

Kinetic Study on the Gelatinization of Barley Starch

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보리전분의 호화에 관한 속도론적 연구

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Abstract

The gelatinization kinetics of barley starch in dilute system (1% w/v concn.) at the temperature range of 60-95°C was investigated. The gelatinization rate was extremely temperature dependent. The gelatinization at the temperature above 90°C was an one step 1st order reaction throughout the gelatinization time, but that below 85°C consisted of two stages which showed different reaction rates. The reaction rate of the 1st stage was greater than that of the 2nd stage. The activation energy of the 1st stage was 31.93 Kcal/g mole and those of the 2nd stage were 78.49 and 23.41 Kcal/g mole above and below 75°C, respectively.

Introduction

The extent of starch gelatinization in starchy foods is of great importance to their physical properties, digestibility and storage behavior. The cooking rates of some cereals and potatoes have been observed by using the texturometer or the plastometer^(1,2, ...7). Yet, in the field of kinetic study of the gelatinization mechanisms of starch, investigation have been rather scarce. In this study, the kinetic investigation of starch gelatinization was accomplished using barley starch. The extent of gelatinization can be expressed as follows;

$$X = \frac{X - X_0}{X_e - X_0} \dots \dots \dots (1)$$

where, X =gelatinization parameter at time t.
X₀=gelatinization parameter at the initial time (t = 0).
X_e=gelatinization parameter at the end

point.

X =extent of gelatinization.

And the reaction rate of gelatinization is

$$\frac{dx}{dt} = K(1 - x)^m \dots \dots \dots (2)$$

where, dx/dt = gelatinization rate (min⁻¹)

K = rate coefficient (min⁻¹)

m = order of the reaction

It was concluded that starch gelatinization was a 1st order reaction by many previous studies (1,3.. ..7). Equation (2) is, thus, converted to Equation (3).

$$\frac{dx}{dt} = K (1 - x) \dots \dots \dots (3)$$

The values of K are derived from Equation (3) as follows;

$$K = - \ln (1 - x)/t \dots \dots \dots (4)$$

And the dependence of gelatinization rate on temperature can be expressed by the Arrhenius equation as follows:

$$K = K_0 \exp(-E_a/RT) \dots \dots \dots (5)$$

where, K_0 = frequency factor (min^{-1})

E_a = activation energy (cal/g mole)

R = gas constant ($1.987 \text{ cal/g mole K}$)

T = absolute temperature (K)

Material and Methods

Material

The starch used in this study was extracted from the barley variety, Sedohadaka, by the method of Kim (9):

Cooking procedure

One percent (w/v) of barley starch suspension was cooked in an Amylograph (Brabender, Duisburg, West Germany) using the Rapid Amylograph Accessories. The schematic view of the Rapid Amylograph Accessories is shown in Fig. 1. The water temperature in outside water jacket was maintained at a given temperature. Barley starch suspension (25 ml) was added to the inner cylinder and cooked for different time periods while both the outside water jacket and the inner cylinder rotated at 75 rpm.

Determination of the extent of gelatinization

The extent of gelatinization at different time intervals was measured by the modified method of Wootton and Chaudhry (10). An aliquot of the cooked starch suspension was transferred to a centrifuge cell and centrifuged at 3000 x G for 30 min. One milliliter of supernatant was transferred to a 100 ml volumetric flask and 0.1 ml of iodine solution (4 % KI, 0.1 %) and 1 ml of 2N HCL were added in succession. The flask was then brought up to 100 ml with distilled water. The absorbance (X) was read at 600 after 30 min. in a spectrophotometer. The absorbance of uncooked 1% barley suspension (X_0) also was measured. A further suspension of barley starch (0.5 g in water (47.5 ml) was pre-

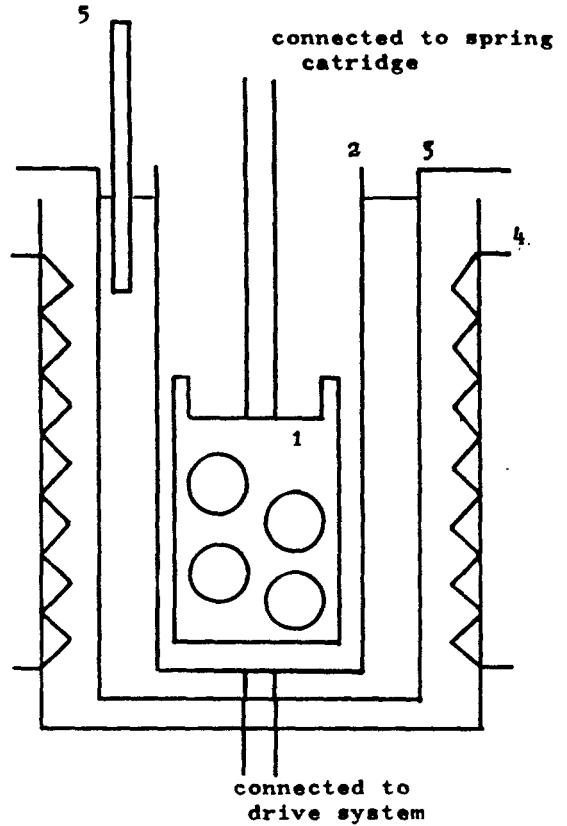


Fig.1. Schematic view of the Rapid Amylograph Accessories (1) sensor/stirrer (2) inner cylinder (3) outside water jacket (4) heating unit (5) thermoregulator

