

## Study of the Rate Equation for the Soaking and Cooking of Red Bean

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(Figs. 1-7, Tables 1-2)

### INTRODUCTION

In order to design various cooking apparatuses, it is necessary to determine the soaking and cooking rate equations from the experimental data of the soaking and cooking of the foods. In a previous paper<sup>1)</sup>, we have studied the soaking and cooking rates of soybean and consequently we have formulated their rate equations. In this paper, we took up the soaking and cooking rate equation of red bean which is a very popular food in Japan, as cooked together with rice. Rice and red bean cooked together called "Sekihan (red cooked rice)" is eaten particularly on feast days such as birthdays, wedding days, New Year and so on.

In this study, we used the weighing method to obtain the soaking and cooking rates of red bean by measuring their change in weight during the process of soaking and cooking. The simple 1st-order rate equation which had been used for the soaking and cooking of soybean<sup>1)</sup>, could not be applied for the soaking and cooking of red bean. The soaking and cooking rate equations of red bean were postulated as a renewed rate equation possessing a S-shape's constant newly defined.

### RATE EQUATION

The relations of the degree of soaking and cooking vs. the soaking or cooking time of red bean did not show monotonous smooth curves, but gave S-shape's curves as shown below. Thus, we postulated the rate equation as follows:

$$dx/d\theta = k_{n,\alpha} (1-x)^n (x+\alpha) \quad (1)$$

where,  $x$  (-) represents the soaking or cooking ratio expressed as in the following equation.  $\theta$  (min) is the soaking or cooking time, and  $k_{n,\alpha}$  ( $\text{min}^{-1}$ ),  $n$ (-) and  $\alpha$ (-) are the rate parameters which can be obtained from the experimental data as shown below.

$$x = (w - w_0) / (w_e - w_0) \quad (2)$$

Where,  $w$  (g) is the soaking or cooking weight of the sample at any given time  $\theta$ , and  $w_0$  and  $w_e$  (g) are the weight at the initial and at the equilibrium states, respectively. The dimensionless values of  $x$  vary from 0 to 1 with the changes of  $w$  from  $w_0$  to  $w_e$ .

The experimental data in the soaking or cooking of red bean were obtained as relationships of  $w$  vs.  $\theta$  as shown below. The rate parameters in Eq. (1) can be calculated from the relationships of  $x$  vs.  $\theta$  which is obtained from the data of  $w$  vs.  $\theta$  by using Eq.(2). Eq. (1) is non-linear in terms of  $k_{n,\alpha}$ ,  $n$  and  $\alpha$ , so we must calculate these values by a non-linear least square method<sup>2)</sup>. Then, the values of the following standard deviation  $\sigma$  (—) for the variable  $x$  were minimized. Eq.(1) was integrated numerically using the Runge-Kutta-Gill method. The FACOM 230-75 digital computer of the Computation Center in Nagoya Univ. was used for these calculations.

$$\sigma = \left\{ \sum_{i=1}^N (x_{obs} - x_{cal})_i^2 / N \right\}^{1/2} \quad (3)$$

The initial values of the rate parameters in Eq.(1) were given as  $n=1.0$  and  $\alpha=0.01$ , and the initial values of  $k_n$ ,  $\alpha$  were estimated by following the integrated equation obtained from Eq.(1).

$$k_{n=1, \alpha} = \frac{1}{(1-\alpha)\theta} \ln \frac{x+\alpha}{(1-x)\alpha} \quad (4)$$

## EXPERIMENTAL

The red bean used as the sample is the so-called "Dainagon". It was harvested in 1977 in the Hokkaido district, Japan. It was bought commercially, sealed in a polyethylene pouch and store in a refrigerator at 5°C. The weight of one grain of red bean was approximately 0.116 g and the volume 0.0899 cm<sup>3</sup> (diameters: 0.47, 0.52, 0.71 cm). It's moisture content was about 15.1 % (wet bases).

The weight red bean (60 grains) was put into a sample basket made of a wire net, and put into water of a desired temperature during a fixed time. Then the cooked red bean was taken out, and poured quickly into water of 30°C for 0.5 minutes to cool off and stop the further cooking of the sample. The surface water of the cooled sample was wiped immediately by a filter paper, and then transfused into a weighing tube. After this, the accurate weight of the sample was taken on a chemical balance.

