Kinetic studies on acid catalysed hydrolysis of starch

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Acid hydrolysis of wheat flour (particle size, 4 µm) was carried out in a batch reactor between 75-95°C at varying acid concentrations (pH 2-5). Maximum (42%) conversion of starch to reducing sugar was obtained at 95°C and pH 3. Reaction follows First-order rate equation with respect to starch concentration and dependence of reaction rate constant \( k \) on pH is incorporated. Activation energy (\( \Delta E \)) and frequency factor (\( A \)) of reaction were 7806 \( R \) and \( 6.583 \times 10^6 \) \( 1/[f(pH)] \) respectively. Time dependent conversion was observed with variation of temperature, pH and initial starch concentration within relative error of 19%.

Keywords: Acid hydrolysis, Batch reactor, Kinetic studies, Starch, Wheat flour

Introduction

Starch is the principal component of most seeds (maize, rice and wheat), tubers (potato) and roots (arrowroot and tapioca). Most commercial starch is produced from maize\(^1\) (61%), followed by wheat (65%), tapioca (63%) and potato (75%). Starch hydrolysis is expressed as\(^2,3\)

\[
(C_6H_{10}O_5)_n + n \text{H}_2\text{O} = n \text{C}_6\text{H}_{12}\text{O}_6. \]

Starch D-glucose

First sweetener created from starch was syrup produced in Japan during the 9th century by action of malt upon arrowroot starch\(^2\). Starch hydrolysis was first practiced in 1842 commercially in USA\(^4\). In 1984, kinetics of hydrolysis of sorghum molasses have been derived from experimentally determined hydrolysis rate constants as function of the acid concentration and temperature\(^5\). In 1997, physico-chemical and functional properties of \textit{Canavalia ensiformis} starch\(^6\) hydrolyzed with HCl were studied. In 2003, kinetics of acid hydrolysis of cellulose\(^7\) was first described as two pseudo-homogeneous consecutive First-order reactions. In 2005, starch was hydrolysed to produce mono- and oligosaccharides under hydrothermal conditions with and without carbon dioxide (CO\(_2\)) in a small batch reactor\(^8\). The yield of glucose produced from hydrolysis of starch at 200°C increased significantly from 3.7% to 53.0% of initial polysaccharides by increasing CO\(_2\) load in a reaction time of 15 min.

This study determines order of hydrolysis reaction, rate constant and its variation with temperature and pH of starch slurry, correlation with Arrhenius equation and studies various parameters that affect kinetics of acid catalyzed hydrolysis of starch.

Materials and Methods

Chemicals were of analytical grade. Analysis of commercially available wheat starch (particle diam, 4 µm) gave following values: starch, 57.8; Protein, 14; fat, 1.0; moisture, 16; ash, 0.8; fiber, 0.6%; and reducing sugar, 9.0%. HCl (35% w/w) was used as catalyst. Fehling solution was prepared by making two solution, one by dissolving \(6.928 \times 10^{-3}\) kg of crystallized CuSO\(_4\) (99% pure) and 4-6 ml concentrated H\(_2\)SO\(_4\) in water (1 l) and other by dissolving \(3.50 \times 10^{-3}\) kg of Rochelle salt (97% pure) and \(1.00 \times 10^{-3}\) kg of NaOH (97% pure) in water (1 l). When equal volume of each solution are mixed the resulting liquid is Fehling solution.

Experimental Procedure

Hydrolysis of starch was performed in a conical shaped glass reactor with thermometer well and sample trapping pocket provided in the middle portion of reactor. A water condenser (standard B 24 joint) is fitted on the
mouth of reactor to avoid loss of HCl and water vapor. This reactor was immersed in a thermostatic water bath. This whole reactor system was housed on a magnetic stirrer operated at a fixed rpm throughout the reaction for all sets of experiments.

Wheat starch (5×10⁻³ kg) was charged into clean reactor. Distilled water (300 ml), heated to a fixed temperature, at which the reaction is to be carried out, is poured into it with simultaneously adding dilute HCl. A mercury glass thermometer (scale 10-150°C) is inserted into contents of reactor. Reaction mixture is always in stirring condition to maintain the reaction medium in suspended state. Contents of reactor attained desired temperature within 10 min. Reactions were conducted at pH 2-5 and temperature 75-95°C. After desired hydrolysis, insoluble protein, fat and some inorganic components present initially in starch were separated by filtration.

Initial concentration of starch (c₀) present in reaction mixture is 9.63 kg/m³. First series of experiments of acid hydrolysis of starch was conducted at 85°C and pH 3 (Fig. 1). Linearity of plot indicates that acid hydrolysis of starch follows First-order reaction. Rate constant obtained from this plot is 1.936×10⁻³ min⁻¹ at 85°C. Other set of experiments was done using 5×10⁻³ starch slurry and dilute HCl maintaining pH 3 at 75 and 95°C (Fig. 2). Rate constants from Fig. 2 at 75°, 85° and 95°C were obtained as 1.340×10⁻³, 1.936×10⁻³ and 4.661×10⁻³ min⁻¹, respectively. Arrhenius equation is as follows:

\[ k = A e^{-\frac{\Delta E}{RT}} \]  

where, k is rate constant at temperature T in K, A is frequency factor (preexponential term), \( \Delta E \) is activation energy.

Reaction mixture (10 ml) was drawn out to analyse the total reducing sugar consisting of maltose, isomaltose, dextrose by titrimetric method⁹.

