Kinetics of in situ and in vitro gelatinization of hard and soft wheat starches during cooking in water

Mahir Turhan a,*, Sundaram Gunasekaran b

a Department of Food Engineering, University of Mersin, Ciftlikkoy, Mersin 33342, Turkey
b Biological Systems Engineering Department, University of Wisconsin, Madison, WI 53706, USA

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Abstract
Kinetics of in situ and in vitro gelatinization of hard (T. durum) and soft (T. aestivum) wheat starches were investigated during cooking in water at 60°C, 70°C, 80°C, 90°C, and 100°C. At the given temperatures, the gelatinization process ceased before 100% completion at a final degree of gelatinization (FDG) for all starches. At the same temperature, the FDG was higher for the in vitro gelatinization than the in situ gelatinization for both hard and soft wheat starches. It was higher for the soft wheat starch than the hard wheat starch for both in situ and in vitro processes. Effect of temperature on the FDG was assessed through a Clausius–Clapeyron type equation. Starch gelatinization followed first-order reaction kinetics for both in situ and in vitro processes. The reaction rate constant \( k_r \) was higher for the in vitro gelatinization than the in situ gelatinization for both starches. It was higher for the soft wheat starch than the hard wheat starch for both processes. The \( k_r \) values were in the order of \( 10^{-5} \) to \( 10^{-4} \) s\(^{-1} \) for the in situ gelatinizations and \( 10^{-4} \) to \( 10^{-3} \) s\(^{-1} \) for the in vitro gelatinizations. The rate of the gelatinization reaction increased with increasing temperature and the effect of temperature on \( k_r \) was evaluated using an Arrhenius type equation. In vitro gelatinizations had an average activation energy \( (E_a) \) of 76 kJ/mol between 60°C and 100°C. In situ gelatinizations had an average \( E_a \) of 137 below 75°C, and 79 kJ/mol above 75°C. Assuming the in vitro gelatinizations were effectively controlled by the reaction of starch with water between 60°C and 100°C, the in situ gelatinizations were effectively controlled by water transfer below 75°C and reaction of starch with water above 75°C. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Cooking of whole grains is the first step in the production of instantized cereal products such as breakfast cereals, hot cereals, and other whole grain foods (Kent & Evers, 1994). The purpose of cooking is to convert the raw grain into a palatable, digestible, and workable form through gelatinization of starch in it. Gelatinization of starch has been recognized as a first-order irreversible reaction and described by the following scheme (Lund & Wirakartakusumah, 1984):

\[
\text{water} + \text{ungelatinized starch} \rightarrow \text{gelatinized starch}_{\text{heat}}
\]

\[
\ln \beta = \ln \beta_0 - k_r t,
\]

where \( \beta \) is concentration of ungelatinized starch (%), \( \beta_0 \) is concentration of ungelatinized starch at the beginning of cooking (100%), \( k_r \) is reaction rate constant (s\(^{-1} \)), and \( t \) is cooking time (s).

Kinetics of starch gelatinization can be investigated in liquid water or steam either in vitro using pure starch or in situ using whole grain. In case of the in vitro gelatinization, there is no physical barrier between starch granules and water molecules, and starch is readily accessible to water. The reaction rate constant \( (k_r) \) obtained from such a system is the true rate constant, only if the starch granules keep the in situ intact characteristics in the whole grain. In case of the in situ gelatinization, starch granules are immobilized in the grain matrix forming physical barrier between water molecules and starch granules. Water must go through the resistance at the kernel surface and within the kernel, and then can meet the starch granules for the reaction. Gelatinization takes place in parts of the whole grain where water content is high enough, e.g., water/starch \( \geq 0.75 \) (Hoseney, 1994).
Water molecules participating in the reaction are held by the gelatinized starch granules while the remaining travel forward (Bakshi & Singh, 1980). The reaction rate constant from such a system is the apparent rate constant, which is a combined form of the true \( k_r \) and the grain resistance against the water transfer.

