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Kimchi Quality Kinetics during Isothermal and Nonisothermal Fermentation Conditions

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Abstract

This study was conducted to develop the fermentation kinetic modeling for the prediction of pH and acidity changes in *kimchi* at isothermal and nonisothermal fermentation temperatures (0~15°C) and salt concentrations (1.5~4.0%) using the traditional two-step method and alternative one-step method. The calculations of the two-step method of pH and acidity change during fermentation followed the patterns of the first order and zero order, respectively. The reaction rate constant of pH by the first order was increased from 0.008 day^{-1} to 0.017 day^{-1} by increasing the temperature from 0°C to 15°C at 2.75% of salt concentration, and was decreased from 0.013 day^{-1} to 0.010 day^{-1} by increasing the salt concentration from 1.5% to 4.0% at 5°C. For the pH and acidity of *Kimchi*, the zero order had a higher correlation than the first order to the estimate of the kinetics parameters by the one-step method. The E_a ranges of pH and acidity were 61.057~66.086 and 62.417~68.772 kJ/mole with different temperatures and salt concentrations. This one-step method had smaller and more realistic estimates of error ($p<0.001$) compared to the two-step method ($p<0.05$). The effective temperatures, T_{eff}, with 0~15°C of square function type of 12 hr intervals were 12.85, 11.48 and 12.46°C as increasing the salt concentration, 1.50, 2.75 and 4.00%, respectively. The T_{eff} were higher values than the mean temperature (7.5°C).

Key words: *kimchi*, isothermal, nonisothermal, kinetic

INTRODUCTION

Kimchi is a Korean traditional fermented vegetable food, which contains various nutrients and bioactive compounds from the ingredients and from the fermentation. *Kimchi* has functional properties such as antimutagenic, anticancer, and antioxidative activities (1,2). The commercial *kimchi* market has grown rapidly in response to consumer demand for convenience and is positioned as an international food. The fermentation reaction rate constant of *kimchi* is strongly dependent on fermentation temperature (3,4), salt concentration (5), and soluble solid content (6,7).

Chemical reactions in *kimchi* are not kinetically simple; they proceed through a number of steps between initial reactants and final products. The changes of pH and acidity in *Kimchi* are mainly due to lactic acid accumulation from anaerobic glycolysis (8). The study of chemical kinetics has provided a powerful mathematical structure that can be used to systemize and model experimental observations and to estimate the shelf-life of food (9). In general, chemical kinetics consists of estimating the reaction rate constant at constants temperature within the range of interest. The procedure most commonly used to determine kinetic parameters has been described as a two-step method and uses linear regression. The first step is to determine the concentration dependence of the rate at a fixed temperature. The temperature dependence of the reaction rate constant is then found using the Arrhenius equation (10). An alternative is the estimation of kinetic parameters by non-linear regression as an one-step method. The minimum for the sum of square differences between experimental and calculated values can be used to determine which kinetic parameters best describe data generated under a statistical software package (11,12).

The objectives of this study were to develop the fermentation kinetic modeling for the prediction of pH and acidity changes in *kimchi* at isothermal and nonisothermal fermentation temperatures (0~15°C) and salt concentrations (1.5~4.0%). It contained the comparison of models' fitness between the traditional two-step method and alternative one-step method.

MATERIALS AND METHODS

Materials

The average height, diameter, weight and moisture content of Chinese cabbages (*Brasica pekinesis* R.) used in this study were 28.25 cm, 12.17 cm, 2.52 kg and 94.17%, respectively. Red pepper powder and commercial bay salt as a salting agent were purchased from a local market and stored in a refrigerator until use. Other ingredients such as green onion, garlic and ginger were purchased on the study day.

Preparation and fermentation of *kimchi*

The Chinese cabbages cut into four parts were salted with 10% (w/v) salt solution at ambient temperature (20°C) to

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reach the desirable salt concentration (1.5 ~ 4.0%). After salting to different salt concentrations of 1.50%, 2.75% and 4.00 %, the reducing sugar contents in salted Chinese cabbages were 2.73%, 1.88% and 1.67%, respectively. The pHs and acidities in salted Chinese cabbages at 1.50%, 2.75% and 4.00 % of salt concentrations were 6.10, 5.95 and 5.88, and 0.16%, 0.18% and 0.21%, respectively. After 1 hr draining of excess water, the salted chinese cabbages were well mixed with ingredients. The composition of standardized *kimchi* materials (13) are shown in Table 1.