**Results and Discussion**

**Kinetic Model**

Integrated form of kinetic equation is

\[ \ln \left( \frac{c_0}{c(t)} \right) = kt + \text{constant} \]

where, \( c_0 \) = initial concentration of starch, kg/m³; \( c \) (\( c_0 - c_{\text{disappear}} \)) = concentration of starch, kg/m³ at time t; and k = rate constant. So, final expression becomes

\[ \ln \left( \frac{c_0}{c_0 - c_{\text{disappear}}} \right) = kt \]

Fig. 1 — Plot of \( \ln(c_0 / c) \) versus reaction time (t) at 85°C and pH 3

Fig. 2 — Plot of \( \ln(c_0 / c) \) versus reaction time (t) at pH 3 and different temperatures of reacting system

Fig.: 3 Arrhenius plot for First order rate constant at 75-95°C and pH 3
Table 1—Experimental and calculated values of rate constant at pH 3

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Experimental best-fit values (min(^{-1}))</th>
<th>Calculated (k) values (min(^{-1})) from Eq. (2)</th>
<th>% Relative error of (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>1.340×10(^{-3})</td>
<td>1.205×10(^{-3})</td>
<td>10.0</td>
</tr>
<tr>
<td>85</td>
<td>1.936×10(^{-3})</td>
<td>2.253×10(^{-3})</td>
<td>-16.4</td>
</tr>
<tr>
<td>95</td>
<td>4.661×10(^{-3})</td>
<td>4.073×10(^{-3})</td>
<td>12.6</td>
</tr>
</tbody>
</table>

Table 2—Experimental and calculated values of rate constant at different pH

<table>
<thead>
<tr>
<th>(k(358.15, \text{pH } n))</th>
<th>Experimental best-fit values (min(^{-1}))</th>
<th>Calculated values (min(^{-1})) from Eq. (3)</th>
<th>% Relative error of (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k(358.15, \text{pH } 2))</td>
<td>1.538×10(^{-3})</td>
<td>1.793×10(^{-3})</td>
<td>-16.6</td>
</tr>
<tr>
<td>(k(358.15, \text{pH } 3))</td>
<td>1.936×10(^{-3})</td>
<td>2.257×10(^{-3})</td>
<td>-16.6</td>
</tr>
<tr>
<td>(k(358.15, \text{pH } 4))</td>
<td>1.761×10(^{-3})</td>
<td>2.069×10(^{-3})</td>
<td>-17.5</td>
</tr>
<tr>
<td>(k(358.15, \text{pH } 5))</td>
<td>1.660×10(^{-3})</td>
<td>1.976×10(^{-3})</td>
<td>-19.0</td>
</tr>
</tbody>
</table>

Using data from Fig. 2 and Fig. 3, \(\Delta E = 64.899 \times 10^6\) J/kmole of starch and \(A = 6.583 \times 10^6\) were obtained. Putting values of \(\Delta E\) and \(A\) in Eq. (1)

\[
k(T)_{pH3} = 6.583 \times 10^6 \exp\left(-7806/T\right)
\]  

(2)

Using Eq. (2), \(k\) values and % relative error \([((\text{experimental best-fit value} \times \text{calculated value}) / \text{experimental best-fit value}) \times 100]\) are calculated (Table 1). In other sets of experiments at 85°C with different pH of starch slurry, \(k\) values with different pH are as follows: pH 2, 1.538×10\(^{-3}\) min\(^{-1}\); pH 3, 1.936×10\(^{-3}\) min\(^{-1}\); pH 4, 1.761×10\(^{-3}\) min\(^{-1}\); and pH 5, 1.660×10\(^{-3}\) min\(^{-1}\).

Effect of pH on Kinetics

Experimental data fit the following polynomial equation:

\[
f(pH) = (-0.066)(pH)^3 + (0.771)(pH)^2 + (-2.862)(pH) + 4.425
\]

Variation of pH is treated as catalytic effect. Assuming average activation energy over the experimental range of temperature \(f(pH)\) is annexed with frequency factor, \(k(T, pH)\) gives variation of \(k\) with pH at temperature \(T\) as (Fig. 4)

\[
k(T, pH) = k(T, pH3) / f(pH)
\]

where, \(k(T, pH3)\) is obtained from Eq. (2). Therefore, kinetic model of rate constant is written from Eq. (2) as (Table 2)
Predictive accuracy of the model is to be verified by experimental data, which are not used for developing kinetic model. For this reason, a set of experimental data was generated by taking concentration of starch \(c_0\) 7.71 kg/m\(^3\) at 85°C and pH 3 (Table 3). Thus experimental best-fit value of rate constant, \(k\) is \(1.936\times10^{-3}\) min\(^{-1}\). This will also confirm that kinetics of hydrolysis reaction is independent of initial concentration of starch at a particular temperature.

### Conclusions

At pH 3, maximum conversion of starch to reducing sugar was 21% (at 85°C) and 42% (at 95°C). Effect of pH on reaction kinetics indicates that hydrolysis of starch occurs via parallel First-order reaction paths. The model is adequate for the range of acid concentration studied at 85°C, predicting experimental conversion data within 19% relative error. On an average, the model is working well. Error comes from scattering of experimental data because of non-attainment of reaction temperature instantaneously within 10 min and titrimetric analysis.

### Acknowledgement

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### References