While the true \( k_r \) is affected by the characteristic attributes of the starch granules, the apparent \( k_r \) is additionally affected by the characteristic and geometrical attributes of the whole grain. In other words, the partition of water molecules between starch granules and cooking medium, and the gelatinization reaction are dominant in the course of the in vitro process. However, during the in situ process, the partition of water molecules between whole grain and cooking medium, and water transfer within the grain in addition to the characteristic attributes of the immobilized starch granules are the dominant factors. The in situ system can also offer much more resistance to the heat transfer from the cooking medium than the in vitro system. Consequently, under the same cooking conditions it takes longer for the in situ gelatinization than the in vitro gelatinization. The relationship between gelatinization in pure starch and whole grain systems is very similar to the relationship between the free and immobilized enzyme systems in terms of the mechanism (Turhan & Mutlu, 1997, 1998).

The true \( k_r \) is the unique and essential data for analyzing any kind of reactional process. True \( k_r \) for the starch gelatinization can be estimated in situ using simultaneous diffusion and reaction equations (Lin, 1993; Cabrera, Pineda, Duran De Bazua, Segurajauregui, & Vernon, 1984; Bakshi & Singh, 1980). The assumptions of simple geometry and homogeneous structure, which are necessary for the use of these equations obviously do not fit the physical situation of the whole cereal grains. Furthermore, in these equations water transfer is assumed to obey Fickian diffusion. Turhan and Gunasekaran (1999) were suspicious if it was really Fickian in durum wheat based on NMR images taken during cooking of whole kernels. The true \( k_r \) can also be obtained in vitro after discarding the effect of the whole grain matrix on the process. Extracting starch from the grain or reducing size of the grain into fine particles are the only experimental ways for this task provided that the resultant samples are only composed of starch granules keeping the in situ intact attributes.

Kinetics of in situ gelatinization of rice starch (Bakshi & Singh, 1980), corn starch (Cabrera et al., 1984) and some legume starches (Kubota, 1979a,b) have been reported in the literature. Jankowski and Rha (1985) studied the phase transition of in situ gelatinization of wheat starch during cooking in water. Stapley, Hyde, Gladden, and Fryer (1997a,b) worked characteristics of the in situ gelatinization of wheat starch during cooking in water and steam. Though wheat is the most popular grain in the manufacture of instantized cereal products (Grider, 1996), kinetics of the starch gelatinization during cooking of whole wheat has not been published. Cooking is not merely the initial step in the production of instantized cereals, but also a vital process, which effectively governs the latter steps of the production and quality of the final product. Accordingly, the kinetical data regarding the starch gelatinization is one of the essential pre-requisites for understanding cooking process of whole grains. The goal of this investigation was to analyze the gelatinization kinetics of wheat starches commercially used in the production of instantized cereals. The specific objectives were to estimate the apparent and true reaction rate constants of the starches and to observe the effect wheat type and temperature on the process.

## 2. Materials and Methods

Hard (\( T. \) durum) and soft (\( T. \) aestivum) wheats were obtained from a commercial mill. Gelatinization was conducted by cooking whole and milled samples of the hard and soft wheats at 60°C, 70°C, 80°C, 90°C, and 100°C in distilled water in test tubes immersed in a water bath. Two groups of experiments were conducted. The first group consisted of many test tubes with approximately 1 g whole wheat (15–20 kernels) each with 30 ml of water. Periodically, one tube was removed from the water bath. The partially gelatinized kernels were immediately transferred to a test tube containing ice water (0–1°C) to prevent residual gelatinization of the starch in the grain and kept there for approximately 30 min. The size of the kernels was reduced using a laboratory blender (Waring, Model 1043, Winsted, CT) into fine particles and kept in a test tube at 4°C for 1–2 h to saturate with water. The saturation was done to obtain the ratio of water/starch \( \geq 0.75 \) for measuring the degree of gelatinization in a differential scanning calorimeter (DSC). The second group consisted of many test tubes each with approximately 1 g milled wheat (passing
through mesh size of 100) and 30 ml water. Milled samples were obtained using the above given laboratory blender. They were treated as the first group except for the size reducing. The first and second groups represented the in situ and in vitro processes, respectively.

