Hydrolysis of Palm Tree Midribs with Hydrochloric Acid for Furfural Formation

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Abstract. Waste material samples as pentosan source of midribs from the Sukkaria date palm tree were collected from different Saudi Arabian agricultural areas, and hydrolyzed using hydrochloric acid (HCl) to produce furfural at different temperatures, liquid to solid ratios (LSR) and acid concentrations. A maximum furfural production with a concentration of 755 gm/m$^3$ (72% furfural yield) was achieved, which was close to the theoretical yield at 15 wt% HCl and 100 ml/g LSR at 120°C. The kinetic model for the pentosan fractional hydrolysis towards the production of furfural was previously proposed and developed. Regression analysis of the experimental data was successfully performed using Polymath software with acceptable predictions precision and regression coefficients of $R^2 \geq 0.96$. Furthermore, regressed rate constants of each reaction step in the proposed kinetic model were developed using modified Arrhenius model with an acceptable accuracy of $R^2 \geq 0.96$. Experimental data showed that hydrolysis using hydrochloric acid could achieve higher furfural yields with lower reaction times in comparison with sulfuric acid hydrolysis, due to lower activation energy of the involved steps.

Keywords: Furfural, Palm tree midribs, Hydrochloric acid, Hydrolysis.

1. Introduction

The industrial applications of furfural and its derivatives have gained more importance as strategic commodities [1] since it is a feedstock for many chemical products. Furfuryl alcohol that is derived by furfural hydrogenation can be used in the production of furan resin and cement materials, which are characterized by their high structural resistances, as well as heat transfer properties [2-4]. Furfural can be used to produce biofuels and value-added chemicals [5-6]. Also, it is mainly used as an effective solvent that selectively dissolves and separates aromatics and olefins in oil refineries [1]. Furfural has other important applications in the production of the key product tetrahydrofuran (THF) and can be used also as a fungicide and herbicide [7].

The main source of furfural production is the hydrolysis in acidic media of the lignocellulosic biomass and hemicelluloses with high pentosan content available in some agriculture residues, such as palm tree midribs [8], olive trees [9], sorghum straw [10] and timber [11]. It can be produced also from food processing plant waste, such as sugar cane bagasse [12], olive stones [13], corncobs [14] and rice hulls [1].

Mineral acids were used as a catalyst for hydrolyzing biomass waste materials to produce furfural. Among these acids are
hydrochloric acid (HCl) \cite{15}, nitric acid (HNO_3) \cite{16}, sulfuric acid (H_2SO_4) \cite{17}, and phosphoric acid (H_3PO_4) \cite{18}.

The higher the hydrolysis pressures (10-25 bar) and temperatures (220-240°C) the higher furfural yields \cite{19} and shorter reaction times \cite{20-21} are. Alternatively, furfural can be formed from hemi-cellulosic materials using the acidic ionic liquid (ILs) characterized by their low vapor pressures and flammability, low temperature sensitivity and high solubility with 60-70% furfural yield \cite{22}. The catalytic coproduction of furfural and the important byproduct 5-hydroxymethyl furfural, 5HMF, has been investigated to improve the economic feasibility of the production process \cite{23-27}. Metal oxides as solid acid catalysts and sulfonated biomass carbon materials have increasingly attracted researchers' attention, due to their strong acidity, high active surface area and low temperature sensitivity \cite{28}. Furthermore, furfural was produced using alginic acid derived from macroalgae over Amberlyst-15 solid acid catalyst \cite{29}. However, ILs and solid catalysts are currently expensive and difficult to synthesize. More extensive research is required to improve their performance. Additionally, the economic feasibility of their industrial synthesis process must be considered.

Hydrolysis of pentosan to pentose takes place in acidic solutions as catalysts to accelerate the dissociation of pentosan molecules, which is dehydrated in a subsequent step to furfural. The actual furfural yield that can be obtained is 50-65%, which is dependent on the hydrolysis reaction temperature and acid concentration \cite{21}, while the maximum reported furfural theoretical yield is 72.7% \cite{7}.

