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Studies on the Soaking and Cooking Rate Equations of Soybean

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(Figs. 1–6, Tables 1–2)

INTRODUCTION

In previous papers$^{1-4)}$, we have studied the soaking and cooking rate equations of rice, potato and so on. From these soaking and cooking rate equations, we have studied the empirical and the semi-theoretical rate equations. In this present paper, we took up the study of the soaking and cooking rate equations of soybean.

The degrees of the soaking and cooking of soybean were obtained by the same weighing method used in the previous papers$^{1,3)}$ on the soaking and cooking of low water content foods. The soaking and cooking rate equations of soybean were postulated as a simple empirical rate equation of 1st-order and as a semi-theoretical one based on the water-soaking-shell model which was used in the previous papers$^{1-3)}$.

RATE EQUATIONS

The rate equations of soaking, cooking and so on have been proposed commonly as a first order rate equation, but a *n*th-order rate equation is most suitable for complicated phenomena. Therefore, we propose the rate equation as follows:

$$dw/d\theta = k_n(w_e - w)^n \tag{1}$$

where, w (g) is the soaking and cooking weight of the sample at any given time θ (min); w_e (g) is the weight at equilibrium state, and k_n (g^{1-n}/min) and $n(-)$ are the rate parameters which can be obtained from the experimental data of w vs. θ.

The soaking or cooking ratio $x(-)$ is expressed in the following equation from the weights of the sample:

$$x = (w - w_0)/(w_e - w_0) \tag{2}$$

where, w_0(g) is the weight at the initial state. From Eqs. (1) and (2), we can obtain the following equation:

$$dx/d\theta = k_n(w_e - w_0)^{n-1}(1-x)^n = k_n^*(1-x)^n \tag{3}$$

An other rate equation that can be used for the soaking and cooking rate equations, is the following equation based on the water-soaking-shell model$^{1-3)}$. This equation was obtained for samples of spherical shape by assuming that the unsoaked core and the soaked shell occuring in the soaking process were cleary divided by the internal plane.

$$\frac{dw}{d\theta}=\frac{4\pi r_c R(C_e-C_0)}{\dfrac{R-r_c}{k_m}+\dfrac{1}{(r_c/R)k_r}} \tag{4}$$

where, R and r_c (cm) are the radius of a sample and of the unsoaked core, and C_0 and C_e ($g-H_2O/cm^3$) are the water concentration of the unsoaked core and the soaked layer, respectively. k_m (cm^2/min) and k_r (cm/min) are the rate parameters which can be obtained from the experimental data of w vs. θ. k_m is the diffusion parameter of water through the soaked layer, and k_r is the reaction parameter of soybean components with the diffused water.

From Eqs. (4) and (2), we can obtain the following equation :

$$\frac{dx}{d\theta}=\frac{4\pi r_c R(C_e-C_0)/(w_e-w_0)}{\dfrac{R-r_c}{k_m}+\dfrac{1}{(r_c/R)k_r}} \tag{5}$$

The radius R and r_c are expressed as the following equations, respectively, and can be calculated from the soaking or cooking ratio x :

$$R=[R_e^3-\{(R_e/R_0)^3-1\}r_c^3]^{1/3} \tag{6}$$

$$r_c=(1-x)^{1/3}R_0 \tag{7}$$

where, R_0 and R_e (cm) are the radius of the sample at the initial and equilibrium state, respectively.

The experimental data of the soaking or cooking of soybean are obtained as the integral data w vs. θ. Therefore, the relations of x vs. θ used the dimensionless valiable x are obtained by Eq.(2). They are convenient for the understanding of the soaking or cooking ratio. Then we give the soaking or cooking rate equation by Eq.(3) or (5) using the valiable x.

For the differential analysis, Eqs. (3) and (5) become as follow:

$$\begin{aligned}\ln(dx/d\theta)&=\ln(k_n)+(n-1)\ln(w_e-w_0)+n\ln(1-x)\\&=\ln(k_n^*)+n\ln(1-x)\end{aligned} \tag{8}$$

$$4\pi r_c R(C_e-C_0)/\{(w_e-w_0)(dx/d\theta)\}=(1/k_m)(R-r_c)+(1/k_r)/(r_c/R) \tag{9}$$

Using Eqs. (8) and (9), we can obtain the rate parameters of k_n or k_n^* and n in Eq. (3) and these of k_m and k_r in Eq.(5), with a linear least square method. When the data of x vs. θ are scattered as in this study, we cannot obtain reliably find the derivative values of $dx/d\theta$ needed in these differential analysis.

