A Fresh Look at the Kinetics of Pentosan Removal from Lignocellulosic Biomass

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Abstract: The effect of time, temperature and concentration of prehydrolyzing agent on the biomass prehydrolysis have been studied for pentosan removal. Basic kinetic parameters i.e. rate constant, order of reaction, energy of activation and frequency factor were calculated. This study on the kinetics of pentosan removal reveals that the rate of pentosan removal does not follow exactly first order kinetics and shifting of order is observed during the reaction. In searching for a kinetic equation for pentosan removal, it was found that the data was well fitted by an order at higher concentration and by another order at lower concentration of prehydrolyzing agent. The order of reaction of pentosan removal lies between 0.8 to 1.40. A regression model was developed for % pentosan removal relating to temperature and time for water prehydrolysis at higher temperatures. This model was well fitted by data given in literature.

Keywords: Hemicelluloses, Pentosan, Prehydrolysis, Arrhenius, Reaction Order

1. Introduction

The interest for producing chemicals from abundant, renewable and low-cost lignocellulosic materials has been increased in the last decade. Biomass residues available from agricultural and forest processing constitute a potential source for production of different chemicals using enzyme or acid catalyzed hydrolysis [18]. Pentosan is one of the important components belonging to hemicelluloses group. In all kinds of fibers of vegetable origin, this group consists of pentacyclic carbohydrates of varying molecular weights with varying degree of polymerization. The unit carbohydrates belonging to this group are termed as pentoses-the monosachharides consisting of D-xylose, D-arabinose, L-arabinose and ribose. Xylose and arabinose are predominant in all natural fibers. The pentosans or pentoses are the major sources of value added products such as Furfural and Hydroxyl methyl furfural which are used in pharmaceutical as well as fuel additives. Furfural is produced by the hydrolysis of xylan rich plant residues. All pentosan containing fibrous materials could be used as raw material for furfural production [18]. Pentosans are also source of bioethanol which can be the major oil substitute in the whole world. The pentosan content in different raw materials is varying from non-wood and wood based fibrous materials. Actually the pentosan content of any fibrous material depends upon the species of that material and the place where it is found. The average pentosan contents of different raw materials are shown in table (1). As shown in table (1), Corn cob has maximum average content of pentosan ranging from 30-40%. Green bamboo, Eucalyptus hybrid has very less pentosan content ranging from 14.50-17.50% and 14.20-15.20% respectively. Non-wood fibrous materials such as rice straw, wheat straw, barley straw, oat straw, rye straw, sugar cane, esparta grasses, sabai grasses, kenaf, jute etc. have higher pentosan content than hardwoods. Coniferous (softwoods) and deciduous (hardwoods) have pentosan content ranging from 7-14% and 19-26% respectively [12]. Attempts have been made by various investigators to produce pentoses and furfural in laboratory as well as in pilot scale. For pentosan removal from different lignocellulosic materials different researchers have been used different acids such as HCl [10], H₂SO₄[1, 22], H₃PO₄ [29] as catalysts and different metallic catalysts such as ZnCl₂, SnCl₂, AlCl₃, CaCl₂ [6] as promoters. Steam treatment (water prehydrolysis at higher
temperature) without any acid catalyst is also used for pentosan removal [9, 16]. Concentration of prehydrolyzing agent, process temperature, liquid to solid ratio and reaction time are main process variables in process of pentosan removal [19]. Liquid to solid ratio did not have very much effect on pentosan removal [9]. In this work experimental data had been taken for analysis from previously published work by different authors. In work of X. Luo et al. [16], green bamboo chips had been used for steam pretreatment. Green bamboo chips heated to different temperatures and maintained here for 0-70 min. The pentosan contents of bamboo chips after steam treatment were determined [9, 16]. Concentration of prehydrolyzing agent can be assumed as constant. For prehydrolysis conditions, reaction involves following steps as described by Bhattacharya et al. [3].

1. The hydrolyzing agent transports from the bulk liquid to the film surrounding the biomass.
2. Diffusion of hydrolyzing agent through the film.
3. Diffusion through the biomass to the reaction sites.
4. Reaction with pentosans.
5. Reaction products follow the reverse path out of the biomass.