Due to the complexity of the liquid phase hydrolysis reactions of solid phase lignocellulosic feedstocks \cite{30}, many investigators proposed reaction steps and used simplified empirical expressions to model the kinetics parameters for each reaction step \cite{31}. Both dilute and concentrated acid hydrolysis can be used to hydrolyze hemicellulose cellulose fractions \cite{9}.

Agriculture wastes are abundantly available with low cost and suitable to produce value-added products. They must be disposed properly. All these factors increase the opportunity of lignocellulosic materials to provide an alternative energy source \cite{9,30}. Saudi Arabia has tremendous quantities of date palm trees. Therefore, it would be more attractive to investigate alternatives that utilize these abundant date palms to produce value-added products, such as furfural and its derivatives.

Recently, we have studied the kinetics and yields of furfural production by hydrolyzing midribs using sulfuric acid \cite{8}. Hydrolysis of lignocellulosic agricultural wastes using hydrochloric acid resulted in a higher yield of furfural as compared to sulfuric acid at the same temperature and acid concentration conditions \cite{32}. Hydrochloric acid is capable of hydrolyzing and breaking the hemicellulosic biomass materials more easily and efficiently than sulfuric acid \cite{33}. Therefore, the purpose of the present work is to study the formation of furfural through the hydrolysis process of the local palm tree midribs, using hydrochloric acid instead of sulfuric acid, which was used in previous work. The key operating parameters of the process, namely reaction temperature, liquid to solid ratio, acid concentration and reaction time were investigated to determine the optimum conditions based on the maximum furfural yield. The obtained experimental data were fit in the previously proposed kinetic model of the hydrolysis reaction to evaluate the derived model.
2. Experimental Procedures

2.1 Raw Materials Preparation and Characterization

Sukkaria palm tree was selected, and midrib samples were collected from agricultural areas in Saudi Arabia. Samples were prepared for analysis and hydrolysis reaction as reported in Bamufleh et al. [8]. In this previous study midrib samples were characterized for pentosan content using Association of Official Analytical Chemists AOAC-36D.

2.2 Hydrolysis Reaction

1500 ml and maximum 10 bars pressure Parr batch glass reactor (5112 model) jacketed and stirred, manufactured by Hastelloy B2 and stainless steel, was used in the hydrolysis reaction. The required acid volume of a given concentration and required raw material with given liquid to solid ratio (LSR) were placed in the reactor. Reaction time was recorded and samples were collected for chemical analysis at specific time intervals. Three values of acid concentrations of 5, 10, and 15 wt %, LSR of 25, 50, and 100 ml/g, and reaction temperatures of 100, 120, and 160°C were experimentally carried out. Detailed reaction procedures were reported in the reference [8].

2.3 Product Analysis

Most articles were likely to have only two levels of headings. 20 μl of periodically collected samples, filtered and diluted with water (1:100 v/v) were injected via a liquid sampling valve for analysis into a Shimadzu HPLC unit. The column 4.6 mm i.d. x 50 mm Shim-Pack XR-ODS was used to investigate the hydrolysis reaction products. A carrier liquid with a composition of 84% of 0.01 N H₂SO₄ and 16% of acetonitrile was utilized. Flow rate of 0.5 ml/min at 4.9 Mpa was regulated during the analysis. The following equation was used to calculate furfural yield:

\[ \text{Yield} = \frac{Y_{act}}{Y_{th}} \times 100 \]  

Where \( Y_{act} \) is the experimental yield (gm) and \( Y_{th} \) is the theoretical yield (gm) when reaction of pentosan to furfural is achieved with 100% conversion. These two yields were calculated as follows:

\[ Y_{act} = C \times V \]  
\[ Y_{th} = \left( \frac{\text{Mwt}_F}{\text{Mwt}_P} \right) \times \left( \frac{\%P}{100} \right) \times W \]

Where \( C \) is the experimental furfural concentration (gm/m³), \( V \) is the mixture volume (m³), \( W \) is the midrib sample mass (gm), \( \% P \) is the pentosan wt% available in the midrib, \( \text{Mwt}_F \) and \( \text{Mwt}_P \) are the furfural and pentosan molecular weights, respectively.