Salted Chinese cabbages mixed with ingredients were packed on a 1 kg basis using a commercial laminated film package (nylon/Al/PE). Fermentation continued for 0 ~ 42 days at 0 ~ 15°C of isothermal and square function type nonisothermal conditions with intervals of 12 hr.

Sample preparation

Two hundred and fifty grams of *kimchi* was blended and a volume of 500 ml was extracted and centrifuged at 10,000 rpm for 20 min (Hitachi, SCR-208, Japan), and then filtered using Tyro No. 2 filter paper.

Chemical analysis

NaCl content was determined by titration with standard $AgNO_3$ using dichlorofluorescein as an indicator (7). Total reducing sugar was determined spectrophotometically using the dinitrosalicylic acid (DNS) method (7). pH was measured by a pH meter (Model-30, Mettler Co., England) and acidity was determined by titration with 0.1 N NaOH solution to a pH 8.2 and calculated on the basis of lactic acid (7).

Fermentation kinetics

Two-step method

The change rate of *kimchi* property at a fixed temperature, acidity or pH as fermentation degree indexes, can be modeled as :

$$\frac{d[A]}{dt} = \pm k[A]^n \qquad (1)$$

where, [A] = *kimchi* property, pH or acidity, k = reaction rate constant (1/days), t = time (day), and n = reaction order.

The temperature dependence of the reaction rate constant at which the reaction proceeds may be described by the following Arrhenius equation.

$$k = k_o \exp\left(-\frac{E_a}{R}\frac{1}{T}\right) \qquad (2)$$

Table. 1. Formula of *kimchi* materials[1)]

Materials	Amounts (g)
Chinese cabbage	1,000
Chinese radish	130
Red pepper powder	35
Green onion	20
Garlic	14
Ginger	6
Salted and fermented shrimp	22
Sugar	10

[1)]Salt concentrations in *kimchi* were adjusted to 1.50, 2.75 and 4.00%.

where, k_0 = pre-exponential factor, E_a = activation energy (J/mole), R=ideal gas constant (8.314 J/mole K), and T = absolute temperature (K).

One-step method

The general time-temperature-dependent kinetic model given by the combination of eqns (1) and (2) is :

$$\frac{d[A]}{dt} = \pm k_o \exp\left(-\frac{E_a}{R}\frac{1}{T}\right)[A]^n \qquad (3)$$

Eqn (3) has three parameters (n, k_o and E_a) that can be derived from experimental data. The parameters for the kinetic model can be estimated using non-linear regression which produces weighted least-squares estimates of the parameters of the nonlinear model (14,15). The non-linear procedure involves simultaneous solutions of eqns (1) and (2) without determining individual rate constant values. The non-linear forms for the zero-order (eqn 4) and first-order (eqn 5) reactions are given from eqn (3), respectively.

$$[A] = [A_0] \pm k_0 t \exp\left(-\frac{E_a}{R}\frac{1}{T}\right) \qquad (4)$$

$$[A] = [A_0] \exp\left[\pm k_0 t \exp\left(-\frac{E_a}{R}\frac{1}{T}\right)\right] \qquad (5)$$

where, $[A_0]$ = initial *kimchi* property [pH or acidity].

Suitable starting estimates of the parameters by the two-step method were put into the program SAS NONLIN procedure (16) for determining the parameter.

Temperature fluctuation

The distribution of commercial *kimchi* products through the marketing channel is not done at a constant temperature. For a variable temperature condition the reaction rate constant is also a function of time : $k_{[T(t)]}$.

Thus, the value of the *kimchi* property function, f [A], at time t can be given (17) by

$$f[A] = \int k_{[T(t)]}dt \qquad (6)$$

where, T (t) = temperature as a function of time.

