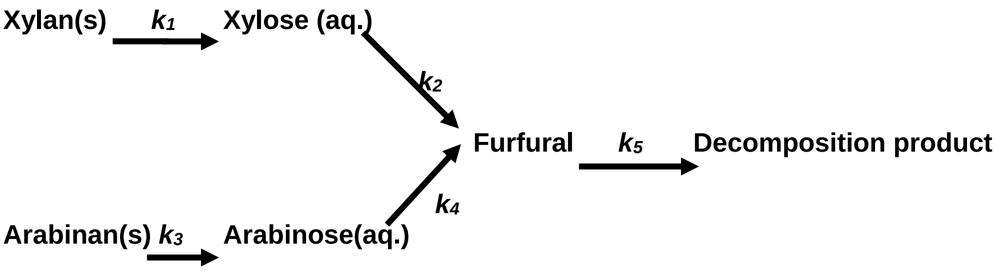

Fig. 1. Proposed kinetics for furfural formation from decomposition of pentosans

The following set of differential equations were obtained based on the above reaction model.

$$\frac{dC_X}{dt} = k_1 C_{xylan} - k_2 C_X \tag{3}$$

$$\frac{dC_A}{dt} = k_3 C_{araban} - k_4 C_A \tag{4}$$

$$\frac{dC_F}{dt} = k_4 C_A + k_2 C_X - k_5 C_F \tag{5}$$

By solving the above differential equations, analytical expressions were obtained for the concentrations of xylose (Eq. 6), arabinose (Eq. 7), and furfural (Eq. 8),

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

$$C_A = \frac{k_3 D_0 (1-\beta)[1-e^{-k_4 t}]}{k_4} + \frac{k_3 D_0 \beta [e^{-k_3 t} - e^{-k_4 t}]}{k_4 - k_3} \tag{7}$$

$$C_F = \frac{k_1 k_2 A_0 (1-\alpha)}{k_2} \left(\frac{1-e^{-k_5 t}}{k_5} - \frac{e^{-k_2 t} - e^{-k_5 t}}{k_5 - k_2} \right) + \frac{k_2 k_1 \alpha A_0}{k_2 - k_1} \left(\frac{e^{-k_1 t} - e^{-k_5 t}}{k_5 - k_1} - \frac{e^{-k_2 t} - e^{-k_5 t}}{k_5 - k_2} \right) + \\ \frac{k_3 k_4 D_0 (1-\beta)}{k_4} \left(\frac{1-e^{-k_5 t}}{k_5} - \frac{e^{-k_4 t} - e^{-k_5 t}}{k_5 - k_4} \right) + \frac{k_3 k_4 D_0 \beta}{k_4 - k_3} \left(\frac{e^{-k_3 t} - e^{-k_3 t}}{k_5 - k_3} - \frac{e^{-k_4 t} - e^{-k_5 t}}{k_5 - k_4} \right) \tag{8}$$

where C_X, C_A, and C_F are the xylose, arabinose, and furfural concentrations (g/L) respectively, α and β are the susceptible fraction of xylan and arabinan respectively, A_0

and D_0 are the total equivalent amount of xylan and arabinan respectively (g/L) initially, k_1 is the rate constant of hydrolysis reaction from xylan to xylose (min^{-1}), k_2 is the rate constant of dehydration reaction from xylose to furfural (min^{-1}), k_3 is the rate constant of hydrolysis reaction from arabinan to arabinose (min^{-1}), k_4 is the rate constant of dehydration reaction from arabinose to furfural (min^{-1}), and k_5 is the rate constant of degradation reaction from furfural into degradation products (min^{-1}). A non-linear regression analysis was performed to fit Eqs. 6 through 8 with experimental data using popular optimization software SOLVER (Microsoft Excel 2007, Redmond, WA, USA), and kinetic parameters and constants were obtained.

RESULTS AND DISCUSSION

Composition of *P. sativum* Waste

The proximate chemical analysis of *P. sativum* waste is shown in Table 1. Its pentosan (xylan and arabinan) content was approximately 17.5%, which is comparable to other lignocellulosic biomass materials commonly used for furfural production such as wheat straw, rice straw, coconut shells, coffee husk, and sugar cane bagasse. The other contents of *P. sativum* waste were in a similar range as reported for other lignocellulosic materials such as wheat straw (Guerra *et al.* 2012), rice straw (Keikhosro *et al.* 2006), sorghum straw (Tellez-Luis *et al.* 2002), and sugar cane bagasse (Rodriguez-Chong *et al.* 2004).