pared and 2.5 of 10M KOH solution was added and the mixture allowed to stand for 5 min. with gentle agitation. The absorbance (X_e) was read by same procedure. The extent of gelatinization was calculated by Equation (1).

Amylograph

An amylogram of barley starch with Na-alginate medium (30 g of barley starch and 9 g of Na-alginate in 450 ml of water) was investigated to reveal the stepwise charact of the gelatinization (11).

Result and Discussion

Fig. 2 shows the extent of gelatinization of

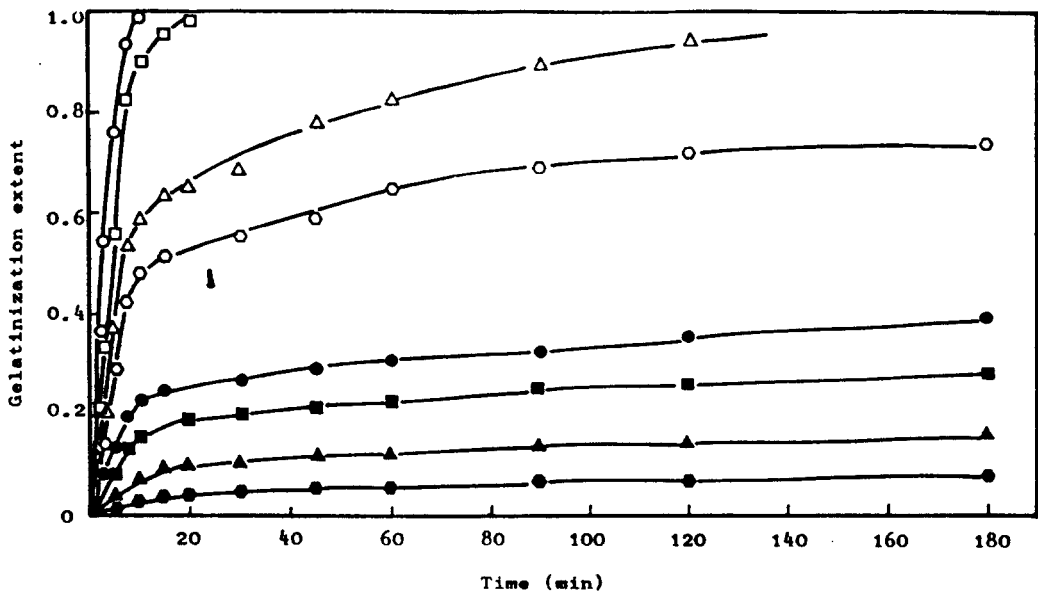


Fig. 2. Change in the extent of gelatinization of 1% barley starch suspension during cooking at the temperature 95 (○), 90 (□), 85 (△), 80 (●), 75 (●), 70 (■), 65 (▲), and 60°C (●)

barley starch suspension at various temperatures and times. The rate of gelatinization was extremely temperature dependent. The plot of $\ln(1/1-x)$ to time, t , are shown in Fig. 3. They were plotted linearly above 90°C. On the other hand, breakpoints were found at the temperatures equal to and lower than 85°C. This indicates that the gelatinization of barley starch above 90°C is an one step 1st order reaction, but consisted of two stages which have different reaction rates (two step 1st order reaction) below 85°C. These results have been confirmed by previous researchers^(12, 13, 14). The reaction rate coefficients of both the 1st and the 2nd stages were calculated from the slopes of each parts of those lines and listed in Table 1. The reaction rate coefficients of both the 1st and the 2nd stages of gelatinization increased as the temperature increased. The reaction rate coefficients of the 2nd stages were smaller than those of the 1st stages at the temperatures below 85°C. This means that it takes a much longer time to obtain complete gelatinization at temperatures below 85°C. This means that it takes a much longer time to obtain complete gelatinization at temper-

atures below 85°C than above 90°C. The estimated times required to get 99% gelatinization, which were calculated from the regression equations are listed in Table 2. The critical time between the 1st and the 2nd stages calculated from interesting points of the regression equations decreased with temperature as shown in Table 3. When the hydrogen bonds that link the starch molecules in the micellar network are disrupted by heat or hydrogen bonds breaking chemicals in the presence of surplus water, the