A useful way of characterizing a known temperature function is by the ratio, α.

$$\alpha = k_{eff} / k_m \qquad (7)$$

where, k_m = the reaction rate at the mean temperature of the fluctuation (T_m), k_{eff} = effective reaction rate constant at T_{eff}, effective temperature, which causes the same pH and acidity changes as the variable temperature condition. The expression of the reaction rate constant as a function of a variable temperature used, is the following Arrhenius approach:

$$T_{eff} = T_m / (1 - (R/E_a) \ln(\alpha) T_m) \qquad (8)$$

RESULTS AND DISCUSSION

Reaction rate of pH and acidity by two-step method

The changes of pH and acidity during *kimchi* fermentation are mainly due to the lactic acid formation from anaerobic glycolysis. Therefore, measurement of pH or acidity could be used to determine the progress of fermentation.

The advantages of the two-step method are the ease of use and the small number of calculations required. Based on the correlation coefficients, the pH changes during *Kimchi* fermentation followed the pattern of the first-order (Table 2) and the reaction could be expressed as $d[A]/dt = \pm k[A]$ from eqn (1). The integrated equation for the quality factor, [A], takes the form $\ln([A]/[A_0])$ as a function of fermentation time and gives a straight line with a slope equal to the first order rate constant, k. Acidity changes during *Kimchi* fermentation followed the pattern of the zero-order. A plot of [A] as a function of fermentation time yields a straight line whose slope equals the zero-order rate constant.

Higher fermentation temperatures, lower salt concentrations and longer fermentation times resulted in lower pH and higher acidity. As the fermentation temperature increased from 0°C to 15°C at 2.75% of salt concentration, the reaction rate constants for pH decreased by the first order increased from 0.008 day^{-1} to 0.017 day^{-1}, and those of acidity were also increased from 0.028 day^{-1} to 0.072 day^{-1}. As the salt concentration increased from 1.5% to 4.0% at 5°C of fermentation temperature, the reaction rate of pH by first order reaction decreased from 0.013 day^{-1} to 0.010 day^{-1}, and those of acidity were also decreased from 0.039 day^{-1} to 0.036 day^{-1} as shown in Table 2.

The correlations of coefficients (r) of pHs and acidities were above 0.822 for the zero order and 0.796 for the first order, whose levels of significance in linear regressions were $p<0.05$. The usage of the two-step method used to calculate the reaction rate constants from the data assumes that the variance is evenly distributed over the raw data. Therefore each data point is assumed to have the same variance or absolute error; quite often it is constant. The result is that data points furthest away from the intercept have the largest influence, even when they are often the least accurate (11).

Activation energy for temperature dependence by two-step method

The influence of fermentation temperature on the reaction rate of pHs and acidities is expressed by an Arrhenius equation (eqn 2). Fig. 1 shows that a plot of a natural log of the reaction rate as a function of the reciprocal of absolute temperature yields a straight line with a slope of $-E_a/R$. Calculation of K_0 by eqn (2) involved finding the intercept at $1/T=0$ or when $T=\infty$. As this point is a long way from where the data points lie on the Arrhenius plot, a small change in E_a causes a large change in K_0. Linear regression of eqn 2 assumed that the two parameters could be determined independantly (9). The E_a describes the temperature sensitivity of the fermentation reaction rate.

The calculated E_a ranges of pH and acidity from 1.5% to 4.0% of salt concentration were 32.727~40.275 kJ/mole and 39.275~45.442 kJ/mole, which were quite low values compared to other literature results, 65.56 kJ/mole and 79.45 kJ/mole, respectively (18). The reason was that a larger magnitude of E_a in *kimchi* fermentation is associated with a higher temperature dependence (4). The commonly employed two-step method has some limitations with respect to statistical analysis of the data. The variability in the reaction rate constant is