The specific gravity of the sample was measured by means of a specific gravity bottle at 30°C. The weight of the sample in it's completely drying state was estimated as being equal to the values of 20 hours drying at 135°C in a dryer.

## RESULTS AND DISCUSSION

The relation at the soaking and cooking temperatures of 20 to 97°C between the weight ratio  $w/w_0$  (—) and the soaking or cooking time  $\theta$  (min) of red bean is shown in Figs. 1~3. This weight ratio is expressed as being the ratio of the weight of soaked or cooked red beans  $w$  (g) and of unsoaked or uncooked ones  $w_0$  (g). In Figs. 1~3, the relationships of  $w/w_0$  vs.  $\theta$  show characteristic S-shape's curves that invite to further

study. Okamura et al.<sup>3)</sup> studied the soaking rate of various kinds of beans at low temperatures of 5~25°C, and obtained the same S-shape's curves by the soaking of red beans.

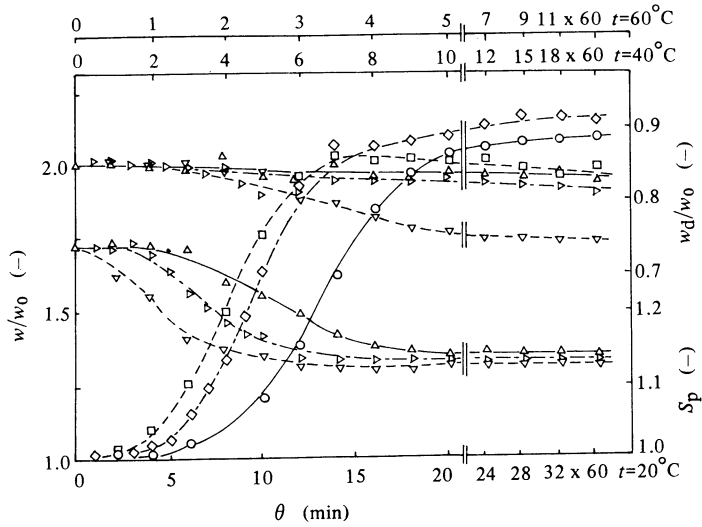


Fig. 1. Relations between the weight ratios  $w/w_0$ ,  $w_d/w_0$ , specific gravity  $S_p$  and the soaking or cooking time  $\theta$  of red bean.

Observed data:  $t = 20, 40, 60^\circ\text{C}$

$\circ \triangle \diamond \square \nabla$

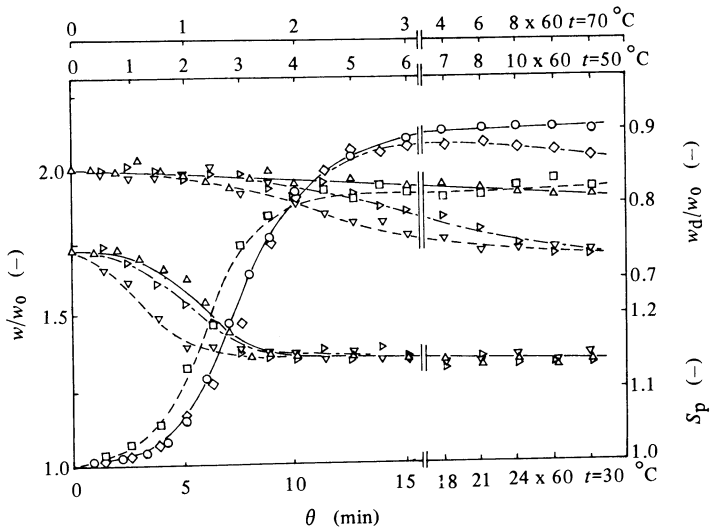


Fig. 2. Relations between the weight ratios  $w/w_0$ ,  $w_d/w_0$ , specific gravity  $S_p$  and the soaking or cooking time  $\theta$  of red bean.

