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Kinetic Modeling for Quality Prediction During Kimchi Fermentation

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Abstract

This study was conducted to develop the fermentation kinetic model for the prediction of acidity and pH changes in Kimchi as a function of fermentation temperatures. The fitness of the model was evaluated using traditional two-step method and an alternative non-linear regression method. The changes in acidity and pH during fermentation followed the pattern of the first order reaction of a two-step method. As the fermentation temperature increased from 4°C to 28°C, the reaction rates of acidity and pH were increased 8.4 and 7.6 times, respectively. The activation energies of acidity and pH were 16.125 and 16.003kcal/mole. The average activation energies of acidity and pH using a non-linear method were 16.006 by the first order and 15.813 kcal/mole by the zero order, respectively. The non-linear procedure had better fitting to experimental data of the acidity and pH than two-step method. The shelf-lives based on the time to reach the 1.0% of acidity were 33.1 day at 4°C and 2.8 day at 28°C.

Key words: kinetic model, acidity, pH, Kimchi

INTRODUCTION

Commercial Kimchi has grown in production rapidly in response to consumer demand for convenience and is positioned as an international food. The primary factors contributing to the fermentation reaction rate of Kimchi are fermentation temperature(1), salt concentration(1,2) and soluble solid content(3,4).

The mathematical structure of chemical kinetics is often used to describe the quality change of foods. The rate of a chemical reaction is measured as the mass of a product produced or reactant consumed per unit time, while the mechanism of a reaction is the sequence of individual chemical events that produce the overall result of the observed reaction(5). The major products produced during Kimchi fermentation are lactic acid, succinic acid and citric acid. The study of chemical kinetics has provided a powerful mathematical structure that can be used to systemize and model experimental observations. In general, chemical kinetics consists of estimating the rate constant at different but constant temperatures within the range of interest. Kinetic parameters and their accuracy are estimated by linear regressions based on the Arrhenius model. This method is known as the two-step method(6). An alternative is the estimation of kinetic parameters by non-linear regression(7). 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 isothermal or non-isothermal conditions. The minimum is found using numerical or analytical optimization techniques(8).

The aims of this study were to develop the fermentation kinetic modeling for the prediction of acidity and pH changes in Kimchi at various fermentation temperatures, and to compare the fitness of models between the traditional two-step method and the alternative non-linear regression method.

MATERIALS AND METHODS

Materials

The average height, diameter, weight, moisture and reducing sugar content of Chinese cabbages(*Brasica pekinesis* R.) used in this study were 28.12cm, 11.56cm, 2.43kg, 93.76% and 18.2mg/ml, respectively.

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Red pepper powder, monosodium glutamate, sugar 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 ginger, garlic, salt-fermented shrimp and green onion were purchased on the study day.

Preparation and fermentation of Kimchi

The Chinese cabbages cut into four parts were soaked in 15%(w/v) salt solution at ambient temperature(21°C) to reach the 3% salt concentration. The salting time, 170min, was determined by preliminary experiments. After draining of the excess water, the salted Chinese cabbages were mixed with ingredients. The composition of Kimchi materials are shown in Table 1, which is the recommended formula of Health and Welfare Ministry(9).

Salted Chinese cabbages mixed with ingredients were packed 1kg basis using a laminated film(nylon/AL/PE). The fermentation temperatures were 4, 12, 20 and 28°C.

Chemical analysis

One hundred grams of Kimchi was blended ; a specific volume(30ml) was extracted and centrifuged at 10,000rpm for 20min(Hitachi, SCR-20S, Japan) and then filtered with a Tyro No.2 filter paper. The filterate was used for chemical analysis.

Concentration of NaCl was determined by titration with standard $AgNO_3$ solution using dichlorofluorescein as an indicator(10). Total reducing sugar was determined spectromitricaly using dinitrosalicyclic acid(DNS) method(11). pH was measured by pH meter(Hanna HI-8519, Italy). Acidity was determined by titration with 0.05N NaOH solution to a pH 8.20 and calculated on the basis of lactic acid(11). All data reported were the mean values from three determinations.