In general, the rate of a particular reaction can be expressed as a function of the concentration of the reactants as well as the temperature at which the reaction is being carried out. If prehydrolysis of wood or any biomass is considered, the rate of prehydrolysis at any time would be related to the polymer contents of wood or biomass as well as the concentration of the active prehydrolyzing agent and the temperature of the reaction system. It can be written as:

\[ -r_p = f(P, C, T) \]  

Assuming pentosan removal follows the order w.r.t. content of pentosan in biomass and a order w.r.t. concentration of prehydrolyzing agent, equation (1) can be written as:

\[ -r_p = kP^n C^a \]  

Where, \( k \) contains the temperature effect along the reaction. When the liquid-solid ratio is very high and the temperature remains constant, the concentration of prehydrolyzing agent can be assumed as constant. For constant temperature and constant prehydrolyzing agent concentration equation (2) can be written as:

\[ -r_p = -\frac{dP}{dt} = kP^n \]  

Taking log (base 10) of equation (3) both side,

\[ \log_{10} \left( -\frac{dP}{dt} \right) = n \log_{10} P + \log_{10} k \]  

Comparing equation (4) with equation of straight line, \( y = mx + c \) Where; \( m \) = slope of straight line,
\( c = \) intercept of straight line.

By plotting equation (4) between \( \log_{10}(P) \) and \( \log_{10}(dP/\text{dt}) \), a straight line will be obtained whose slope will give the order of reaction and intercept will give the value of \( \log_{10}(k) \) for reaction. This method is called differential method of analysis of reaction data described elsewhere [14].

\( t = \) time after starting of constant temperature period.

X. Luo et al. [16] studied the pentosan solubility during steam treatment in wide range of reaction conditions. In the heating up period (non isothermal) about 29.5%, 38%, 45% and 58% pentosan was removed till achieving final constant cooking temperatures 160°C, 170°C, 180°C and 190°C respectively. It indicates that during heating up-period some fraction of the pentosan degradates. After heating up period, constant temperature period starts. In table (2), correlations with \( R^2 \) values are given between % pentosan removed and time in min. for Green Bamboo steam pretreatment. From table (2), it is concluded that as reaction temperature increases, the linear relation between two variables becomes less significant. Actually the pentosan removal mechanism is divided into two stages namely the main pentosan degradation phase and the residual pentosan degradation phase [15]. Main pentosan easily degradates but residual pentosan is difficult to degrade. According to Fig.1a, at lower temperatures 160°C to 180°C, no residual pentosan degradates but at higher temperatures such as 190°C residual pentosan degradates. For initial period of reaction when pentosan content is high, the rate of removal of pentosan is high. After initial period, pentosan content in biomass reduces. At this stage rate of removal of pentosan becomes low which indicates residual pentosan degradation phase. Maximum pentosan removed in work of X.Luo and coworkers [16] is about 90% at 190°C for 70 min of reaction period. It shows that it requires more steam pretreatment period for whole pentosan removal at these reaction conditions. According Fig.1b, in heating up period for prehydrolysis of Eucalyptus hybrid about 19.5% pentosan was removed. After heating up period correlation between % Pentosan removal and time is given as %\( PR = 0.503t + 15.91 \) with \( R^2 = 0.975 \). In work of Guha et al. [9] degradation of only main pentosan occurs. It is concluded after study of work of Guha et al. [9] and X. Luo et al. [16] that without using any catalyst and steam pretreatment of biomass till temperature of 180°C, removal of only main part of pentosan takes place. Fig. 1(c) represents work of Bains et al. [2] in which rice straw was hydrolysed using sulphuric acid. Fig.1c clearly shows that as time increases, the rate of pentosan removal decreases. In their work Bains et al. [2] has shown removal of both parts of pentosan. For initial phase of reaction when main pentosan removes correlation is %\( PR = 0.646t + 1.533 \) with \( R^2 = 0.994 \) and for later phase when the degradation of residual pentosan takes place, the

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Correlation</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>160°C</td>
<td>%( PR = 0.456t + 23.76 )</td>
<td>0.987</td>
</tr>
<tr>
<td>170°C</td>
<td>%( PR = 0.446t + 33.47 )</td>
<td>0.983</td>
</tr>
<tr>
<td>180°C</td>
<td>%( PR = 0.477t + 40.58 )</td>
<td>0.917</td>
</tr>
<tr>
<td>190°C</td>
<td>%( PR = 0.335t + 57.58 )</td>
<td>0.857</td>
</tr>
</tbody>
</table>

\( t = \) time after starting of constant temperature period.