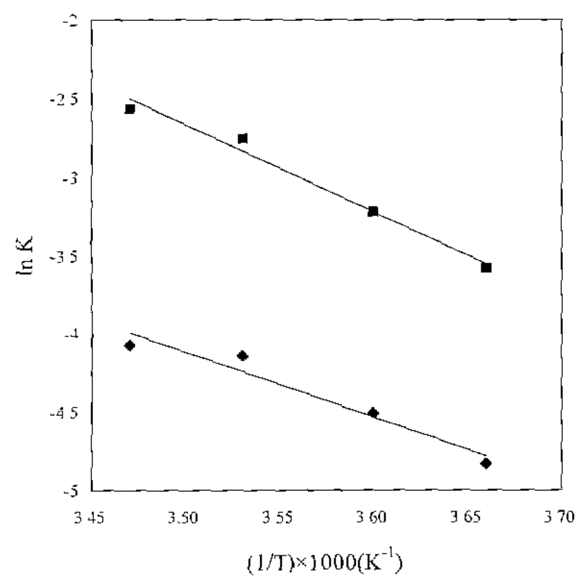

Fig. 1. Influence of fermentation temperatures on kinetics of pH and acidity at 2.75% of salt concentration. -◆- pH, -■- Acidity

Table 2. Rate constants for pHs and acidities in *kimchi* as a function of fermentation temperatures and salt concentrations by the two-step method

Reaction order	Fermentation temperature (°C)	1.50%[1)] pH K (day^{-1})	1.50% pH r	1.50% Acidity K (day^{-1})	1.50% Acidity r	2.75% pH K (day^{-1})	2.75% pH r	2.75% Acidity K (day^{-1})	2.75% Acidity r	4.00% pH K (day^{-1})	4.00% pH r	4.00% Acidity K (day^{-1})	4.00% Acidity r
0	0	0.044	0.973***	0.013	0.973***	0.041	0.910**	0.010	0.926**	0.032	0.895**	0.010	0.930**
	5	0.054	0.901**	0.020	0.957***	0.051	0.961***	0.018	0.967***	0.050	0.967***	0.017	0.981***
	10	0.080	0.879**	0.036	0.941**	0.078	0.870*	0.032	0.925**	0.061	0.876**	0.027	0.871*
	15	0.087	0.822*	0.054	0.896**	0.080	0.876**	0.053	0.947**	0.069	0.854*	0.051	0.964***
1	0	0.009	0.964***	0.034	0.993***	0.008	0.902**	0.028	0.966***	0.006	0.886**	0.027	0.966***
	5	0.013	0.924**	0.039	0.888**	0.011	0.968***	0.038	0.946**	0.010	0.972***	0.036	0.966***
	10	0.017	0.902**	0.071	0.878**	0.016	0.887***	0.064	0.871*	0.014	0.888***	0.057	0.856*
	15	0.019	0.858*	0.074	0.796*	0.017	0.903**	0.072	0.873*	0.015	0.876**	0.070	0.903**

1)Salt concentration. *$p<0.05$, **$p<0.01$ and ***$p<0.001$

Table 3. Activation energy for pHs and acidities in *kimchi* as a function of fermentation temperatures and salt concentrations by the one-step method[1)]

Reaction order	Fermentation temperature (°C)	1.50%[2)]						2.75%						4.00%					
		pH			Acidity			pH			Acidity			pH			Acidity		
		K_0	Ea[3)]	F[4)]	K_0	Ea	F	K_0	Ea	F	K_0	Ea	F	K_0	Ea	F	K_0	Ea	F
0	0	1.28E11	65.367	6101	8.30E10	67.182	527	1.24E11	65.823	1900	7 90E10	67.639	242	7.90E10	65.367	2452	1.09E11	68 772	182
	5	1.34E11	65.643	726	7.00E10	65.567	311	1.42E11	64.915	3150	7.50E10	65.823	513	1.29E11	64.915	4227	6.50E10	65.823	896
	10	5.40E10	63.057	443	5 00E10	65.408	238	6.40E10	61.509	570	1.25E11	65 367	208	1.19E11	63.099	746	1.17E11	65.597	168
	15	1.26E11	66.086	259	1.35E11	67.764	111	1.13E11	62.643	467	1.36E11	64.459	234	5.00E10	61.057	535	5.20E10	62.417	372
1	0	1.08E11	68.772	144	1.06E11	65 141	1037	1.32E11	69.228	146	1.24E11	66.049	279	1 17E11	70.136	126	1.18E11	66.505	108
	5	6.50E10	67.722	103	8.50E10	64.948	75	6.50E10	67.722	103	9.00E10	64.233	169	7.00E10	67.182	290	1.25E11	65.367	288
	10	9.90E10	68.233	87	5.20E10	63 526	73	9.90E10	68 233	87	1 16E11	63.325	70	9.80E10	66.275	84	8 00E10	62.873	66
	15	1.16E11	69.676	59	1.19E11	66.086	45	1.16E11	69.676	59	1.08E11	62 643	68	1.24E11	66 731	69	8.00E10	61.764	87