Table 1. Main Components of *P. sativum* (Pea Pod) Waste

Constituent	Method	Mass Fraction in Percentage(%) of Oven-Dried Material
Glucan	ASTM E 1758-01(2015)	36.80
Xylan	ASTM E 1758-01(2015)	15.20
Arabinan	ASTM E 1758-01(2015)	2.30
Ash	ASTM D 1102- 84(2013)	4.60
Moisture	ASTM D 1106-96(2013)	7.12
Lignin(Klason +Acid-soluble)	ASTM E1758-01(2015)	16.90
Ethanol-benzene solubility	ASTM D1107-96(2013)	3.14

Production of Furfural

The effect of different combinations of acid concentration, reaction temperature, reaction time and liquid-to-solid ratio (LSR) on the furfural yield were determined and discussed below.

Effect of acid concentration

Figure 2 shows the effect of acid concentration on the concentration of furfural. At lower acid concentrations (3% and 6%), hydrolysis of pentosan in *P. sativum* waste occurred at a slower rate than observed at 9% acid concentration. Maximum furfural concentration of 3.78 g/L (29.12% yield based on total conversion of pentosans) was obtained after 60 min of reaction time while hydrolyzing at 9% acid concentration. At 3% and 6% acid concentrations, maximum yields were 13.09% and 23.34% respectively. These findings show that higher acid concentration favors degradation of xylose and arabinose into furfural. At higher acid concentrations, loss of furfural also takes place due to side reactions, which lead to condensation and formation of resins. Due to degradation of furfural, concentration of furfural decreases after attaining maximum concentration during reaction at higher acid concentrations. It is also due to the fact that at higher acid concentrations, after attaining maximum furfural concentration, the rate of degradation of furfural is higher than rate of formation of furfural. For higher furfural yields, acid concentrations of 6 to 9% and reaction times of 60 to 120 min are favorable.

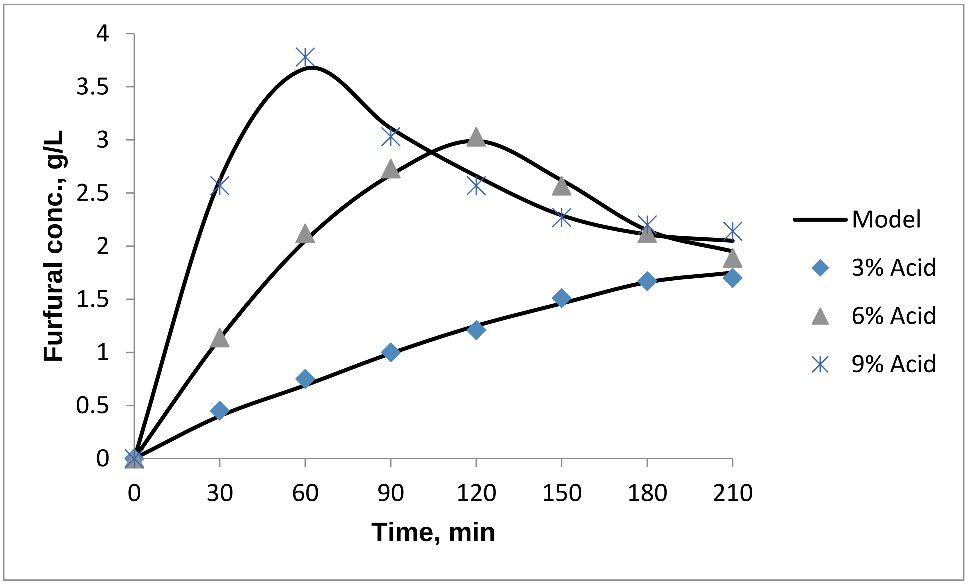

Fig. 2. Dependence of furfural concentration on various acid concentrations. Other reaction conditions were constant at a reaction temperature of130 °C and LSR of 10:1.