For the integral analysis, Eq.(3) becomes as follows :

For $n=1$:

$$k_n=[\{1/(1-x)\}^{n-1}-1]/\{(w_e-w_0)^{n-1}(n-1)\theta\} \quad \text{or}$$

$$k_n^*=[\{1/(1-x)\}^{n-1}-1]/\{(n-1)\theta\} \tag{10}$$

For $n = 1$:

$$k_{n=1} = k_{n=1}^{*} = -\ln(1-x)/\theta \tag{11}$$

However, Eq. (5) cannot be integrated analytically. We must solve it numerically by a digital or an annalogue electric computer. The numerical integral analysis using a digital electric computer is most satisfying in various analyses. Then, Eqs. (3) and (5) were integrated numerically using the Runge-Kutta-Gill method, and the rate parameters in Eqs. (3) and (5) were calculated by a non-linear least square method[5] using a digital electric computer (used "HITAC 8700–OS7" in the Computation Center of Hiroshima Univ.).

The values of the following standard deviation δ (–) for the valiable x were minimized.

$$\sigma = \left\{ \sum_{i=1}^{N} (x_{obs} - x_{cal})_i^{\,2} / N \right\}^{1/2} \tag{12}$$

The initial values of the rate parameters in Eq. (3) were calculated by Eq. (11) assuming n=1.0, and the initial values of k_{m} and k_{r} in Eq. (5) were calculated by the following equations which were obtained for the cases of only a partry control of diffusion or reaction rate.

For diffusion controlling :

$$k_{\mathrm{m}} = \rho_{\mathrm{h}} [\{ R_0^{\,2} R_{\mathrm{e}}^{\,3} - r_{\mathrm{c}}^{\,2} (R_{\mathrm{e}}^{\,3} - R_0^{\,3}) \} - R_0 \{ R_0^{\,3} R_{\mathrm{e}}^{\,3} - r_{\mathrm{c}}^{\,3} (R_{\mathrm{e}}^{\,3} - R_0^{\,3}) \}^{2/3}] / \{ 2 (R_{\mathrm{e}}^{\,3} - R_0^{\,3}) (C_{\mathrm{e}} - C_0) \theta \} \tag{13}$$

For reaction controlling:

$$k_r = \rho_{\mathrm{h}} R_0 \{ 1 - (r_{\mathrm{c}} / R_0) \} / \{ (C_{\mathrm{e}} - C_0) \theta \} \tag{14}$$

where, ρ_{h} (g-$H_2$0/cm^3) is the increasing water concentration by the soaking or cooking.

EXPERIMENTAL

The soybean used as the sample is the so-called "Nishiki-Daizu" harvested in 1977 in Okayama district, Japan. It was bought from the market, and stored in a refrigerator at 5°C. The weight and volume of one grain of soybean were approximately equal to 0.281 g and 0.231 cm^3 (diameters : 0.69, 0.79 and 0.81 cm), respectively, and the moisture content was about 13.7% (wet basis).

The weighed soybeans (30 grains) were put into a sample basket and entered into water of the desired temperature for a fixed time. The cooked soybean was poured out quickly into water of 30°C for 0.5 minutes in order to stop the cooking of the sample. After the surface water was wiped away, the weight of the sample was weighed on a chemical balance.

The specific gravity of the sample was measured by a specific gravity bottle at 30°C. The weight of the completely drying state of the sample was estimated as being the value of 20 houres drying at 135°C in a dryer.

RESULTS AND DISCUSSION

The relation between the weight rations of soaked or cooked soybean $w/w_o(-)$ and

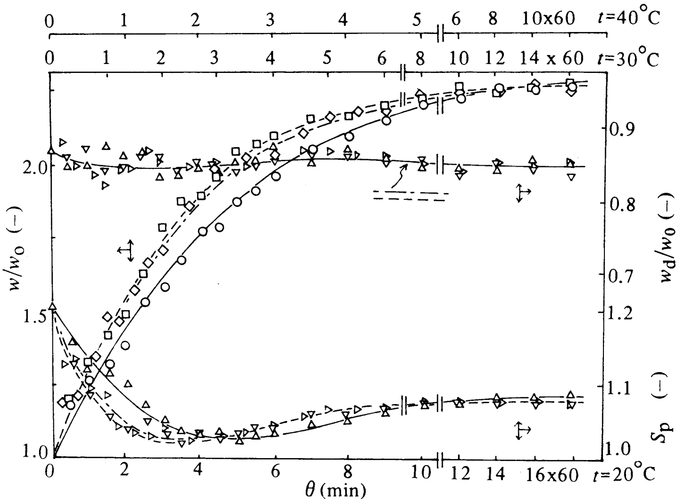

Fig. 1.