### Figures

- **Figure 1a.** Effect of time and temperature on removal of Pentosan. Data taken from X. Luo et al. [16].
- **Figure 1b.** Effect of time at 150°C on removal of pentosan. Data taken from Guha et al. [9].
- **Figure 1c.** Effect of time at 150°C on pentosan removal. Data Taken from Bains et al. [2].

### Table 2. Correlations between %Pentosan removed with time at different temperatures. Data taken from X. Luo et al. [16].

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<td>0.857</td>
</tr>
</tbody>
</table>
correlation is \( PR = 0.076t + 62.26 \) with \( R^2 = 0.997 \). In work of Bains and coworkers [2], about 79\% pentosan removed in 200 min. at reaction temperature 150°C using 1.6\%(w/w) sulphuric acid. In this work about 19\% pentosan removed in heating up period for 40 minutes using 1.6\%(w/w) sulphuric acid but in work of Guha et al. [11] same amount of pentosan removed in 90 minutes using hot water at 150°C. It can be concluded that when acid catalysts are used, high pentosan removal can be obtained at low temperatures also.

In table (3), Kinetic equations for steam pretreatment of Green Bamboo according to work of X. Luo et al. [16] are summarized with \( R^2 \) values. At higher temperature shifting of order of reaction is observed. The shifting of order during biomass prehydrolysis reaction is also observed by some other researchers [5, 30]. According to Fig. 2b, pentosan removal from Eucalyptus hybrid at 150°C hydrolyzed with water has kinetic relation as \( \log_{10} \left( \frac{-dP}{dt} \right) = 1.24 \log_{10} P - 1.122 \) with \( R^2 = 0.97 \) and for low pentosan content region the kinetic equation is \( \log_{10} \left( \frac{-dP}{dt} \right) = 0.81 \log_{10} P - 1.793 \) with \( R^2 = 0.99 \). So order of reaction at high pentosan content region (main pentosan removal) is 1.24 and at low pentosan content region (residual pentosan removal) is 0.81. \( k \) value for high pentosan content region is 0.0755 min\(^{-1}\) and for low pentosan content region is 0.0161 min\(^{-1}\). Wilder et al. [31] had taken data from Walter...
et. al. [30] and shown that pentosan removal follows zero order kinetics. In present study the data of Walters [30] was analyzed and found that at higher temperatures pentosan removal follows order of shifting. Following table (4) has shown the kinetic equations obtained from Walters data [30] in present study.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Kinetic equation</th>
<th>Order of reaction</th>
<th>k</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>173°C (Main Pentosan)</td>
<td>( \log_{10}\left( \frac{dP}{dt} \right) = 1.36\log_{10} P - 2.5836 )</td>
<td>1.36</td>
<td>0.0755</td>
<td>0.98</td>
</tr>
<tr>
<td>186°C (Main Pentosan)</td>
<td>( \log_{10}\left( \frac{dP}{dt} \right) = 1.27\log_{10} P - 2.437 )</td>
<td>1.27</td>
<td>0.0874</td>
<td>0.99</td>
</tr>
<tr>
<td>200°C (Main Pentosan)</td>
<td>( \log_{10}\left( \frac{dP}{dt} \right) = 1.28\log_{10} P - 2.247 )</td>
<td>1.28</td>
<td>0.1057</td>
<td>0.98</td>
</tr>
<tr>
<td>200°C (Residual Pentosan)</td>
<td>( \log_{10}\left( \frac{dP}{dt} \right) = 1.05\log_{10} P - 2.3528 )</td>
<td>1.05</td>
<td>0.0951</td>
<td>0.99</td>
</tr>
<tr>
<td>210°C (Main Pentosan)</td>
<td>( \log_{10}\left( \frac{dP}{dt} \right) = 1.16\log_{10} P - 1.9456 )</td>
<td>1.16</td>
<td>0.1429</td>
<td>0.99</td>
</tr>
<tr>
<td>210°C (Residual Pentosan)</td>
<td>( \log_{10}\left( \frac{dP}{dt} \right) = 0.96\log_{10} P - 2.1742 )</td>
<td>0.96</td>
<td>0.1137</td>
<td>0.97</td>
</tr>
</tbody>
</table>

According to Fig. 3a, % pentosan removed vs. temperature relationship is given as \( \%PR = 1.212T - 158.6 \) with \( R^2 = 0.995 \). This shows approximately a straight line relationship. According to Fig. 3b, the work of Guha et al. [9] shows that at low temperature % pentosan removal increases by lower rate by increasing temperature, but at higher temperature it increases at higher rate by increasing the temperature. The relationship between % pentosan removed vs. temperature is given by \( \%PR = 1.108T - 115.4 \) with \( R^2 = 0.993 \). According to Fig. 3(c), the work of Bains et al. [2] shows that % pentosan removal and temperature relation is of irregular type. A correlation for this data is as \( \%PR = 0.429T + 10.05 \) with \( R^2 = 0.90 \). In all cases, it is shown that at higher temperature, % pentosan removal is greater than lower temperature at higher temperature.