Observed data:  $t = 30, 50, 70^\circ\text{C}$

$\circ \triangle \diamond \square \nabla$

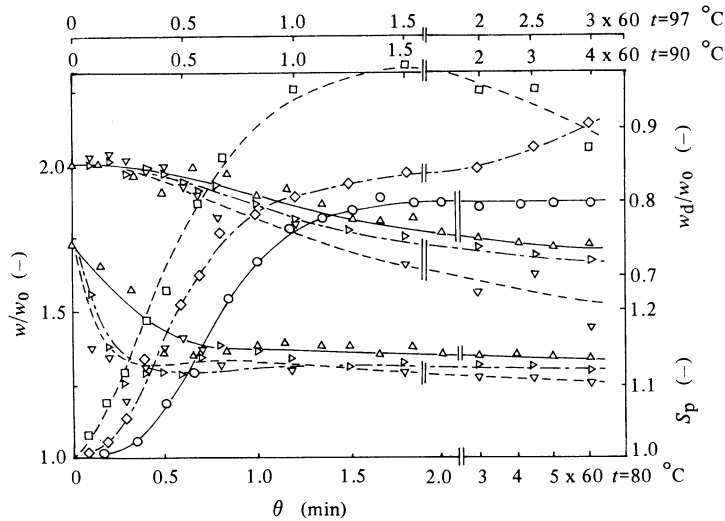


Fig. 3. Relations between the weight ratios  $w/w_0$ ,  $w_d/w_0$ , specific gravity  $S_p$  and the soaking or cooking time  $\theta$  of red bean.

Observed data :  $t = 80, 90, 97^\circ\text{C}$

$\triangle \diamond \square \nabla$

The relations between the weight ratio of the completely drying state and the initial state  $w_d/w_0$  (—); the specific gravity  $S_p$  (—) and the soaking or cooking time  $\theta$  are shown in Figs. 1~3, too. These relationships too show these characteristic S-shape's curves.

The red beans soaked at a soaking temperature under  $40^\circ\text{C}$  were able to germinate on water-absorbed cotton at  $30^\circ\text{C}$ . The red beans soaked at  $50, 60, 70, 80$  and  $90^\circ\text{C}$  were only able to germinate for soaking times below 3 hours, 1 hour, 15 minutes, 1 minute and 10 seconds, respectively, and were not able to germinate when the soaking times were about 3.5 hours, 45 minutes, 5 minutes and 30 seconds, respectively. Therefore, we can consider that the phenomena under  $40^\circ\text{C}$  are the soaking phenomena of the beginning of the germinating process, and the phenomena above  $50\sim 60^\circ\text{C}$  are the real soaking and cooking phenomena. The starting positions of the soaking and cooking phenomena were regular at soaking or cooking temperatures of 20 until  $80^\circ\text{C}$ , but from  $90\sim 97^\circ\text{C}$  on the positions became irregular, as shown in Fig. 4.

The relationships of  $x$  vs.  $\theta$  used for determination of the rate parameters  $k_{n,\alpha}$ ,  $n$  and  $\alpha$  in Eq.(1) are shown in Figs. 5 and 6. The values of  $x$  were calculated by Eq. (2) using the values of  $w_e/w_0 = 2.13 \times 3, 2.06, 1.99, 1.92, 1.85, 1.98$  and  $2.34$  at  $t = 20, 30, \dots, 90$  and  $97^\circ\text{C}$ , respectively.

The calculated values of  $k_{n,\alpha}$ ,  $n$  and  $\alpha$  in Eq.(1) are listed in Table 1, and the calculated values of  $x$  for the obtained  $k_{n,\alpha}$ ,  $n$  and  $\alpha$  are illustrated by broken lines in Figs. 5 and 6. These calculated results are satisfactory enough. The calculated values of  $k_{n=1}, \alpha=0.01$  fixed  $n$  and  $\alpha$  are listed in Table 2. The calculated values of  $x$  are illustrated by solid lines in Figs. 5 and 6. The calculated results visualized by solid lines can be used effectively at  $t = 20\sim 80^\circ\text{C}$ , but they are not satisfactory at  $t = 90$  and  $97^\circ\text{C}$ . The reason is that the