Relations between the weight ratio w/w_0, w_d/w_0, specific gravity S_p and the soaking or cooking time θ of soybean. Observed data : t = 20, 30, 40 °C

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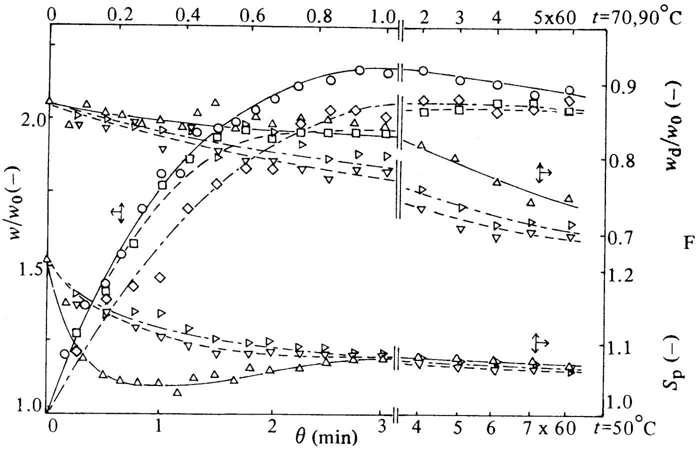

Fig. 2.

Relations between the weight ratio w/w_0, w_d/w_0, specific gravity S_p and the soaking or cooking time θ of soybean. Observed data: t = 50, 70, 90 °C

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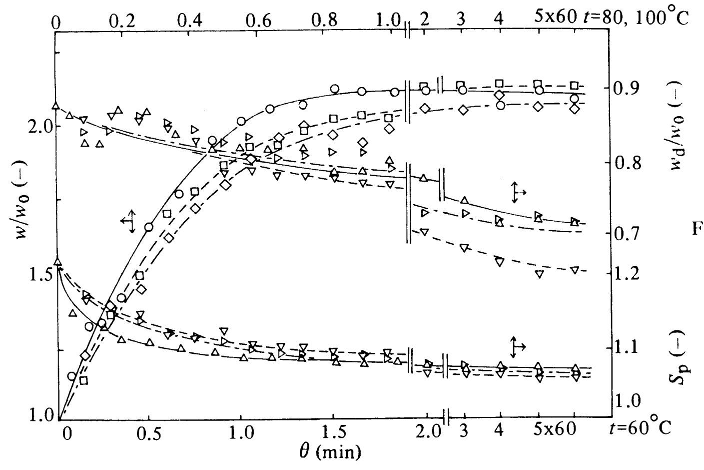

Fig. 3.

Relations between the weight ratio w/w_0, w_d/w_0, specific gravity S_p and the soaking or cooking time θ of soybean. Observed data : t=60, 80, 100°C

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the soaking or cooking time θ (min) at each temperature is shown in Figs. 1~3. The weight ratio of the sample is expressed as the ratio of the weight of soaked or cooked soybean w (g) and of unsoaked or uncooked one w_0 (g).

The relation between the specific gravity of the sample $S_p(-)$ and the soaking or cooking time θ at each temperature, and the relation between the weight ratios of the completely drying state and the initial state $w_d/w_0(-)$ and the soaking or cooking time θ, are shown in Figs. 1~3, too.

The soybeans soaked at a temperature below 40°C can germinate on a water-absorbing cotton at 30°C. The soybeans soaked at 50, 60 and 70°C can germinate only for soaking times below 90, 4 and 2 minutes, respectively. The soybeans soaked at a temperature above 80°C cannot germinate for about 1 minute. Therefore, we can considered two processes : one the soaking process as the start of the germinating phenomena at lower temperatures, and the other the soaking process as the start of cooking phenomena at higher temperatures. The results obtained at 50°C seem to be the intermediate process.