Degree of gelatinization (DG) in whole and milled wheat samples during cooking was determined using a DSC (Modulated 2920, TA Instruments, New Castle, DE). The DSC was calibrated frequently with an aluminum oxide standard (TA Instruments, 1996). Partially gelatinized samples kept at 4°C (10–15 mg) were sealed in a hermetic aluminum pan and heated at 10°C/min from 30°C to 90°C in the DSC to obtain the energy for gelatizing the ungelatized portion of starch in the sample. After removing the pan from the DSC, a small hole was made in its lid and kept at 105°C in a moisture analyzer (Mettler Toledo LJ16, Columbus, OH) until constant mass to bone dry the sample. The gelatinization energy from the DSC was converted into dry basis. The DG was determined by comparing gelatinization energies of cooked samples (partially gelatinized) and the control (0% gelatinized). Gelatinization energy for the control was obtained using both milled durum and soft wheat samples. The uncooked milled samples were kept in water at 4°C for 1–2 h to saturate with water as done for the partially gelatinized samples. Average gelatinization energy for the control was obtained to be 8.7 J/g dry sample. The DSC measurements were stopped when at least two successive gelatinization energies were the same.

3. Results and discussion

3.1. Progress of the gelatinization

Degree of gelatinization during the in situ and in vitro processes followed an exponentially raising path against cooking time. Figs. 1 and 2 show the trend of the in situ and in vitro gelatinization of the hard wheat starch. The rate of the gelatinization increased with increasing cooking temperature as expected (Bakshi & Singh, 1980; Lund & Wirakartakusumah, 1984). At the same conditions, the rate of the in vitro gelatinization was higher than that of the in situ gelatinization for both hard and soft wheat starches.

The in situ and in vitro gelatinizations for the hard and soft wheat starches never completed 100% at the given cooking temperatures. The process stopped at a final degree of gelatinization (FDG) which increased with increasing cooking temperature (Fig. 3). The higher FDG points the comparatively higher fraction of the starch granules, which are able to gelatinize. The in vitro gelatinization exhibited higher FDG values than the in situ gelatinization for the soft and hard wheat starches (Fig. 3), since starch granules are more accessible to

Fig. 1. Progress of the in situ gelatinization of the hard wheat starch at different cooking temperatures.

Fig. 2. Progress of the in vitro gelatinization of the hard wheat starch at different cooking temperatures.

Fig. 3. Effect of the cooking temperature on the FDG of the starch samples.
water molecules in the former than the latter. Besides, the fraction of the damaged starch facilitating the gelatinization reaction is supposed to be much more in the in vitro samples than the in situ samples because of the milling (Hoseney, 1994). The slightly higher FDG in the soft wheat starch than the hard wheat starch during the in situ gelatinization (Fig. 3) can be due to characteristic differences between the wheats. In durum wheat, starch granules are covered with a protein layer which is not available in soft wheats, and endosperm cells are more closely packed than soft wheats (Hoseney, 1994). Both differences cause more hindrance to water molecules to reach the starch granules in durum wheat compared to soft wheat. The higher FDG in the soft wheat starch than the hard wheat starch during the in vitro gelatinization (Fig. 3) can be explained by the same way considering the milled wheat samples had non-starchy parts together with starch granules. The presence of FDG and its increasing trend with temperature have been reported for the gelatinization of other starches. It was 87% and 97% at 80°C and 100°C, respectively, during in situ gelatinization of rice starch (Birch & Priestly, 1973), and 3% and 99% at 52.5°C and 65.3°C, respectively, during in vitro gelatinization of potato starch (Shiotsubo, 1983).

The effect of temperature on the FDG was assessed through a Clausius–Clapeyron type equation

\[
\ln \text{FDG} = -\frac{\Delta H_{\text{FDG}}}{R} \frac{1}{T} + \text{constant} \quad (2)
\]

where \(\Delta H_{\text{FDG}}\) is the heat of FDG (kJ/mol), \(T\) the temperature (K) and \(R\) is the gas constant (8.314 kJ/mol K).