Table 1. Formula of Kimchi materials

Materials	Amounts(%)
Chinese cabbage	85.9
Garlic	1.0
Red pepper powder	3.0
Green onion	2.0
Salted and fermented shrimp	1.4
Ginger	0.5
Salt[1)]	5.0
Sugar	1.0
Monosodium glutamate	0.2

[1)]Salt concentration in Kimchi was adjusted to 3%

Fermentation kinetics modeling

The study of chemical kinetics, however, has provided a powerful mathematical structure that can be used to systemize and model experimental observations. The rate of a chemical reaction is measured as the mass of a product produced(or reactant consumed) per unit time, while the mechanism of a reaction is sequence of individual chemical events that produce the overall result of the observed reaction(7).

The rate of change of Kimchi property, 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(acidity or pH), k=reaction rate constant(1/day), t=time(day) and n=reaction order.

The temperature dependence of the rate at which the reaction processes may be described by the following Arrhenius relationship.

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

where k_o=pre-exponential factor, E_a=activation energy (cal/mole), R=ideal gas constant(1.987cal/mole K) and T=absolute temperature(K).

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

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

Eq. 3 has three parameters(n, k_o and Ea) 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 nonlinear models(7,12,13). The non-linear procedure involves simultaneous solution of eqns (1) and (2) without determining individual rate constant values. The non-linear form for the zero-order and first-order reactions are given from eqn (3), respectively.

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

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

where $[A_o]$=initial Kimchi property(acidity or pH).

Data on changes during fermentation can be coded into a computer data array, and the kinetic parameters determined using the SAS NONLIN procedure(14).

RESULTS AND DISCUSSION

Reaction rate of acidity and pH by two step method

The acidity and pH changes as a function of fermentation time at various temperatures are shown in Fig. 1. The changes in pH and titratable acidity showed good accordance with fermentative gas pressure(15). The changes of pH during Kimchi fermentation are mainly due to the lactic acid formation from anaerobic glycolysis. Therefore, measurement of acidity or pH could be used to determine the progress of fermentation. The reaction order of eq. 1, n, is set to 0 or 1 for most modes of food reaction, though some, for example, pure lipid oxidation, have a different value of n(7).

Acidity and pH changes during Kimchi fermentation followed the pattern of the first-order reaction(n=1) and the reaction could be expressed from eq. 1. $d[A]/dt=\pm k[A]$ and the integrated equation for the quality factor, [A], takes the form $\ln([A]/[A_o])=\pm kt$. Thus, a plot of $\ln([A]/[A_o])$ as a function of fermentation time gives a straight line with a slope equal to the first order rate constant, k(Fig. 1 and Table 2).

As expected, higher fermentation temperatures and longer fermentation times resulted in higher acidity and lower pH. As the fermentation temperature increased

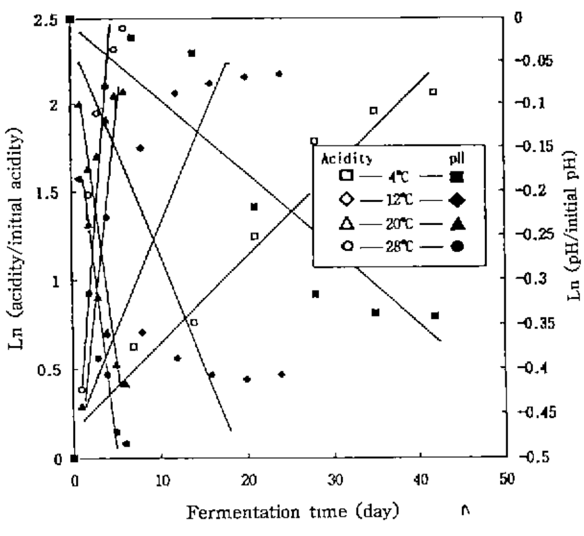

Fig. 1. Changes in acidities and pHs of Kimchi during fermentation at various temperature.