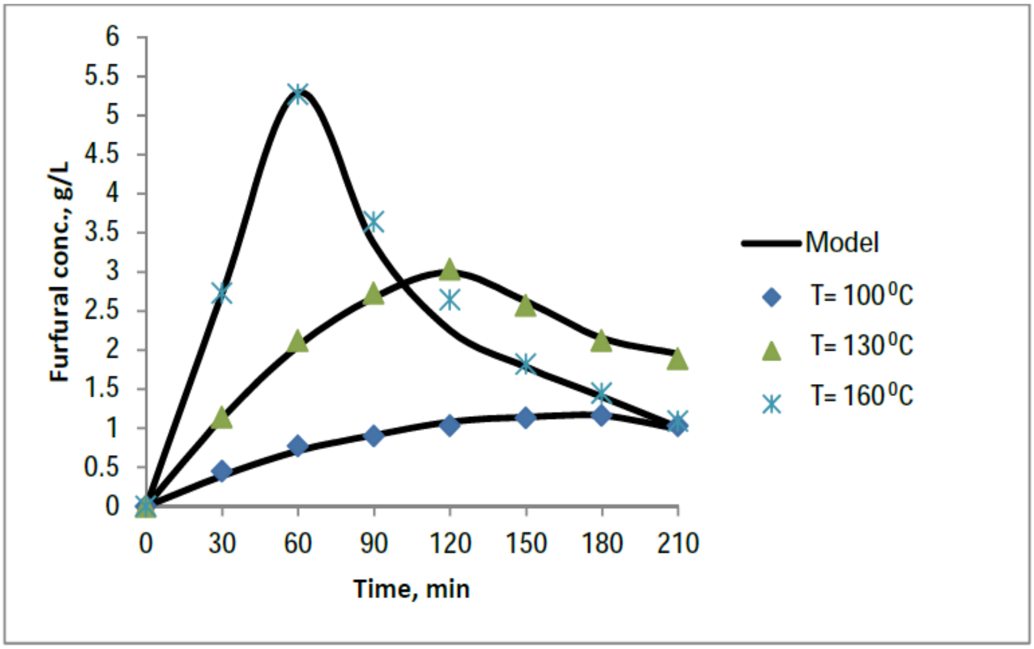

Fig. 3. Dependence of furfural concentration on various reaction temperatures. Other reaction conditions were constant at a 6% acid concentration and LSR of 10:1.

Effect of temperature

Dependence of furfural concentration on different reaction temperatures is shown in Fig. 3. Other reaction parameters were constant at some particular value. It is shown that as reaction temperature was increased, the rate of furfural formation also increased up to a maximum concentration of furfural. While reacting at 160 °C, maximum furfural concentration of 5.27 g/L (40.6% yields) was obtained after completion of only 60 min of reaction time. This value (5.27 g/L) is much higher than other maximum value of 3.03 g/L obtained reacting at a lower temperature of 130 °C. After reaching these maximum values (5.27 g/L and 3.03 g/L), furfural concentration started to decrease due to acid-catalyzed degradation of furfural into destructive products such as resins, and during this, the rate of furfural degradation reactions was higher than the rate of furfural formation reactions. These observations indicate that higher temperature gives higher furfural yield in lesser time of reaction period than lower temperatures, and after attaining maximum concentration, the rate of degradation reaction of furfural becomes higher than rate of formation of furfural. At 130 °C, reacting for 90 min, the maximum furfural yield is only 51.80% of that obtained at 160 °C. This shows slower rates for formation of furfural at this temperature. However, after achieving maximum concentration at this temperature, rate of net loss of furfural was slower than that observed after attaining maximum at the higher temperature of 160 °C. This indicates that at lower temperatures the rate of degradation of furfural was also slow. Further, at a lower temperature of 100 °C, it was observed that the rate of formation of furfural was very slow and no dominant degradation stage was observed. During the entire experimental run period (0 to 210 min), net furfural concentration steadily increased and reached up to concentration of 1.09 g/L (8.39% yield) until a reaction time of 210 min. Thus, low reaction time and higher reaction temperatures produced a higher furfural yield from *P. sativum* waste.

Effect of liquid solid ratio (LSR)

Dependence of furfural concentration on different LSR is show in Fig. 4.