Within the same temperature range, the lower \(\Delta H_{\text{FDG}}\) value comparatively reflects the existence of higher number of starch granules having the ability for the gelatinization reaction. The \(\Delta H_{\text{FDG}}\) for the in situ and in vitro gelatinization of the starches was determined to be constant between 60°C and 80°C (Table 1) and the fit of Eq. (2) gave the coefficients of determination greater than 0.99. The decreasing trend of the heat of FDG above 80°C with increasing temperature (Table 1) shows the decreasing energy demand to increase the fraction of starch granules with the ability of gelatinization. The decreasing \(\Delta H_{\text{FDG}}\) vs increasing temperature is in accordance with the behavior of heat of reaction of a typical endothermic reaction (Cooper & Jeffreys, 1971). The in vitro gelatinization exhibited lower \(\Delta H_{\text{FDG}}\) values than the in situ gelatinization for the hard and soft wheat starches within the same temperature ranges. In the former, \(\Delta H_{\text{FDG}}\) accounts for the energy to increase the number of starch granules capable of the gelatinization, however in the latter it additionally accounts for the energy for overcoming the resistance by the whole grain against the water transfer. Soft wheat starch had slightly lower \(\Delta H_{\text{FDG}}\) values than the hard wheat starch during the in situ and in vitro gelatinizations within the same temperature ranges. It can be due to the more accessibility of the former to water than the latter because of the characteristic differences between durum and soft wheats as discussed above (Hoseney, 1994). The \(\Delta H_{\text{FDG}}\) values of the in situ gelatinization of wheat starches were comparable to that of rice starch (6000 kJ/mol) between 90°C and 100°C (Birch & Priestly, 1973). However, between 60°C and 80°C they were not in agreement with that of the rice starch (337 000 kJ/mol) (Lund & Wirakartakusumah, 1984).

The concept of \(\Delta H_{\text{FDG}}\) can be exploited in estimating the ultimate ability of a starch for the gelatinization at a specific cooking temperature, the cooking temperature giving the desired ultimate gelatinization, energy needed for increasing the FDG from a level to the desired level. It can also be useful in analyzing and comparing thermodynamic properties of different starches.

### 3.2. Kinetics of the gelatinization

The fit of Eq. (1) to experimental data resulted in high coefficients of determination at all cooking temperatures indicating that the in situ and in vitro gelatinizations of the hard and soft wheat starches follow a first-order reaction kinetics. Figs. 4 and 5 show the fit of the first-order reaction kinetics to the in situ and in vitro gelatinizations of soft wheat starch. Reaction rate constants \((k_c)\) estimated for the in situ and in vitro gelatinizations

<table>
<thead>
<tr>
<th>Cooking temperature (°C)</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>In situ</td>
<td>36000</td>
<td>10000</td>
<td>7000</td>
<td>6000</td>
<td></td>
</tr>
<tr>
<td>In vitro</td>
<td>27000</td>
<td>7000</td>
<td>1000</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.985</td>
<td>0.932</td>
<td>0.970</td>
<td>0.999</td>
<td>0.995</td>
</tr>
</tbody>
</table>

Fig. 4. First-order reaction kinetics of the in situ gelatinization of the soft wheat starch at different cooking temperatures.

Table 1

Heat of FDG (\(\Delta H_{\text{FDG}}, \text{kJ/mol}\)) for the in situ and in vitro gelatinization of hard and soft wheat starches

<table>
<thead>
<tr>
<th>Cooking temperature (°C)</th>
<th>Hard wheat In situ</th>
<th>In vitro</th>
<th>Soft wheat In situ</th>
<th>In vitro</th>
</tr>
</thead>
<tbody>
<tr>
<td>60–80</td>
<td>36000</td>
<td>27000</td>
<td>34000</td>
<td>23000</td>
</tr>
<tr>
<td>80–90</td>
<td>10000</td>
<td>7000</td>
<td>11000</td>
<td>4000</td>
</tr>
<tr>
<td>90–100</td>
<td>7000</td>
<td>1000</td>
<td>6000</td>
<td>1000</td>
</tr>
</tbody>
</table>
of the hard and soft wheat starches using Eq. (1) are listed in Table 2.