1)Using modified Gauss-Newton method in SAS, 2)Salt concentration, 3)Unit of activation energy is kJ/mol, 4)$F(0.001, 1, 6)=35.50$

generally ignored when calculating E_a and K_0, and there is less utilization of the raw data, resulting in the kinetic parameters being associated with only a small number of degrees of freedom, which resulted in large confidence intervals (11).

Estimating the kinetic parameters by the one-step method

Table 3 shows the comparison of kinetic parameters and fitness between the zero order (eqn 4) and first order (eqn 5) of non-linear regression procedure using a modified Gauss-Newton method in SAS. The method can be used for complicated multi parameter models, and the estimated parameter values are reliable because it produces weighted least-square method (16). The E_a range of pH in *kimchi* were 61.057 ~ 66.086 kJ/mole for the zero order and 66.275 ~ 70.136 kJ/mole for the first order, respectively. Those of acidity in *kimchi* were 62.417 ~ 68.772 kJ/mole for the zero order and 61.764 ~ 66.505 kJ/mole for the first order respectively. Both the zero order and the first order had excellent correlation existing between experimental data and non-linear regression ($F>45$). The levels of significance in regression were $p<0.001$. This one-step method had smaller and more realistic estimates of error, and more degrees of freedom associated with E_a and k_0, compared to the two-step method. For the pH and acidity of *kimchi*, the zero order had a higher correlation than the first order to the estimate of the kinetics parameters.

Comparison between isothermal and nonisothermal conditions

The fermentation degree and its usefulness for the shelf-life of commercial *kimchi* are strongly dependent on its temperature exposure history, from production, through distribution to consumption. In this experiment, the nonisothermal condition (0 ~ 15°C) was based on the real temperature fluctuation in *kimchi* distribution system (19). Fig. 2 shows the changes in pH and acidity of *kimchi* at isothermal (0°C and 15°C), and nonisothermal (0 ~ 15°C) conditions with 2.75% of salt concentration. Based on calculations of eqns (7) and (8), the effective temperature, T_{eff}, which causes the same acidity changes as the variable temperature condition (0 ~ 15°C) with square function type of 12 hr intervals at 1.50, 2.75 and 4.00% of salt solutions were 12.85, 11.48, and 12.46°C, respectively. The effective temperatures were higher values than the mean temperature (7.5°C).

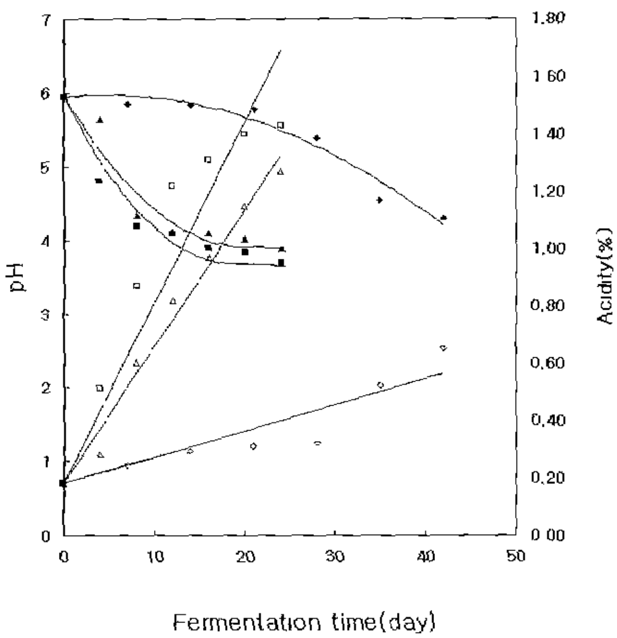

Fig. 2. Changes in pHs and acidities of *kimchi* at isothermal and nonisothermal temperatures with 2.75% of salt concentration. pH and acidity -◆-, -◇- at 0°C; -■-, -□- at 15°C; -▲-, -△- at 0 ~ 15°C.