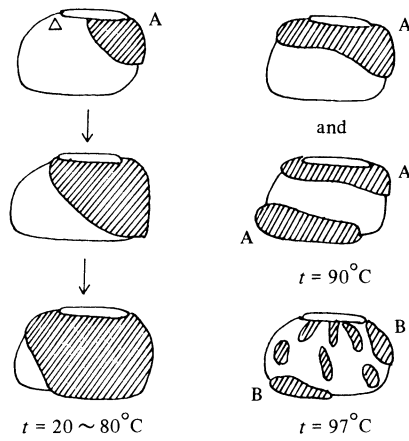


Fig. 4. Starting positions on the soaking and cooking of red bean.  
 A : Soaking position  
 B : Gas space position  
 $\triangle$  : Germinating position at  $30^\circ\text{C}$

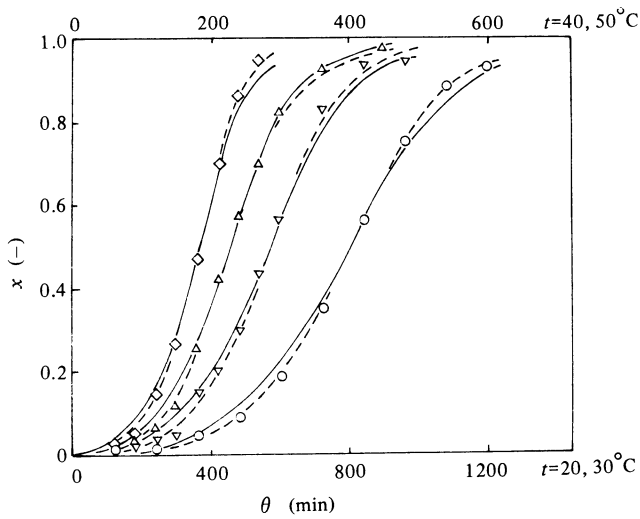


Fig. 5. Relations between the soaking or cooking ratio  $x$  and the soaking or cooking time  $\theta$  of red bean.  
 Observed data :  $t = 20, 30, 40, 50^\circ\text{C}$   
 $\circ \quad \triangle \quad \nabla \quad \diamond$   
 Calculated values : — for  $k_n=1, \alpha=0.01$  in Table 2.  
 - - - for  $k_n, \alpha, n$  and  $\alpha$  in Table 1.

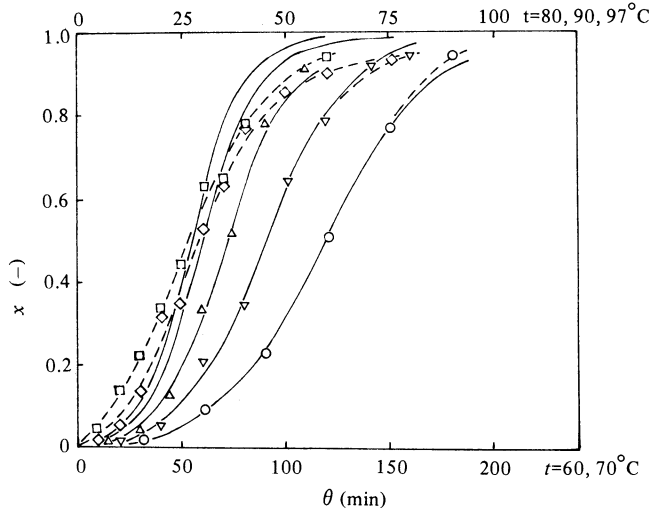


Fig. 6. Relations between the soaking or cooking ratio  $x$  and the soaking or cooking time  $\theta$  of red bean.

Observed data :  $t = 60, 70, 80, 90, 97^\circ\text{C}$   
 $\circ \triangle \nabla \diamond \square$

Calculated values : — for  $k_n=1, \alpha=0.01$  in Table 2.  
 ---- for  $k_n, \alpha, n$  and  $\alpha$  in Table 1.

values at 90 and 97°C are higher than the fixed value of 0.01 as shown Table 1. The S-shape's tendency becomes looser at the higher temperature, and the value of  $\alpha$  increases with the increasing of the soaking or cooking temperatures as shown in Table 1.