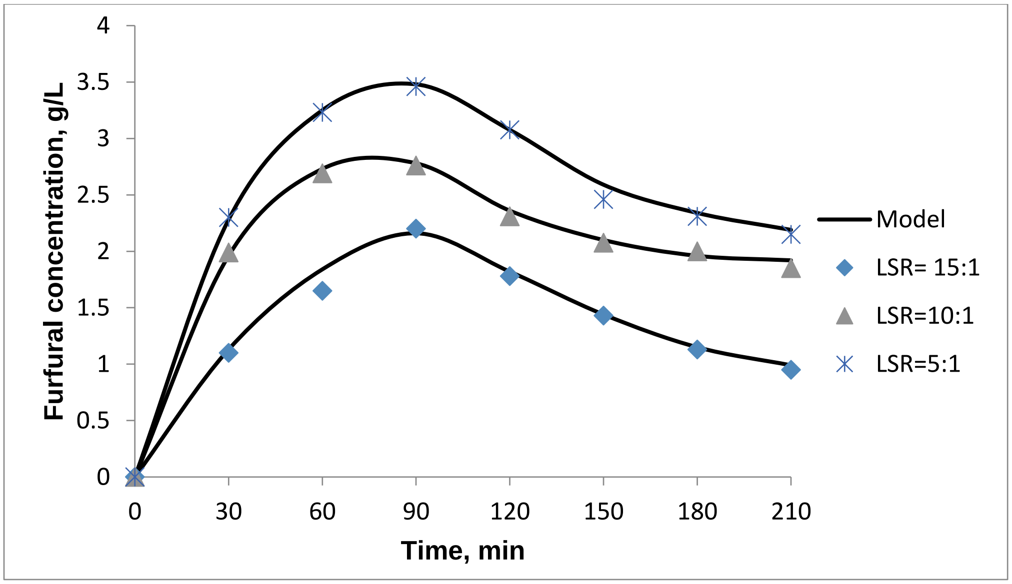

Fig. 4. Dependence of furfural concentration at different liquid-solid mass ratios, while other reaction parameters were constant (acid concentration = 6%, Temperature=130 °C)

According to Eq. 2 for maximum potential concentration of furfural, it is shown that as LSR increased, maximum potential concentration of furfural decreased. Maximum potential concentration at different LSR 5, 10, and 15 were 26.09, 12.98, and 8.62(g/L), respectively. This is due to the increase in total reaction volume while keeping a limiting reactant constant. On changing LSR, mass percentage of acid remained constant; only increasing the volume of water, despite the mass percentage of acid, did not affect the results appreciably. It was observed that as LSR was increased, furfural concentration decreased, but the yield of furfural increased (based on potential conversion). The rate of furfural degradation was also higher at higher LSR.

Kinetic Modeling of Furfural Concentration

Table 2 shows the kinetic and statistical parameters obtained after fitting Eq. 8 for furfural formation.

Table 2. Kinetic and Statistical Parameters of Furfural Formation for the H_3PO_4 Hydrolysis of *P. sativum* (Pea Pod) Waste

H_3PO_4 (wt.%)	T(°C)	α	β	k_1	k_2	k_3	k_4	k_5	R^2
3	100	0.29	0.24	0.0268	0.0002	0.0714	0.0002	0.00015	0.981
3	130	0.39	0.31	0.1311	0.0012	0.1023	0.00061	0.00082	0.940
3	160	0.48	0.39	0.1701	0.0035	0.1419	0.0030	0.00382	0.909
6	100	0.44	0.38	0.0584	0.0047	0.1440	0.00176	0.00462	0.982
6	130	0.59	0.48	0.2574	0.0075	0.3420	0.00186	0.01842	0.883
6	160	0.65	0.53	0.5738	0.0364	0.5814	0.00316	0.06472	0.926
9	100	0.54	0.41	0.2406	0.0025	0.5613	0.00232	0.1685	0.867
9	130	0.71	0.58	1.061	0.0791	1.4028	0.00493	0.7627	0.960
9	160	0.84	0.67	2.361	0.9682	1.6142	0.00691	0.9472	0.896

Table 4 shows that susceptibility (α and β) of pentosans and kinetic coefficients of reactions were highly dependent on acid wt.% and reaction temperature. Kinetic coefficients of generation reactions were much higher than coefficients of degradation reaction. The values of α were in the range 0.29 to 0.84. These are similar to the values reported for dilute-acid hydrolysis of other materials. Abad *et al.* (1997) reported values of α in the range 0.66 to 0.78 for eucalyptus acid hydrolysis. Ramirez *et al.* (2004) found values of α in the range of 0.54 to 0.83 for hydrolysis of sugar cane bagasse. The values of β (0.24 to 0.67) in this study were also similar to the range of β value (0.31 to 0.42) reported by Rodriguez-Chong *et al.* (2004). β was also reported lower (0.225 to 0.319) than this study by Guerra-Rodriguez *et al.* (2012) for wheat straw hydrolysis. There were strong correlations between kinetic parameters at different acid concentrations and temperatures, as shown by the correlation coefficients ($R^2 \geq 0.90$) and Fig. 5. This result also showed the adequacy of model to describe the furfural concentration during *P. sativum* waste hydrolysis. The k_1 and k_3 values showed that generation reactions for formation of pentose sugars were faster than degradation of pentose sugars to form furfural. Kinetic constants (both formation and degradation) usually increased with increasing acid concentration and reaction temperature, as shown in Table 2. A modified Arrhenius type equation, containing an acid term, was used to describe the effect of reaction temperature and acid concentration on the reaction coefficients (k_i), similar to other reports (Chang *et al*. 2009; Arslan *et al.* 2012). The modified Arrhenius equation was written as shown in Eq. 9.