Arrhenius equation is given by,

\[
k = Ae^{\frac{E_a}{RT}}
\]

Taking natural log both side of Arrhenius equation.

\[
\ln k = -\frac{E_a}{RT} + \ln A
\]
A Plot of $\ln k$ versus $\frac{1}{T}$ should yield straight line of slope $-\frac{E_a}{R}$ and intercept $\ln A$. From Fig. 4a to Fig. 4d, the equations between $\ln k$ vs. $\frac{1}{T}$ with pre-exponential factor and activation energies are summarized here.

**Figure 4a.** Relationship between $\ln k$ and $1/T$. Data taken from X. Luo et al.[16].

**Figure 4b.** Relationship between $\ln k$ and $1/T$. Data taken from Guha et al.[9].

**Figure 4c.** Relationship between $\ln k$ and $1/T$. Data taken from Bains et al. [2].

**Figure 4d.** Relationship between $\ln k$ and $1/T$. Data taken from Bains et al. [2].

**Figure 4e.** Relationship between $\ln k$ and $1/T$. Data taken from Wilder et al. [31].

**Table 5.** $\ln k$ vs. $\frac{1}{T}$ relations for different raw materials.

<table>
<thead>
<tr>
<th>Raw material and process</th>
<th>$\ln k$ vs. $\frac{1}{T}$ relation</th>
<th>$E_a$ (kJ/mol)</th>
<th>$A$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green bamboo, steam pretreatment</td>
<td>$\ln k = -4966.0 \frac{1}{T} + 6.889$</td>
<td>41.287</td>
<td>981.45</td>
<td>0.993</td>
</tr>
<tr>
<td>Eucalyptus hybrid, hot water prehydrolysis</td>
<td>$\ln k = -4454.0 \frac{1}{T} + 5.829$</td>
<td>37.031</td>
<td>340.018</td>
<td>0.934</td>
</tr>
<tr>
<td>Rice straw, sulphuric acid prehydrolysis (main pentosan removal)</td>
<td>$\ln k = -3903.0 \frac{1}{T} + 8.291$</td>
<td>32.445</td>
<td>3987.82</td>
<td>0.931</td>
</tr>
<tr>
<td>Rice straw, sulphuric acid prehydrolysis (residual pentosan removal)</td>
<td>$\ln k = -5242.0 \frac{1}{T} + 7.240$</td>
<td>43.582</td>
<td>1394.1</td>
<td>0.941</td>
</tr>
<tr>
<td>Aspenwood, Neutral sulfite pulping</td>
<td>$\ln k = -7696.0 \frac{1}{T} + 12.79$</td>
<td>63.984</td>
<td>$3.58 \times 10^6$</td>
<td>0.98</td>
</tr>
</tbody>
</table>
Wilder and coworkers [31] analyzed Walter Pulping Data and found that Pentosan removal kinetics have activation energy 30.800 KJ/mol and pre exponential factor is $4.26 \times 10^{4.26}$. Findley et al. [5] performed experiments on Red maple (Acer rubrum) and found that log-log plot of reaction rate vs. remaining pentosan resulted in a series of straight lines but the slopes of these lines varies with cooking conditions. They have indicated that pentosan removal follows two first order reactions, one is rapid and other is slow but they could not gave any indication that these reactions are parallel or consecutive. The reaction constants of these two reactions vary with temperature. According to Arrhenius equation the range of these two reaction constants are $3.0.71 \times 10^{-} \text{min}^{-1}$ to $3.68 \times 10^{-3} \text{min}^{-1}$ and $5.12 \times 10^{-3} \text{min}^{-1}$. Activation energy represented by Findley et al. [5] for these two reactions are 294.315 and 209.512 KJ/mol which are very high than other reported values by other authors. X. Luo et al. [16] assumed that pentosan removal follows pseudo-homogenous first order kinetics and reported pre-exponential factor 4331 and activation energy 48.06 KJ/mol. In present study these values are found different than these reported values.