In Figs. 1~3, the curves of the specific gravity at the soaking temperature above 60°C are monotonous, but the curves at below 50°C are not monotonous and have minimum states. The reason may be perhaps that the production of respiratory gases and so on progress in the space between the surface film tissue and the inner components or the soybeans. The surface film tissue of the soybeans expanded initially and creased, but got rid of the creases along with the expanding of the inner components accompanied by the increasing of the soaking or cooking time. At the higher cooking temperatures, these phenomena occured momentarily. The starting position of the creases on the surface film tissue was not regular. At the intermediate states of the soaking or cooking of soybean, the inner components showed two parts ; a softer shell and a harder core. Accordingly, the water-soaking-shell model mentioned in Eq.(5) could be applied approximately. At the higher cooking temperatures, the extra water that permeated through the surface film tissue could be observed in the space between the two hemispherical inner components at the initial cooking states. The these initial atates, the water-soaking-shell model cannot be applied satisfactory.

The relationships of x vs. θ for determining the rate parameters $k_n{}^*$, n, k_r and k_m in Eqs. (3) and (5) are shown in Figs. 4 and 5. The values of x were calculated from the values of the weight ratio w/w_0 in Figs.1~3 by Eq. (2) using the values of w_e/w_0 = 2.26, 2.26, 2.26, 2.19, 2.12, 2.05, 2.05, 2.05 and 2.13, at 20, 30, . . . 100°C, respectively. The initial and calculated values of $k_n{}^*$ and n in Eq. (3) are listed in Table 1. As the values of n in Table 1 can be approximately expressed by 1.0, the calculated values of $k_{n=1}{}^*$ fixing n=1.0 in Eq.(2) are listed in Table 1, too. The calculated values of x for the obtained $k_{n=1}{}^*$ are illustrated by the solid lines in Figs. 4 and 5. The calculated results are satisfactory enough.

The initial and calculated values of k_r and k_m in Eq. (5) are listed in Table 2. In Table 2, the calculated values of k_m differ too much from the initial values. The reason

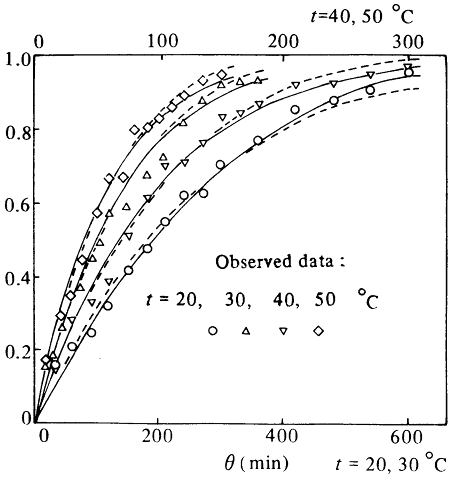

Fig. 4. Relations between the soaking or cooking ratio x and the soaking or cooking time θ of soybean.
Calculated values:
——— for $k_{n=1}$* in Table 1
- - - - - for k_r in Table 2

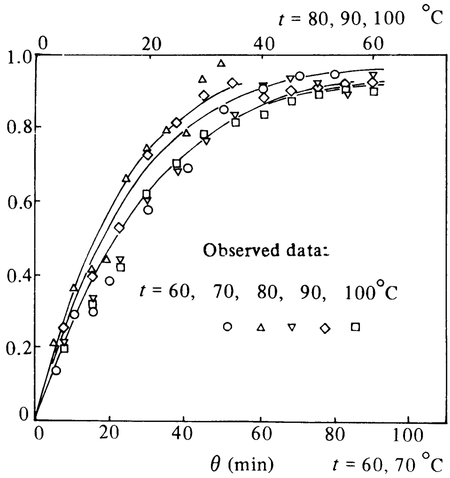

Fig. 5. Relations between the soaking or cooking ratio x and the soaking or cooking time θ of soybean.
Calculated values:
——— for $k_{n=1}$ * in Table 1

Table 1. Initial and calculated values of k_n*. n and $k_{n=1}$* on the soaking and cooking of soybean

Temp. t (°C)	Initial values k_n* (min^{-1})	n (−)	δ (−)	Calculated values k_n* (min^{-1})	n(−)	δ (−)
20	4.02 x 10^{-3}	1.0	0.0346	3.33 x 10^{-3}	0.725	0.0219
30	7.62 〃	1.0	0.0327	6.73 〃	0.852	0.0273
40	1.07x10^{-2}	1.0	0.0313	9.35 〃	0.817	0.0253
50	1.78 〃	1.0	0.0305	1.53 x 10^{-2}	0.801	0.0232
60	3.15 〃	1.0	0.0514	2.41 〃	0.606	0.0317
70	4.56 〃	1.0	0.0690	3.21 〃	0.554	0.0503
80	4.67 〃	1.0	0.0392	3.96 〃	0.784	0.0320
90	5.57 〃	1.0	0.0438	5.85 〃	1.021	0.0428
100	4.37 〃	1.0	0.0297	4.26 〃	0.944	0.0290