The \(k_r\) values of the in vitro gelatinization were greater than the in situ gelatinization for the hard and soft wheat starches at the same temperature (Table 2) suggesting that the in vitro gelatinization is faster than the in situ gelatinization. The \(k_r\) values obtained from the in situ gelatinizations are the apparent rate constants including the control of the gelatinization reaction and resistance of the grain to the water transfer. The \(k_r\) values from the in vitro gelatinizations could be considered true rate constants if the milled wheat samples were composed of only pure starch keeping the in situ characteristics. These could not be possible due to inevitable damaging effect of the milling on the starch granules, and association of the non-starchy parts of wheat with starch granules and their presence in the cooking medium. Therefore, \(k_r\) from the in vitro process can be termed as the pseudo true rate constant. Even if pure starch could have been extracted and used in the study, the true reaction rate constant would not be obtained truly because of the modification and damaging effect of the extraction process on the starch granules (Hart & Blanshard, 1982).

At the same temperature, \(k_r\) values of the soft wheat starches were greater than those of the hard wheat starches during the in situ and in vitro gelatinizations (Table 2). This may be because of the aforementioned characteristic differences between hard and soft wheats (Hoseney, 1994). The ratio between \(k_r\) values of the soft and hard wheat starches during the in situ and in vitro gelatinizations was around 1.4 at all temperatures (Table 2). The almost equal \(k_r\) ratios for both processes regardless of the cooking temperature indicates that the characteristic attributes of the samples are apparently dominant on the kinetics of the gelatinization. Besides, the same \(k_r\) ratios for the in vitro gelatinizations imply that the milling affects the gelatinization ability of hard and soft wheat starches to the same extent between 60°C and 100°C.

Gelatinization kinetics of all starches available in the literature were reported as a first-order reaction with one \(k_r\) value except for barley starch with two \(k_r\) values depending on the DG (Mok, Lee, Nam, & Min, 1985). The findings of this study were in agreement with the literature in terms of the order of magnitude of the \(k_r\) values (Table 2). However, no agreement was observed between pseudo true rate constants of the hard and soft wheat starches used in the study, and true rate constants of rice and brown rice starches (Bakshi & Singh, 1980), and corn starch (Cabrera et al., 1984).

### 3.3. Effect of temperature on the gelatinization

The \(k_r\) values of the in situ and in vitro gelatinizations increased with increasing temperature due to increasing starch–water reactivity and/or water transferability. The effect of temperature on the gelatinization process was evaluated considering the behavior of \(k_r\) vs temperature through an Arrhenius type equation

\[
\ln k_r = \ln A - \frac{E_a}{R} \frac{1}{T}
\]

where \(A\) is the pre-exponential factor (s\(^{-1}\)) and \(E_a\) is the activation energy (kJ/mol).

Eq. (3) conformed to experimental data very well (Table 3). The fit exhibited one linear curve between 60°C and 100°C for the in vitro gelatinizations with almost equal slopes giving an average \(E_a\) of 76 kJ/mol (Table 3). For the in situ gelatinizations, the fit resulted in two linear curves crossing around 75°C with almost same slopes within the same temperature ranges. The

### Table 2

<table>
<thead>
<tr>
<th>Cooking temperature (°C)</th>
<th>Hard wheat</th>
<th>Soft wheat</th>
<th>Soft wheat/Hard wheat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In situ</td>
<td>In vitro</td>
<td>In situ</td>
</tr>
<tr>
<td>60</td>
<td>1.4</td>
<td>15.1</td>
<td>1.7</td>
</tr>
<tr>
<td>70</td>
<td>4.7</td>
<td>30.0</td>
<td>5.4</td>
</tr>
<tr>
<td>80</td>
<td>21.5</td>
<td>69.9</td>
<td>30.0</td>
</tr>
<tr>
<td>90</td>
<td>54.8</td>
<td>139.9</td>
<td>67.2</td>
</tr>
<tr>
<td>100</td>
<td>85.7</td>
<td>238.8</td>
<td>134.3</td>
</tr>
</tbody>
</table>

Average 1.3 1.3
average \( E_a \) values were 137 kJ/mol below 75°C, and 79 kJ/mol above 75°C which was very close to that of the in vitro gelatinizations between 60°C and 100°C.