3. Kinetics Model

Based on reported literature complexity of the lignocellulosic materials, hydrolysis reactions kinetics were simplified by proposing pseudo-homogenous first order irreversible reactions [9,15,30]. This approach was applied with the assumption that a fraction of pentosan in the raw material was easy and fast to hydrolyze, while the remaining pentosan fraction was difficult and slow to hydrolyze. Accordingly, the parameter \( \alpha \) was introduced in the kinetic model as the fast-decomposed mass fraction of pentosan [13,31]. The first reaction started with the formation of pentose from pentosan, then progressively continued to other undesired decomposition products, as shown below [9,15,30,31].

\[
\begin{align*}
\text{Pentosan (s)} & \xrightarrow{k_1} \text{Pentose (aq)} \\
& \xrightarrow{k_2} \text{Furfural (aq)} \\
& \xrightarrow{k_4} \text{Decomposition products (aq)} \\
& \xrightarrow{k_3} \text{Decomposition products (aq)}
\end{align*}
\]

Where \( k_1, k_2, k_3 \) and \( k_4 \) are the rate constants in (min⁻¹). The previously derived kinetic model of the differential equations describing the above reactions system was as follows [8]:

\[ C_P = \alpha C_{P0} e^{-k_1 t} \]  
\[ C_S = \frac{\alpha k_1 C_{P0}}{(k_2+k_3)-k_1} \left( e^{-k_1 t} - e^{-(k_2+k_3)t} \right) \]
\[
C_F = \frac{a k_1 k_2 C_{P0}}{(k_2 + k_3) - k_1} \left( \frac{e^{-k_3 t} - e^{-k_4 t}}{k_4 - k_1} - \frac{e^{-(k_2 + k_3) t} - e^{-k_4 t}}{k_4 - (k_2 + k_3)} \right)
\] (7)

Where \(C_F\) is the concentration of pentosane, \(C_{P0}\) is the initial concentration of pentosan in the raw material, \(C_S\) is the concentration of pontose, \(C_F\) is the furfural concentration (mol/liter) and \(t\) is hydrolysis time (min).

4. Experimental Data Analysis

4.1 Characterization of Midribs

Midribs’ pentosan content was determined in the previous study by Bamufleh et al. \[8\] as 14.52 wt% providing a reasonable amount of pentosan in comparison to that available in other reported lignocellulosic materials employed as raw materials for furfural production.

4.2 Furfural Production

Various conditions of acid concentration, reaction temperature and LSR of the hydrolysis reaction were selected to study their parametric effects on furfural concentration and yield. The experimental results were analyzed and discussed in the following subsections.

4.3 Acid Concentration Parameter

Hydrolysis reactions were carried out at acid concentrations of 5, 10 and 15 wt%, at a LSR of 100 and a temperature of 120°C. Furfural concentrations at various elapsed times were plotted, as shown in (Fig. 1). As shown in this figure, higher furfural yields were obtained at faster times with higher acid concentrations. Figure 1 shows clearly that for 15% acid concentration maximum furfural concentration is achieved faster at 755 gm/m³ in 10 mins compared to 5% and 10% with maximum furfural concentrations at 640 gm/m³ in 210 min and 700 gm/m³ in 60 min respectively. Furfural concentration started to decrease after reaching its maximum value, the point beyond which the rate of furfural production was expected to be less than the rate of furfural decomposition. The first point with 10 wt% acid didn't fall in the same trend with the rest of the points and it occurs in the early stage of the main reactions toward furfural production. It is apparently due to other rapid side reaction(s) that proceed to produce furfural and other side products.

4.4 Reaction Temperature Parameter

Hydrolysis reactions at temperatures of 100, 120 and 160 °C, at 10% acid concentration and 50 ml/g LSR were shown in Fig. 2. Data in this figure indicated that the maximum concentration of 1266 gm/m³ (a maximum furfural yield of 60%) was obtained at 120°C after 60 minutes of hydrolysis, after which it decreased rapidly, because the furfural loss rate was much faster than the formation rate. Increasing the reaction temperature from 100°C to 120°C increased the obtained furfural concentrations, indicating that higher furfural concentration and yield were favored by higher temperatures within this range. On the other hand, increasing the reaction temperature to 160°C, a maximum furfural concentration value of 400 gm/m³ (a maximum furfural yield of 19%) was obtained after 5 minutes hydrolysis time compared to 1266 gm/m³ (a maximum furfural yield of 60%) after 60 minutes hydrolysis time at 120°C. This clearly indicated that furfural competing reactions were more pronounced at 160°C. This might also be attributed to the effect of the higher temperature, which reduced hydrogen ion concentration, thus lowering the water dielectric constant and consequently making an insignificant impact of the acid concentration on the furfural formation kinetics data.