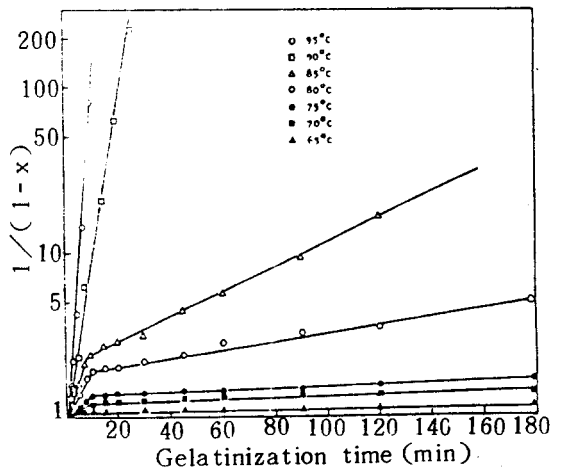


Fig. 3. Semi-logarithmic plot of $1/(1-x)$ to t

Table 1. Reaction rate coefficients of the 1st and 2nd stages of the gelatinization of barley starch

| Temperature(°C) | Reaction rate coefficient (min ⁻¹) | |
|-----------------|--|-------------------------|
| | 1st stage | 2nd stage |
| 95 | 0.4621 | — |
| 90 | 0.2056 | — |
| 85 | 0.1072 | 0.0170 |
| 80 | 0.0758 | 5.88 x 10 ⁻³ |
| 75 | 0.0285 | 1.22 x 10 ⁻³ |
| 70 | 0.0191 | 7.01 x 10 ⁻⁴ |
| 65 | 9.66 x 10 ⁻³ | 4.92 x 10 ⁻⁴ |
| 60 | 3.80 x 10 ⁻³ | 2.53 x 10 ⁻⁴ |

Table 2. Estimated time required for 99% gelatinization

| Temperature(°C) | Required time for 99% gelatinization (min) |
|-----------------|--|
| 95 | 11.16 |
| 90 | 22.79 |
| 85 | 230.04 |
| 80 | 676.81 |
| 75 | 3,544.04 |
| 70 | 6,277.88 |
| 65 | 9,162.61 |
| 60 | 10,872.70 |

Table 3. Critical time between the 1st and 2nd stage of gelatinization

| Temperature (°C) | Critical time (min) |
|------------------|---------------------|
| 85 | 8.44 |
| 80 | 9.75 |
| 75 | 10.65 |
| 70 | 11.91 |
| 65 | 12.09 |
| 60 | 13.99 |

hydration of the network is encouraged and an irreversible process of swelling is started. The swelling rate is dependent on the sizes of starch granules and on the molecular weight of starch molecules. Larger granules of the same species usually start to swell at lower temperature than the smaller ones. The swollen granules have a greater chance of coming into contact with each other and the viscosity of solution increases. The dispersed starch molecules, mostly amylose, exuded from the starch granules also contributes to the viscosity increase. The process of leaching starts with dissolving molecules of low molecular weight from the surface of the granules, whereas those of higher molecular weight are still left in swollen and elastic meshes^(15, 16). The difference in the reaction rates between the 1st and the 2nd stages was thought to be partially due to differences in granule size and in the molecular weight of starch.

Blanshard⁽¹⁴⁾ proposed a semi-cooperative process for the explanation of gelatinization. He focused on the crystallites within the granules which have slightly different energy characteristics. The imposition of a small temperature jump may result in certain starch granules being totally gelatinized but, in others, only some of the crystallites will have their gelatinization threshold exceeded. It is envisaged that, within such gelatinized granules, there is the possibility of a rearrangement of the polymer chains of the amylose and amylopectin. With such arrangements taking place, the energy characteristics of adjacent crystallites will also be moderated and some of these may fall within the temperature range where melting occurs, with a consequent loss of X-ray orders and birefringence. This rearrangement was believed to be responsible for the slow, time-dependent process.

Starch molecule can be thought to be a parcel-like matter done up with string with many knots (representing the crystallites and junction zones) and ties (representing the entangled

chains in amorphous regions). There are two way to undo the parcel, by a rapid process of cutting the knots, or by a slow process of disentangling the ties. If sufficient cuts are made there is no need for the slow disentangling process, the parcel opened up and the starch granule swells⁽¹²⁾. The results obtained in this study can be fully explained by such a theory. In the 1st stage of gelatinization, some cuts are made by heat and the process is fast. In the 2nd stage, on the other hand, the slow disentanglement of the ties occurs. At the temperature above 90°C enough energy was provided to cut the string sufficiently. Thus only the fast process, the 1st stage, occurred. An intensive study on the gelatinization kinetics of various starches using different starch particle size fractions is needed to reveal the gelatinization mechanism.