The values of the logarithm of  $k_{n=1}, \alpha = 0.01$  are plotted in Fig. 7 against the reciprocal of the absolute temperature. The Arrhenius equation is formulated as follows:

$$k_{n=1, \alpha=0.01} = 9.46 \times 10^4 \exp(-9.70 \times 10^3 / R_g T) \tag{5}$$

Table 1. Calculated values of  $k_n, \alpha, n$  and  $\alpha$  on the soaking and cooking or red bean

Soaking and cooking temp. $t$ ( $^\circ\text{C}$ )	Calculated values			Standard deviation $\sigma$ (-)
	$k_n \alpha (\text{min}^{-1})$	$n$ (-)	$\alpha$ (-)	
20	$7.35 \times 10^{-3}$	1.06	0.00274	0.00555
30	$1.34 \times 10^{-2}$	1.26	0.00283	0.00884
40	$1.97 \times 10^{-2}$	1.06	0.00385	0.0162
50	$2.80 \times 10^{-2}$	0.898	0.00535	0.00675
60	$3.61 \times 10^{-2}$	0.871	0.0112	0.00909
70	$5.90 \times 10^{-2}$	0.844	0.0120	0.0177
80	$1.04 \times 10^{-1}$	1.09	0.00973	0.0207
90	$1.39 \times 10^{-1}$	1.45	0.0252	0.0255
97	$9.30 \times 10^{-2}$	1.16	0.0876	0.0256

Table 2. Calculated values of  $k_{n=1}$ ,  $\alpha=0.01$  fixed  $n=1.0$  and  $\alpha=0.01$  on the soaking and cooking of red bean

Temp. $t$ ( $^{\circ}\text{C}$ )	$k_{n=1}, \alpha=0.01$ ( $\text{min}^{-1}$ )	$\sigma$ (-)	Temp. $t$ ( $^{\circ}\text{C}$ )	$k_{n=1}, \alpha=0.01$ ( $\text{min}^{-1}$ )	$\sigma$ (-)
20	$5.70 \times 10^{-3}$	0.0313	70	$6.39 \times 10^{-2}$	0.0213
30	$1.00 \times 10^{-2}$	0.0202	80	$1.01 \times 10^{-1}$	0.0228
40	$1.60 \times 10^{-2}$	0.0266	90	$1.52 \times 10^{-1}$	0.0714
50	$2.53 \times 10^{-2}$	0.0295	97	$1.65 \times 10^{-1}$	0.0913
60	$3.83 \times 10^{-2}$	0.0148			

where,  $T$  ( $^{\circ}\text{K}$ ) is the soaking or cooking temperature and  $Rg = 1.987$  cal/g-mol  $\cdot$   $^{\circ}\text{K}$  is the gas constant. The observed values at the higher cooking temperature were scattered from the calculated line. The reasons are due to the loosely S-shape's tendency and the scattered values of  $w_e$ .

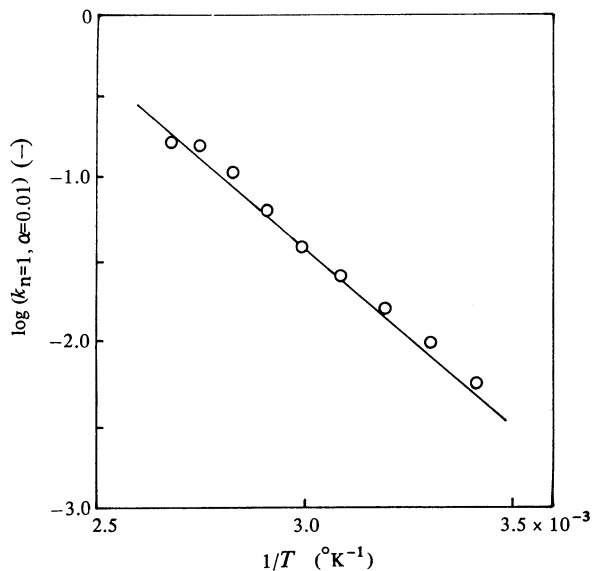


Fig. 7. Arrhenius plot of the rate parameter  $k_{n=1}, \alpha=0.01$  on the soaking and cooking of red bean.