4.5 LSR Parameter

The effect of LSR at values of 25, 50 and 100 at 120 °C and 10 wt% acid concentration on
the measured furfural concentrations during the hydrolysis reaction was depicted in Fig. 3. Higher LSR values, which implied a lower limiting reactant, decreased the obtained furfural concentration with time. The maximum furfural concentration for all LSRs was obtained at 60 minutes. Moreover, the maximum achievable furfural concentration was decreased from 2097 gm/m³ (50% furfural yield) to 1266 gm/m³ (60% furfural yield) and 700 gm/m³ (66% furfural yield) at LSR of 25, 50 and 100 respectively since only LSR changed, while the kinetic parameters (k₁-k₄) remained unchanged at the same reaction temperature and acid concentration.

4.6 Side Products Formation

The cost of the furfural production process was considerably influenced by the maximum achievable furfural yield with the accompanied side products. Moreover, the formation of side products required a separation process for a treatment purpose to achieve the desired product specifications. Table 1 summarizes the reaction time required to produce the maximum furfural yield and concentration obtained at different operating conditions, along with the corresponding concentration of furfuryl alcohol, 5-hydroxymethyl furfural (5HMF), 5 methyl furfural (5MF) and 2 acetyl furan side products. Table 1 shows that the highest achieved furfural yield was 72%, which was produced in 20 minutes at an acid concentration of 15 wt%, LSR of 100 and 120°C. Figure 4 shows furfural yield at this operating condition measured at different reaction times.

Side products were considered as valuable products, due to their industrial applications. For example, furfuryl alcohol was used for the production of tetrahydrofurfuryl alcohol, fibers, rubbers and for enforcing ceramic resins [34]. Also, 5-hydroxymethyl furfural (5HMF) was used for plastics productions [35]. However, it should be noted that the side product content of 5 methyl furfural (5MF) should be less than 1% in furfural product specification [7]. Side products concentrations with time at the optimum operating condition are shown in Fig. 5.

4.7 Kinetics Parameters

Derived nonlinear model presented in Eq. 7 was used to fit the collected kinetic data of furfural yield from palm tree midribs at different experimental conditions. Polymath 5.1 software was used in the nonlinear regression analysis. Table 2 presents the optimum regression analysis values of k₁ to k₄, and α for all acid hydrolysis reactions at different operating conditions.

Table 2 shows that all k values increased with reaction temperature and acid concentration. Regressed α values, (0.60-0.94), fell within the same reported ranges of (0.84-0.86) and (0.55-1) reported by Eken-Saracoglu et al. [20] and Aguilar et al. [31] respectively. Regression of the experimental data at different acid concentrations and reaction temperatures using Eq. 7 resulted in satisfactory fit, as evidenced by R² ≥0.9 as shown in Fig. 1-3. The higher value of k₁ compared to k₂-k₄ values indicated a faster rate of pentosan to pentose reaction step, and the reaction steps that followed controlled the final furfural production.

The modified Arrhenius equation was used to estimate the rate constant for a given reaction temperature and acid concentration. It was expressed as follows [9,13,30,31,36]:

\[ k_i = aC^b exp\left(-\frac{E}{RT}\right) \]  

(8)

Where a and b are regression parameters, C is the acid concentration in wt%, E is the activation energy in kJ/mol, R is the universal gas constant in kJ/(mol K), and T is the reaction temperature in K.
Fig. 1. Date Tree midribs, 0.25-0.5mm, Acid = HCl, 5-15wt%, LSR =100, Hydrolysis Temp = 120°C.

Fig. 2. Date Tree midribs, 0.25-0.5mm, Acid = HCl, 10wt%, 250ml, LSR =50 Hydrolysis Temp = 100-160°C.