The activation energies of both the 1st and the 2nd stage of gelatinization are given by Arrhenius plots and shown in Fig. 4. The activation energy of the 1st stage was 31.93 *Kal/g* mole and those of the 2nd stage were 78.49 and 23.41 *Kcal/g* mole at the temperatures above and below 75°C, respectively.

The activation energy of the gelatinization of barley starch was much smaller than that of potato starch, 230 *Kcal/g* mole⁽⁷⁾. The activation energy of the gelatinization of rice starch was in the range of 9.6 – 31.7 *Kcal/g* mole according to varieties and temperature ranges^(1,6,7,8). It can be concluded, therefore, that the cooking of barley at a higher temperature is desirable in case of cooking barley with rice from the viewpoint of energy efficiency.

The amylogram of barley starch with Na-alginate dispersion medium is shown in Fig. 5. The gelatinization of barley starch consisted of two stages and the initial gelatinization temperature was 55°C. The 2nd stage started at 79°C and accelerated around 90°C. It means that enough heat was provided to gelatinize barley starch at the temperature above 90°C. This

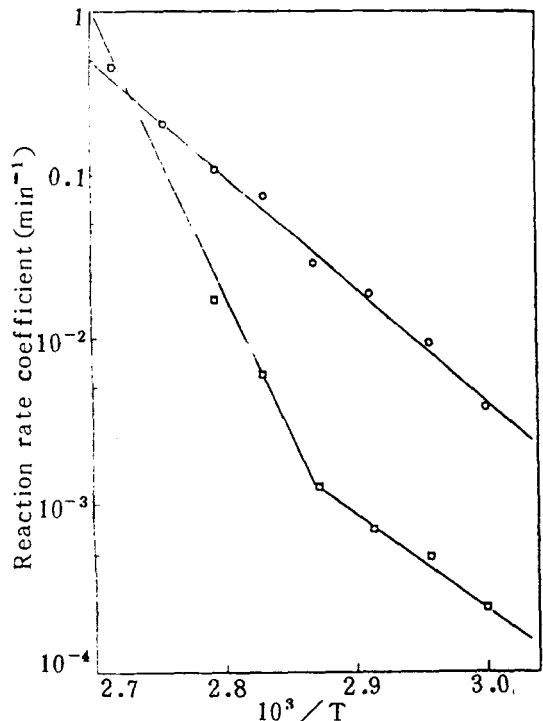


Fig. 4. Arrhenius plots of rate coefficients of the 1st stage (O) and the 2nd stage (□) of the gelatinization of barley starch

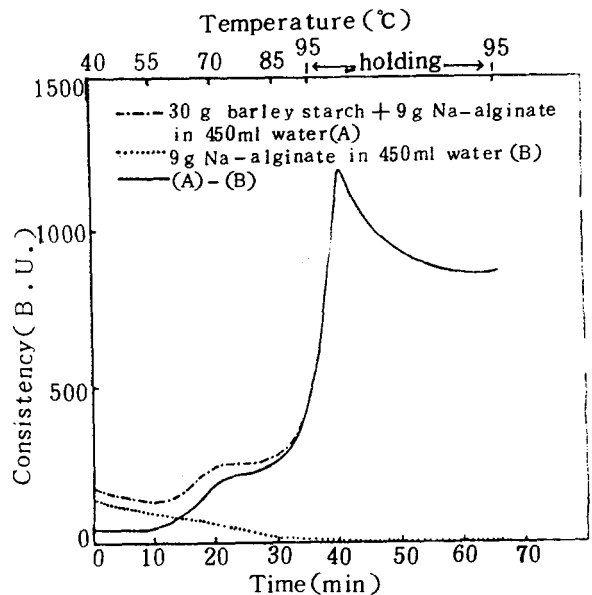


Fig. 5. Amylogram of barley starch with Na-alginate dispersion medium fact confirms the change of the activation energy of the 2nd stage at 75°C and the phenomenon showing only 1st stage above 90°C.

요 약

60~95℃의 온도범위에서 보리전분회석액의 호화를 속도론적으로 조사분석하였다. 보리전분의 호화속도는 온도의존성이 컸으며 90℃이상에서의 호화는 1단계의 1차반응에 속하였으나 85℃이하에서는 2단계의 1차 반응으로 구성됨을 확인하였다. 85℃이하의 온도에서 반응제 1단의 반응속도는 반응제 2단의 경우에 비하여 큰값을 나타내었다. 반응제 1단의 활성화에너지는 31.93 Kcal/g mole 이었으며 반응제 2단의 활성화에너지는 75℃이상에서는 78.49Kcal/g mole, 75℃이하에서는 23.41 Kcal/g mole 이었다.

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