Temp. t (°C)	Cal. values $k_{n=1}$* (min^{-1})	δ (−)	Temp. t (°C)	Cal. values $k_{n=1}$* (min^{-1})	δ (−)
20	3.87 x 10^{-3}	0.0323	70	4.18 x 10^{-2}	0.0632
30	7.33 〃	0.0307	80	4.56 〃	0.0385
40	1.05 x 10^{-2}	0.0306	90	5.77 〃	0.0428
50	1.74 〃	0.0297	100	4.42 〃	0.0295
60	3.04 〃	0.0503			

is due to the interrelation of k_r and k_m and to the reaction-rate controlling. The values of k_r for the reaction-rate controlling are listed in Table 2, also. The calculated values of x for the obtained k_r at 20 ~ 50°C are illustrated by the broken lines in Fig. 4. As the values of standard deviation δ in Tables 1 and 2 are similar, the simple empirical rate equation of Eq.(3) is more useful than the equation of Eq.(5).

Table 2. Initial and calculated values of k_r and k_m on the soaking and cooking of soybean

Temp. t (°C)	Initial values k_r(cm/min)	k_m(cm^2/min)	δ (–)	Calculated values k_r(cm/min)	k_m(cm^2/min)	δ (–)
20	1.06×10^{-3}	7.21×10^{-5}	0.190	1.06×10^{-3}	1.04×10^{-3}	0.0220
30	1.89 〃	1.21×10^{-4}	0.206	2.36 〃	6.05×10^{-4}	0.0283
40	2.60 〃	1.98 〃	0.206	3.06 〃	1.35×10^{-3}	0.0277
50	4.10 〃	3.00 〃	0.230	5.16 〃	1.99 〃	0.0241
70	1.12×10^{-2}	8.06 〃	0.208	1.06×10^{-2}	1.71×10^{-2}	0.0514
80	1.14 〃	9.12 〃	0.205	1.21 〃	1.23 〃	0.0341
90	1.60 〃	1.44×10^{-3}	0.148	4.60×10^{-3}	1.85 〃	0.0540
100	1.19 〃	9.64×10^{-4}	0.178	3.09 〃	1.48 〃	0.0363

Temp. t(°C)	Cal. values k_r(cm/min)	δ (–)	Temp. t (°C)	Cal. values k_r(cm/min)	δ (–)
20	9.93×10^{-4}	0.0226	70	1.06×10^{-2}	0.0514
30	1.86×10^{-3}	0.0334	80	1.13 〃	0.0344
40	2.63 〃	0.0294	90	1.45 〃	0.0554
50	4.34 〃	0.0270	100	1.10 〃	0.0413
60	7.72 〃	0.0324			

where, 60°C in upper results : cannot obtain by overflow.

The values of logarithm of $k_{n=1}{}^*$ and k_r are plotted in Fig. 6 against the reciprocal of the absolute temperature. The calculated results at the higher cooking temperatures excepted 100°C were higher than the calculated lines. This is due to the extra permeated water in the space of the two hemispherical inner components. The result at 100°C is however lower. This is due to the splitting of the surface film tissue. The Arrhenius equations are shown as follow:

$$k_{n=1}{}^* = 1.392 \times 10^3 \ \exp(-7.310 \times 10^3 / R_g T) \qquad (15)$$

$$k_r \quad = 3.183 \times 10^2 \ \exp(-7.246 \times 10^3 / R_g T) \qquad (16)$$

where, T(°K) is the soaking or cooking temperature and R_g=1.987 cal/g-mol·°K is the gas constant. The values of the apparent activation energy for the soaking and cooking of soybean is less than the values obtained from the cooking of rice[1,2] and potatos[4]. The values of the activation energy of a chemical reaction is generally about from 10 to 100 kcal/g-mol. From the above results, we may infer that the cooking phenomena of