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REFERENCES

1. Park, K. Y., Baek, K. A , Rhee, S. H. and Cheigh, H. S. : Antimutagenic effect of *kimchi. Foods and Biotechnology*, **3**, 141 (1995)
2. Park, K. Y. : The nutritional evaluation, and antimutagenic and anticancer effects of *kimchi. J. Korean Soc. Food Nutr.*, **24**, 169 (1995)
3. Choi, S. Y., Lee, M. K., Choi, K. S., Koo, Y. J. and Park, W.

S. : Changes of fermentation characteristics and sensory evaluation of *kimchi* on different storage temperature. *Korean J. Food Sci. Technol.*, **30**, 644 (1998)
4. Mheen, T. I. and Kwon, T. W. : Effect of temperature and salt concentration on *kimchi* fermentation. *Korean J. Food Sci. Technol.*, **16**, 443 (1984)
5. Park, W. P. and Kim, Z. U. : The effect of salt concentration on *kimchi* fermentation. *J. Korean Agri. Chem. Soc.*, **34**, 295 (1991)
6. Shin, S. T., Kim, K. J. and Kyung, K. H. : Effect of soluble solids contents of Chinese cabbage on *kimchi* fermentation. *Korean J. Food Sci. Technol.*, **22**, 278 (1990)
7. Yu, H. G., Kim, K. H. and Yoon, S. : Effect of fermentable sugar on storage stability and modeling prediction of shelf-life in *kimchi*. *Korean J. Food sci. Technol.*, **24**, 107 (1992)
8. Lee, K. H., Cho, H. Y. and Pyun, Y. R. : Kinetic modelling for the prediction of shelf-life of *kimchi* based on total acidity as a quality index. *Korean J. Food Sci. Technol.*, **23**, 306 (1991)
9. Taoukis, P. S. and Labuza, T. P. : Applicability of time-temperature indicators as shelf life monitors of food products. *J. Food Sci.*, **54**, 783 (1989)
10. Mallikarjunan, P. and Mittal, G. S. : Meat quality kinetics during beef carcass chilling. *J. Food Sci.*, **59**, 291 (1994)
11. Munes, R. V., Rhin, J. W. and Swartzel, K. R. : Kinetic parameter evaluation with linear increased temperature profile : Integral method. *J. Food Sci.*, **56**, 1433 (1991)
12. Wells, J. H. and Singh, R. P. : The application of time-temperature indicator technology to food quality monitoring and perishable inventory management. In "*Mathematical modelling of food processing operations*" Thorne, S. (ed.), Elsevier Applied Science, New York. p.271 (1992)
13. Cho, E. J., Lee, S. M., Rhee, S. H. and Park, K. Y. : Studies on the standardization of Chinese cabbage *kimchi*. *Korean J. Food Sci. Technol.*, **30**, 324 (1998)
14. Haralmpu, S. G., Saguy, I. and Karel, M. : Estimation of Arrhenius parameters using three least square methods. *J. Food Process and Preservation*, **9**, 129 (1985)
15. Arabshahi, A. and Lund, D. B. : Considerations in calculating kinetic parameters from experimental data. *J. Food Process Engineering*, **7**, 239 (1985)
16. SAS Institute : *SAS User's Guide : Statistics*. SAS Inst. Inc., Cary, NC (1990)
17. Taoukis, P. S. and Labuza, T. P. : Reliability of time-temperature indicators as food quality monitors under nonisothermal conditions. *J. Food Sci.*, **54**, 789 (1989)
18. Ku, K. H., Kang, K. O. and Kim, W. J. : Some quality changes during fermentation of *kimchi*. *Korean J. Food Sci. Technol.*, **20**, 476 (1988)
19. Chung, W. S. : Problems in *kimchi* industry and prospective direction. *Food Industry and Nutrition*, **1**, 15 (1996)

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