Fig. 3. Date Tree midribs, 0.25-0.5 mm, Acid = HCl, 10wt%, LSR =25-100, Hydrolysis Temp = 120°C.
Table 1. Summary of different reaction conditions with corresponding maximum furfural yields and concentrations using hydrochloric acid.

<table>
<thead>
<tr>
<th>Acid Conc. (wt%)</th>
<th>LSR (ml/g)</th>
<th>Temp, (°C)</th>
<th>Time (min)</th>
<th>Max Yield (%)</th>
<th>Max Furfural Concentration (ppm)</th>
<th>5HMF</th>
<th>5MF</th>
<th>Furfural Alcohol</th>
<th>2 Acetyl Furan</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>100</td>
<td>120</td>
<td>210</td>
<td>60</td>
<td>640</td>
<td>15</td>
<td>2</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>140</td>
<td>30</td>
<td>41</td>
<td>435</td>
<td>15</td>
<td>2</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>25</td>
<td>120</td>
<td>60</td>
<td>50</td>
<td>2097</td>
<td>70</td>
<td>14</td>
<td>21</td>
<td>7</td>
</tr>
<tr>
<td>10</td>
<td>50</td>
<td>100</td>
<td>330</td>
<td>44</td>
<td>924</td>
<td>16</td>
<td>2</td>
<td>12</td>
<td>4</td>
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<tr>
<td>5</td>
<td>50</td>
<td>120</td>
<td>60</td>
<td>60</td>
<td>1266</td>
<td>37</td>
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<td>60</td>
<td>66</td>
<td>700</td>
<td>18</td>
<td>2</td>
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<tr>
<td>15</td>
<td>25</td>
<td>120</td>
<td>5</td>
<td>25</td>
<td>1063</td>
<td>72</td>
<td>1</td>
<td>332</td>
<td>145</td>
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<tr>
<td>15</td>
<td>100</td>
<td>120</td>
<td>10</td>
<td>72</td>
<td>755</td>
<td>15</td>
<td>2</td>
<td>45</td>
<td>2</td>
</tr>
</tbody>
</table>

Fig. 4. Furfural yield using 0.25-0.5 mm date tree midribs, 15 wt% HCl, LSR=100, Temp=120°C.

Fig. 5. Side products distribution using 0.25-0.5 mm date tree midribs, 15 wt% HCl, LSR=100, Temp=120°C.
It is advantageous to validate and compare the model prediction of $k$ values with reported 
models in the literature that used closer acid 
concentrations, temperature ranges and different 
agricultural wastes. Herrera and his workers [30] 
proposed the kinetic parameters $k_1$ and $k_2$ for the 
hydrolysis of sorghum, using 2-6 wt% HCl at 
122°C as follows:

$$k_1 = 0.00261C_a^{1.41}$$

$$k_2 = 0.0009C_a^{0.93}$$

Where $C_a$ is the wt% acid concentration. Eq. 9 
and 10 underpredict the value of $k_1$ (0.016 
compared to regressed value of 0.111) and $k_2$ 
(0.004 compared to regressed value of 0.015) 
at 5wt% HCl and 120°C. This might be due to 
different raw materials used in both cases and 
thus different side products.

Since there was no correlation available in 
literature that was suitable for predicting k 
values at acid concentrations higher than 6 
wt%, modified Arrhenius correlations to 
predict $k_1$-$k_4$ at acid concentrations in the 
range of 5 to 15 wt%, could be developed by 
nonlinear regression analysis of $k$ values at 
different conditions, using Polymath 5.1 
software. The resulted correlations showed 
satisfactory predictions with the correlation 
coefficients $R^2 \geq 0.96$ as presented in Table 3.

Where C is HCl concentration in wt %, T is 
the hydrolysis reaction temperature in Kelvin 
and $R$ is the universal gas constant in kJ/mol 
K. It was observed from Equation (11) that the 
pentosan hydrolysis to pentose reaction ($k_1$) 
had the lowest activation energy which 
indicated that this reaction was the fastest step 
relative to the other reaction steps and thus 
highest $k_1$ values. The activation energies for 
the other reactions were higher than the first 
reaction, due to lower $k_2$-$k_4$ values and slower 
reaction rates accordingly.