$$k_i = k_i^{'} C^{m_i} \left({}^{-E_i}/_{RT} \right), \quad i = 1{,}2{,}3{,}4 \text{ and } 5 \qquad (9)$$

where k_i is the rate constant of corresponding reaction, k_i' is the pre-exponential factor, C is the acid mass percentage (wt%), m_i is the exponent of acid concentration, E_i is the activation energy, R is universal gas constant (8.314 J.mol^{-1}.K^{-1}) and T is the reaction temperature (^{o}K). Non-linear regression fitting was applied to Eq. 9 using values of acid concentrations, reaction temperatures, and kinetic coefficients to find out the values of pre-exponential factor, exponent of acid concentration, and activation energy. Non-linear regression of the modified Arrhenius equation resulted in the correlations for kinetic coefficients of reactions (Table 3). The values of pre exponential factors, exponent of acid concentration, and activation energy of different reactions predicted by different researchers using modified Arrhenius equations are given in Table 4.

Table 3. Modified Arrhenius Correlations for Kinetic Coefficients

Correlations	R^2
$k_1 = 5.32 \times 10^7 C^{0.85} \exp(^{-96.8}/_{RT})$	0.94
$k_2 = 2.48 \times 10^{11} C^{1.14} \exp(^{-106.93}/_{RT})$	0.88
$k_3 = 2.08 \times 10^7 C^{0.71} \exp(^{-98.7}/_{RT})$	0.91
$k_4 = 1.76 \times 10^9 C^{1.26} \exp(^{-103.9}/_{RT})$	0.89
$k_4 = 1.41 \times 10^7 C^{0.75} \exp\left(^{-71.85}/_{RT}\right)$	0.92

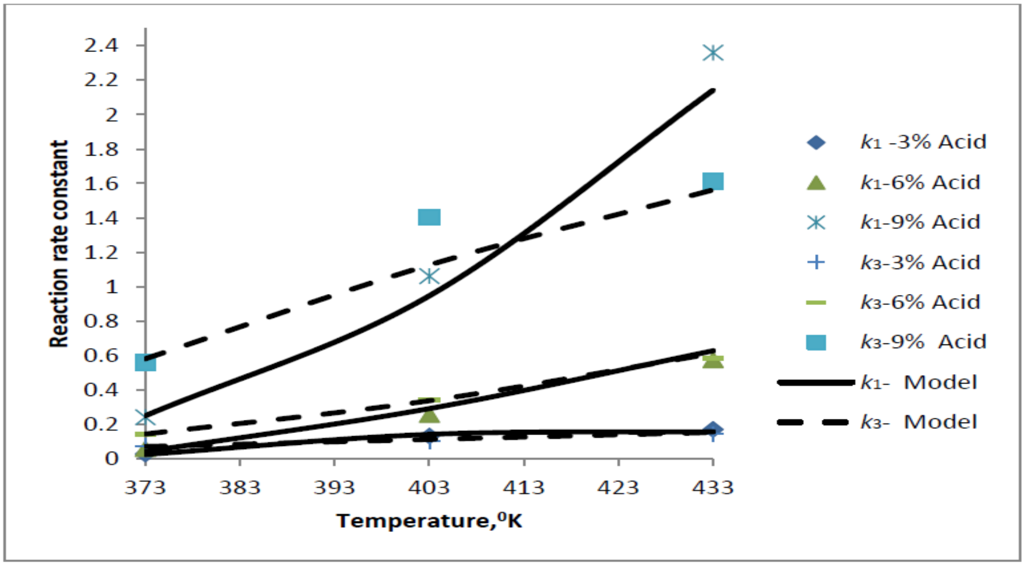

Fig. 5. Dependence of reaction rate constants on reaction temperatures and acid concentrations