Activation energy is a useful tool to deduce how a process is sensitive to temperature. The higher the activation energy, the more the sensitive process to temperature. Within the same temperature ranges, the same \( E_a \) values for the hard and soft wheat starches during both in situ and in vitro gelatinizations (Table 3) suggests that temperature affects the gelatinization ability of the starches to the same extent. Activation energy also signifies the minimum energy needed by the reactants for undergoing reaction (Fogler, 1999). Higher \( E_a \) values for the in situ gelatinization than the in vitro gelatinization for hard and soft wheat starches below 75°C shows that the in situ gelatinization needs some extra energy for overcoming the resistance of the grain to water transfer above going to the reaction. The suddenly decreasing \( E_a \) value of the in situ gelatinizations above 75°C points some textural changes in the whole wheat grains leading to the higher rate of the water transfer compared to the rate of the gelatinization reaction. The average \( E_a \) value for the in situ gelatinizations above 75°C was very close that of the in vitro gelatinizations between 60°C and 100°C (Table 3). Assuming the process was effectively controlled by the gelatinization reaction during in vitro gelatinizations between 60°C and 100°C, it was effectively governed by the water transfer below 75°C and by the gelatinization reaction above 75°C during the in situ gelatinizations.

The observed behavior of activation energy for the gelatinization of hard and soft wheat starches vs temperature was consistent with the literature. It decreased from 78 to 44 kJ/mol above 85°C during in situ gelatinization of corn starch (Cabrera et al., 1984). In vitro gelatinizations of some extracted starches exhibited one \( E_a \) value which was 234 kJ/mol for cowpea starch between 67°C and 86°C (Okechukwu & Rao, 1996), 110 kJ/mol for potato starch between 53°C and 65°C (Shiotsubo, 1983), 42 kJ/mol for rice starch between 73°C and 92°C (Kubota, Hosokawa, Suzuki, & Hosaka, 1979), and 3325 kJ/mol a starchy food tarhana between 60°C and 120°C (Ibanoglu & Ainsworth, 1997).

### Table 3

<table>
<thead>
<tr>
<th>Starch</th>
<th>Cooking temperature (°C)</th>
<th>( E_a ) (kJ/mol)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>In situ</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hard wheat starch</td>
<td>60–75</td>
<td>133</td>
<td>0.993</td>
</tr>
<tr>
<td></td>
<td>75–100</td>
<td>76</td>
<td>0.966</td>
</tr>
<tr>
<td>Soft wheat starch</td>
<td>60–75</td>
<td>140</td>
<td>0.984</td>
</tr>
<tr>
<td></td>
<td>75–100</td>
<td>82</td>
<td>0.999</td>
</tr>
<tr>
<td>In vitro</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hard wheat starch</td>
<td>60–100</td>
<td>73</td>
<td>0.997</td>
</tr>
<tr>
<td>Soft wheat starch</td>
<td>60–100</td>
<td>78</td>
<td>0.995</td>
</tr>
</tbody>
</table>

4. Conclusions

The in situ and in vitro gelatinization of hard and soft wheat starches was not 100% complete within the temperature range 60–100°C. The FDG was higher for the in vitro gelatinization than the in situ gelatinization for both hard and soft wheat starches. It was higher for the soft wheat starch than the hard wheat starch for both in situ and in vitro processes. The in situ and in vitro gelatinizations obeyed first-order reaction kinetics. The rate of the process was faster for the in vitro gelatinization than the in situ gelatinization for both hard and soft wheat starches. It was faster for the soft wheat starch than the hard wheat starch for both in situ and in vitro processes. The discrepancy between the in situ and in vitro gelatinization in terms of the FDG and the rate of the gelatinization reaction is supposed to be due to resistance of whole grain to the water transfer in the former, which is comparatively ineffective in the latter. The discrepancy between the soft and hard wheat starches was due to characteristic textural and structural differences between the wheat types. Assuming the gelatinization process was effectively controlled by the starch–water reactivity during the in vitro gelatinization. It was effectively controlled by the water transfer below 75°C and by the starch–water reactivity above 75°C during in situ gelatinization of both wheat starches.

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References