Natural log of $k_1$, $k_2$, $k_3$, and $k_4$ versus 
the reciprocal of the absolute reaction 
temperature (1/T) were plotted as shown in 
Fig. 6 at 10 wt % acid concentration and LSR 
of 50. Modified Arrhenius equation was 
satisfied, since kinetic data were fit in almost 
straight lines for all $k$ values with their 
corresponding reaction temperatures. The low 
$R^2$ value associated with fitting $k_2$ and $k_3$ are 
probably due to other side reactions beside $k_2$ 
and $k_3$ corresponding reaction steps which 
were not considered in the proposed full 
reaction configuration.

Romero and his workers [9] proposed a 
correlation that predicted insoluble fraction, 
100(1-α) g/100 g raw material, linearly with 
temperature and nonlinearly with acid 
concentration. With an attempt to correlate α 
regression output of this work with the 
corresponding temperatures and acid 
concentrations using similar proposed 
correlation, the following correlation was 
obtained:

| Table 2. Regression values of $k_1$- $k_4$ and $\alpha$ at different acid concentrations and temperatures. |
|---|---|---|---|---|---|---|
| HCl %wt | T °C | $a$/g | $k_1$/(min)$^{-1}$ | $k_2$/(min)$^{-1}$ | $k_3$/(min)$^{-1}$ | $k_4$/(min)$^{-1}$ | $R^2$ |
| 5  | 120 | 0.600 | 0.111 | 0.015 | 0.001 | 0.001 | 0.99 |
| 5  | 140 | 0.658 | 0.221 | 0.152 | 0.069 | 0.009 | 0.97 |
| 10 | 100 | 0.741 | 0.326 | 0.004 | 0.0001 | 0.003 | 0.99 |
| 10 | 120 | 0.843 | 0.390 | 0.080 | 0.037 | 0.012 | 0.96 |
| 10 | 160 | 0.917 | 0.447 | 0.410 | 0.269 | 0.136 | 0.99 |
| 15 | 120 | 0.940 | 0.996 | 0.136 | 0.065 | 0.031 | 0.99 |

| Table 3. Modified Arrhenius correlations for $k_1$-$k_4$. |
|---|---|
| Correlations | $R^2$ |
| $k_1 = 0.0172 \times C^{2.152}e^{(-0.5874 \times 10^4)/RT}$ | 0.96 |
| $k_2 = 1.01 \times 10^5C^{0.749}e^{(-5.093 \times 10^4)/RT}$ | 0.96 |
| $k_3 = 1.008 \times 10^4C^{1.028}e^{(-5.49 \times 10^4)/RT}$ | 0.96 |
| $k_4 = 9.991 \times 10^5C^{1.702}e^{(-6.295 \times 10^4)/RT}$ | 0.97 |
\[ \beta = (842.524 - 4.172T)C^{-1.299} \quad (15) \]

Where \[ \beta = 100(1 - \alpha) \quad (16) \]

The regression output for fitting the experimental data with (5-15 wt%) HCl and (100-160°C) to Eq. 15 yields \( R^2 = 0.95 \). The regression parameters of Eq. 15 were quite different from Remero's correlation, which might be attributed to the difference in the raw material composition used in both cases. However, this correlation, beside Eq. (11-14), could be used in the hydrolysis of midribs from date palm tree reactor design.

5. **Comparison with Sulfuric Acid Hydrolysis**

Hydrolysis data of midribs with hydrochloric acid was compared with sulfuric acid hydrolysis data in our previous work [8]. The optimum condition obtained with HCl hydrolysis gave an excellent furfural yield (72%), which was close to the theoretical yield (72.7%) at 15 wt% HCl, 120°C and 100 LSR compared to H2SO4 hydrolysis, which gave a furfural yield of (53%) at 15wt% and 120°C and 50 LSR. In addition to the higher furfural yield obtained with HCl hydrolysis, a lower initial concentration was required as compared to hydrolysis with H2SO4 (LSR of 100 with HCl compared to 50 with H2SO4).