The value of the apparent activation energy on the soaking and cooking of red bean is nearly equal to the value of 7 kcal/g-mol obtained on the cooking of soybean at 20~100 $^{\circ}\text{C}$  in previous paper<sup>1</sup>).

Quast et al.<sup>4</sup>) have studied the effects of temperature on the cooking rates of black bean, brown bean and soybean at higher temperatures ranging from 98~127 $^{\circ}\text{C}$  using a share press method. They obtained an apparent activation energy of 35.5~43.5 kcal/g-mol. This value is considerably higher than the values obtained in our studies on the cooking of soybean and red bean.

The values of the apparent activation energy of a chemical reaction are generally about 10 to 100 kcal/g-mol, and the general diffusion phenomena are under 10 kcal/g-mol. From the above considerations, we can suppose that the cooking phenomena of red bean at a temperature under 100°C are mainly physical hydrating phenomena between the red bean components and the soaked water, and that above 100°C they are perhaps a chemical reaction between the components and the water.

This paper has been presented at part of the Food Chemical Engineering Symposium at the 13th Autumn Meeting of the Society of Chemical Engineers, Japan (October 20, 1979 ; Nagoya).

### SUMMARY

In a former paper <sup>1)</sup>, the rate equations on the soaking and cooking of soybean have been investigated. In the present paper, we took up the soaking and cooking of red bean.

The soaking and cooking rates were measured by a weighing method at temperature ranges of 20~97°C. For the soaking and cooking of red bean, the simple *n*th-order rate equation, which had been used for the soaking and cooking of soybean, could not apply. The rate equation of red bean was postulated as the following equation with a S-shape's constant  $\alpha$ .

$$dx/d\theta = k_{n,\alpha} (1-x)^n (x+\alpha)$$

$$k_{n,\alpha} = 9.46 \times 10^4 \exp(-9.70 \times 10^3 / R_g T) \text{ (min}^{-1}\text{)},$$

$$n = 1.0 \text{ (-)}, \quad \alpha = 0.01 \text{ (-)}, \quad R_g = 1.987 \text{ cal/g-mol} \cdot ^\circ\text{K}$$

where,  $x$  (-),  $\theta$  (min) and  $T$  (°K) are the soaking or cooking ratio, time and temperature, respectively.

### NOTATIONS

- $k_{n,\alpha}$  : Rate parameter in Eq.(1), (min<sup>-1</sup>)  
 $N$  : Total number of the experimental points,(-)  
 $n$  : Order in Eq. (1), (-)  
 $S_p$  : Specific gravity of sample, (-)  
 $T$  and  $t$  : Soaking or cooking temperature, (°K) and (°C)  
 $w$  : Weight of sample, (g)  
 $x$  : Soaking or cooking ratio by Eq. (2), (-)  
 $\alpha$  : S-shape's constant in Eq.(1), (-)  
 $\theta$  : Soaking or cooking time, (min)  
 $\sigma$  : Standard deviation by Eq. (3), (-)

Subscripts ;

- o, e and d : Initial, equilibrium and completely drying states  
 obs and cal : Observed and calculated values



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## 小豆の浸漬，蒸煮速度式に関する研究

久保田 清

前報<sup>1)</sup>において，大豆の浸漬，蒸煮速度式に関する研究を行なった。本報では，前報に引続き，小豆の浸漬，蒸煮について研究をした。

浸漬，蒸煮速度を，温度 20～97℃において重量法により求めた。小豆の浸漬，蒸煮では，大豆の浸漬，蒸煮において使用できた簡単な n 次速度式が利用できないことが分った。小豆の浸漬，蒸煮速度式は S 型形状係数  $\alpha$  を含んだ次式で表わされた。

$$dx/d\theta = k_{n, \alpha} (1-x)^n (x+\alpha)$$

$$k_{n, \alpha} = 9.46 \times 10^4 \exp(-9.70 \times 10^3 / R_g T) (\text{min}^{-1})$$

$$n = 1.0 (-), \alpha = 0.01 (-)$$

$$R_g = 1.987 \text{ cal/g-mol} \cdot ^\circ\text{K}$$

ここで， $x$  (-)， $\theta$  (min) および  $T$  (°K) は，それぞれ浸漬，蒸煮率，時間および温度である。