Table 4. Predicted Values Using the Modified Arrhenius Equation

Reference	Raw Material	k_1'	k_2'	k_3'	k_4'	k_5'	m_i	*E*
Eken-Saracoglu *et al*. (1998)	Corn cob	1.486 x 10^{10}	2 x10^{10}	--	--	--	1.21(k_1) 1.86(k_2)	80.34(k_1) 85.679(k_2)
Qiang *et al*. (2011)	Corn stover	1.4 x 10^{14}	--	3.3 x 10^{10}	--	--	0.68(k_1) 0.40(k_2)	111.6(k_1) 95.7(k_3)
Rodriguez-Chong *et al*. (2004)	Sugar cane bagasse	9.66 x 10^{12}	--	--	--	--	--	85.6(k_1)
Aguilar *et al*. (2002)	Sugar cane bagasse	2.15 x 10^{13}	--	--	--	--	0.734(k_1)	108.6(k_1)
Hisham S. Bamufleh et al. (2013)	Midribs of date-palm trees	4.14x10^5	4.53x10^8	--	--	4.14 x10^5	0.387(k_1) 4.345(k_2) 0.462(k_3)	15.66(k_1) 94.97(k_2) 59.54(k_3)
Danon B. *et al*. (2014)	Pure xylose and arabinose	---	0.06027	---	0.0238	--	--	133.3(k_2) 121.4(k_4)
Present study	*P*. sativum (Pea pod)	5.32x10^7	2.48x10^{11}	2.08x10^7	1.76x10^9	1.41x10^7	0.85(k_1) 1.14(k_2) 0.71(k_3) 1.26(k_4) 0.75(k_5)	96.8(k_1) 106.93(k_2) 98.7(k_3) 103.9(k_4) 71.85(k_5)

"--" indicates that these values are not available in the literature

CONCLUSIONS

1. Furfural can be produced from acid hydrolysis of *P. sativum* waste using H_3PO_4 at various conditions of reaction temperature and liquid-to-solid ratio.
2. *P. sativum* waste contains approximately 17.30% (w/w) pentosan, which makes it a suitable raw material for the production of furfural by acid hydrolysis.
3. Kinetic models were developed to predict the concentration of furfural under varying acid concentration and temperature conditions.
4. The maximum furfural yield obtained during hydrolysis of *P. sativum* waste was 40.6% at 160 °C, 6 wt.% acid concentration, and liquid-to-solid ratio of 10. Under all reaction conditions, furfural yield was highly dependent on reaction temperature, acid concentration, and liquid-to-solid ratio.
5. Based on correlation coefficients, kinetic models were highly correlated with experimental values. Kinetic coefficients highly depend upon reaction parameters, which are described by a modified Arrhenius equation with high values of correlation coefficients ($R^2 \geq 0.88$).
6. *P. sativum* waste can be used for furfural production successfully because the yield of furfural using this as a raw material is high and it has ability to replace previously used raw materials.

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NOMENCLATURE

A_0	initial total amount of xylan in raw material (g/L)
α	susceptible fraction of xylan (g/g)
β	susceptible fraction of araban (g/g)
Cacid	concentration wt % (mass per mass)
C_A	arabinose concentration in liquid media (g/L)
C_{araban}	equivalent xylan concentration in raw material (g/L)
C_F	furfural concentration in liquid media (g/L)
C_x	xylose concentration in liquid media (g/L)
C_{xylan}	equivalent xylan concentration in raw material (g/L)
D_0	initial total amount araban in raw material (g/L)
E_i	activation energy (kJ/mol)
F_0	theoretical maximum concentration of furfural(g/L)
k_1	kinetic coefficient for generation of xylose from xylan(min^{-1})
k_2	kinetic coefficient for degradation of xylose into furfural (min^{-1})
k_3	kinetic coefficient for generation of arabinose from arabinan(min^{-1})
k_4	kinetic coefficient for degradation of arabinose into furfural (min^{-1})
k_i	pre-exponential factor
LSR	liquid to solid ratio (mL/g)
m_i	exponent for acid concentration
$\%P$	pentosan mass %
ρ	density of hydrolyzate (kg. m^{-3})
R	universal gas constant (=8.314 J . mol^{-1} . K^{-1})
T	reaction temperature (K)
t	reaction time (min.)

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