According to Fig.5a, % pentosan removed vs. sulphuric acid plot had been drawn according data taken from Bains and coworkers [2]. The regression relation is written as 

$$
\% PR = 10.11(\%S) + 53.66 \quad \text{with } R^2 = 0.94.
$$

When sulphuric acid percentage is increased then % pentosan removal is also increased. In the work of Bains et al. [2] at 3.5% sulphuric acid about 90% pentosan is removed in 2 hours. In Fig. 5b, % pentosan removal vs. Liquor to solid ratio is shown from data of Guha et al. [9]. The regression relation is written as 

$$
\% PR = 2.35(\text{LSR}) + 39.43 \quad \text{with } R^2 = 0.99.
$$

It is shown that when liquid to solid ratio increased from 3:1 to 5:1, the pentosan removal increased from 46% to 51%. It is concluded that liquid to solid ratio have less effect than other variables.

### 3. Model Development for Pentosan Removal

A non-linear regression model has been developed using Levenberg-Marquardt (LM) algorithm for finding the % pentosan removed in biomass steam pretreatment process for different time and temperatures. The objective function that is minimized is the sum of squares of the errors. To develop this model data is taken from Guha et al. [9] and X. Luo et al. [18]. The non-linear model is as follows.....

$$
y = a_0 + a_1 t + a_2 T + a_3 t T
$$

Where $y$ = % Pentosan removed (Based on total pentosan initially in oven dry material) 
$t$ = time, min., $T$ = temperature in °C.

The values of Different parameters and statistical parameters of this model are as tabulated in Table (6) & (7) respectively.

#### Table 6. Model Parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>95% confidence</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$</td>
<td>-48.96257</td>
<td>25.49</td>
</tr>
<tr>
<td>$a_1$</td>
<td>0.0028025</td>
<td>0.002308</td>
</tr>
<tr>
<td>$a_2$</td>
<td>0.5473429</td>
<td>0.208568</td>
</tr>
<tr>
<td>$a_3$</td>
<td>0.0015339</td>
<td>0.318765</td>
</tr>
</tbody>
</table>

#### Table 7. Statistical Parameters.

<table>
<thead>
<tr>
<th>Statistical Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^2$</td>
<td>0.97</td>
</tr>
<tr>
<td>$R^2_{\text{adj}}$</td>
<td>0.96</td>
</tr>
<tr>
<td>Rmsd</td>
<td>1.0208</td>
</tr>
<tr>
<td>Variance</td>
<td>14.06</td>
</tr>
</tbody>
</table>
4. Conclusion

It has been observed that there is a wide variation in the average pentosan content of the different materials worldwide. In steam prehydrolysis till 170°C only main part of pentosan removes. At higher temperatures residual part of pentosan also degradates. Residual pentosan can also be removed at lower temperatures using acid catalysts. During prehydrolysis of biomass, the order of pentosan removal alters as reaction proceeds. For initial stage of reaction, %pentosan content in biomass is high. For this stage rate of pentosan removal and order of reaction is high. At low pentosan content, rate of removal and order of reaction is low. The order of pentosan removal given by different researchers and found out in this study vary with each other. Average order for main pentosan removal found in this study is approximately 0.84-1.43. For residual pentosan removal approximate order is 0.80-0.97. Activation energy for main pentosan removal lies between 30-40 kJ/mol. For residual pentosan removal it is about 43 KJ/mol. Pre-exponential factor have also large range of variation given by different researchers and found in present study. Pre-exponential factor lies in the range of 340 to 3.58×10⁶. For pentosan removal temperature, time and acid concentration are the main important process variables to affect the process. Solid-liquid ratio has very little effect on pentosan removal.

Nomenclature

\[-r_p = \text{rate of pentosan removal, grams pentosan removed/(100 g. O.D. wood)(min.)}\]

\[n = \text{order of reaction}\]

\[P = \text{unreacted pentosans, gram pentosans/(100g. O.D.charged material)}\]

\[C = \text{concentration of active prehydrolyzing agent}\]

\[k = \text{reaction rate constant, units consistent with order of reaction}\]

\[\%PR = \text{percentage pentosan removed (based on total initial pentosan in material)}\]

\[T = \text{temperature, °C}\]

\[t = \text{time, min.}\]

\[E_a = \text{activation energy, kJ/mol}\]

\[A = \text{pre-exponential factor}\]

\[R = \text{universal gas constant}\]

\[\%S = \text{percentage sulphuric acid (w/w)}\]

References