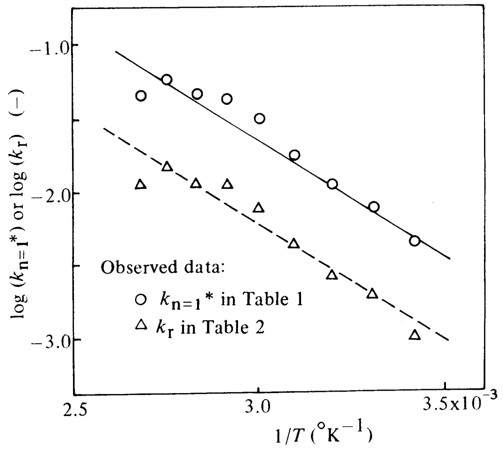

Fig. 6. Arrhenius plots of $k_{n=1}{}^*$ and k_r for the soaking and cooking of soybean.
Calculated values : ——— for Eq.(15)
------ for Eq.(16)

rice and potatos are chemical changes of starch components such as α-conversion and so on, and that the phenomena of the soaking or cooking of soybean are perhaps physical transformations such as hydrating or bonding phenomena between the soybean components and the soaked water. The obtained values of the apparent activation energy are very complicated and perhaps higher than those of the physical transformations in the inner component, because the sample weights at the higher cooking temperatures contain the weights of the extra water in the space of two hemispherical inner components.

The effects of the temperature on the cooking of soybean have been determined by Quast *et al.*$^{6)}$ at higher temperatures ranging from 89~127°C using a share press method. The values of the apparent activation energy at higher temperatures was 43.5 kcal/g-mol. This value is considerably higher than the value obtained at 20~100°C. From these results, we may infer that the cooking phenomena of soybean at above 100°C is perhaps the chemical reaction between the soybean components and the soaked water.

The soaking or cooking rations by the weighing method used in this study are the values corresponding to the mainly physical changes of soybean. If the cooking rations are measured by the other method which that allows a better observation of the chemical changess of the inner components, we may foresee that the apparent activation energy at 20~100°C might be increased to higher value than those obtained in this study. Therefore, it is necessary to carry out further experiments with the various methods in order to reach more accurate results.

SUMMARY

In former papers$^{1-4)}$, we studied the cooking rate equations of rice, potato and so on. This time, we took up the soaking and cooking rate equations of soybean whose components differ greatly from those of starch foods such as rice, potato and so on.

The results of this investigation can be summarized as follows :

(1) The soaking and cooking rates of soybean were obtained by the weighing method at 20 ~ 100°C.

(2) The rate equations were postulated in two types: one type is a first order empirical rate equation and the other is a semi-theoretical rate equation based on the water-soaking-shell model.

(3) The apparent activation energy was about 7 kcal/g-mol. This value is considerably less than the values in the cooking of soybean at 98~127°C obtained by Quast *et al.*$^{6)}$ From these results, we may deduce that the cooking phenomena of soybean consist perhaps in the physical and the chemical transformations at about below and above 100°C, respectively.

NOTATIONS

C	:	concentration of water, (g-H_2O/cm^3)
k_m	:	diffusion rate parameter of water in soybean component, (cm^2/min)

k_n and k_n^* : rate parameter of nth-order empirical rate equation, (g^{1-n}/min) and (1/min)
k_r : reaction rate parameter of soybean component with water, (cm/min)
n : order of empirical rate equation, (−)
R and r_c : radius of sample and unsoaked or uncooked core, (cm)
S_p : specific gravity of sample, (−)
T and t : soaking or cooking temperature, (°K) and (°C)
w : weight or sample, (g)
x : soaking or cooking ratio by Eq.(2), (−)
θ : soaking or cooking time, (min)
ρ_h : increasing concentration of water, (g–H_2O/ cm^3)
δ : standard deviation by Eq.(12), (−)

Subscripts;
0, e and d : initial, equilibrium and completely drying states

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大豆の浸漬，蒸煮速度に関する研究

久保田　清

前報[1-4]において，米，ジャガイモなどの蒸煮速度式に関する研究を行なってきた。本研究は，米，ジャガイモなどデンプン類食品と主成分を異にしている大豆の浸漬，蒸煮速度式に関する研究を行なったものである。

(1) 大豆の浸漬，蒸煮速度を，温度20～100℃において重量法により求めた。

(2) 浸漬，蒸煮速度式は，1次の経験的速度式と殻状吸水モデルに基づいた半理論的速度式で表わすことができた。

(3) 見掛の活性化エネルギーは，約7 kcal／g－mol となり，本研究より高い温度98～127℃においてQuastら[6]が求めてきている値43.5 kcal／g－mol よりかなり小さい値となった。大豆の蒸煮現象は，約100℃以下で物理的変化，また，これ以上で化学的反応が主体になっているのではないかと考えられる。