Furthermore, faster reactions and higher furfural yields were observed with HCl acid as compared to H2SO4 at the same conditions. For example, at 5 wt% HCl and 120°C, maximum furfural yield of 60% was achieved at 210 minutes, while it took 240 minutes to reach a maximum yield of 22% at the same conditions with sulfuric acid hydrolysis. Similarly, at 10 wt% HCl and 120°C the maximum furfural yield of 60% was achieved at 60 minutes as compared to 180 minutes to reach a maximum yield of 25% at the same conditions. Increasing HCl concentration from 5 to 15 wt% expedited the reaction significantly, while in the case of H2SO4 the concentration increase did not affect the hydrolysis time, until 15% was used. On the other hand, increasing the temperature with HCl hydrolysis caused faster reactions and higher furfural yields than H2SO4 hydrolysis. This could be attributed to lower activation energy values for furfural formation reactions steps with HCl as compared to the corresponding ones using H2SO4 hydrolysis as shown in Table 4. The activation energy for the reaction steps \( k_1 \) through \( k_4 \) are estimated from the natural exponential term \( e^{-E/RT} \) in the Equations 11 through 14 respectively.

So, hydrolysis of palm tree midrib in hydrochloric acid produced more furfural as compared to sulfuric acid, and hence it was recommended to consider the application of hydrochloric acid with higher concentrations as a catalyst in the industrial hydrolysis process of palm tree midribs to achieve higher yields and produce more desirable furfural products.

6. **Conclusions**

Furfural could be produced by HCl hydrolysis of pentosane that exists in palm tree midribs as an agricultural waste with an achievement of 72% maximum furfural yield. This actual yield was close to the theoretical yield (72.7%) at reaction conditions of temperature as 120°C, acid concentration as 15 wt% and LSR as 100. Experimental data showed that furfural yield is function of reaction temperature, acid concentration and LSR. The kinetic model of the furfural production reactions that was derived in a previous work was used in the regression of the experimental furfural concentrations obtained in this work with acceptable predictions and regression coefficients of \( R^2 \geq 0.96 \). Furthermore, the rate constants of the reaction steps as well as the hydrolyzed fraction were correlated using modified Arrhenius model at the reaction conditions. The derived correlations could provide a
preliminary design basis for the optimization of the hydrolysis reactor configuration. Finally, comparison with the sulfuric acid hydrolysis showed that using hydrochloric acid higher furfural yields were achieved and lower reaction times were required due to lower activation energy of the involved step.

![Graph showing ln(k1) vs. 1/T for HCl](image)

Fig. 6. Fitting k1-k4 values with (1/T) at 10 wt% HCl.

Table 4. Activation energy comparison for the reactions steps with HCl and H2SO4.

<table>
<thead>
<tr>
<th>Reaction Step</th>
<th>Activation Energy, kJ/mol</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>With HCl</td>
</tr>
<tr>
<td>k1</td>
<td>5.87</td>
</tr>
<tr>
<td>k2</td>
<td>50.93</td>
</tr>
<tr>
<td>k3</td>
<td>54.90</td>
</tr>
<tr>
<td>k4</td>
<td>62.95</td>
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</tbody>
</table>

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Hydrolysis of Palm Tree Midribs with Hydrochloric Acid for Furfural Formation


309-318.


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The present study deals with the collection of palm tree fronds from different geographical locations in Saudi Arabia as a source of pentose, followed by its hydrolysis using hydrochloric acid (HCl) at different temperatures and concentrations of liquid to solid ratio (LSR) for furfural production. The maximum furfural yield of 755 g/kg (72% of the highest yield) was obtained under 15% weight percent of hydrochloric acid and 100/1 LSR at 120 °C. In a previous study, a mathematical model for partial hydrolysis of pentose to furfural was proposed and validated by the software Ploymath. The correlation between the predicted results and the experimental data was found to be R² ≥ 0.96. In addition, a mathematical model for the reaction rate constant for each step using the Arrhenius model was proposed, and the correlation between the predicted results and the experimental data was found to be R² ≥ 0.96. The experimental results showed that hydrolysis using HCl acid can produce higher furfural quantities in shorter times compared to using sulfuric acid, due to a decrease in the activation energy of the step involved.

Keywords: Furfural, Palm fronds, Hydrochloric acid, Hydrolysis.