Table 2. Rate constants(k) for acidities and pHs in Kimchi as a function of fermentation temperatures

Fermentation temp.(°C)	Acidity		pH	
	$k(day^{-1})$	r^2	$k(day^{-1})$	r^2
4	0.0504	0.9616***	0.0099	-0.9017**
12	0.0878	0.7632*	0.0146	-0.6821*
20	0.3685	0.8671**	0.0723	-0.9376***
28	0.4227	0.8892**	0.0755	-0.8763**

*$p<0.05$, **$p<0.01$ and ***$p<0.001$

from 4°C to 28°C, the reaction rates of acidity were increased from 0.0504 day^{-1} to 0.4227 day^{-1}, and those of pH were also increased from 0.0099 day^{-1} to 0.0755 day^{-1}, as shown in Table 2. The rate constants for acidity and pH in Kimchi were increased rapidly with the fermentation temperature increased from 12°C to 20°C. While, the rate constants for pH were increased slowly with the fermentation temperature increased from 20°C to 28°C.

The correlation determinations of coefficients(r^2) were above 0.6821 and the levels of significance in linear regressions were $p<0.05$, which meant good correlations existed between experimental data and linear regressions.

Activation energy for temperature dependence by two step method

The influences of fermentation temperature on the reaction rate of Kimchi property(acidity or pH) are expressed by Arrhenius equation(eq. 2). Fig. 3 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 $-E_a/R$. The activation energy(E_a) describes the temperature sensitivity of the fermentation reaction rate. Larger magnitude of E_a is associated with higher temperature dependence.

The calculated activation energies(E_a) of acidity and pH were 16.215kcal/mole and 16.003kcal/mole, respectively. The Arrhenius relationship of the acidity and pH, and fermentation temperature were straight lines with good linear fits($r>0.9384$, Fig. 3). The level of significance in linear regression was $p<0.05$.

Estimating the kinetic parameters by non-linear regression method

Table 3 shows that the comparison of kinetic parameters and fitness between the zero order(eq. 4) and

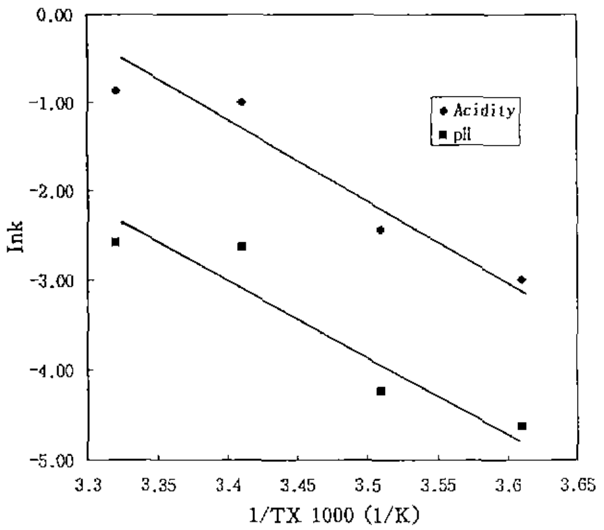

Fig. 2. Influence of fermentation temperatures on kinetics.

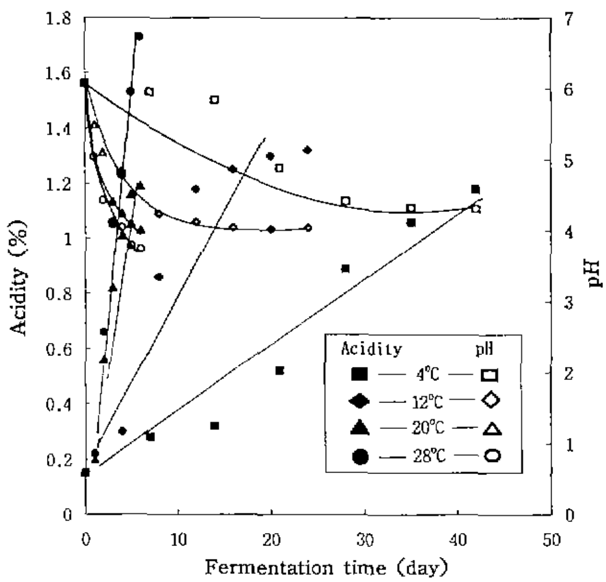

Fig. 3. Predicted and observed changes in acidities and pHs of Kimchi at various fermentation temperatures.

*Acidity was based on zero order and pH was based on first order.

first order(eq. 5) of non-linear regression procedure using a modified Gauss-Newton method in SAS which can be used for complicated multiparameter models and the estimated parameter values are reliable because it produces weighted least-squares estimates(14). The average activation energies(E_a) of acidity in Kimchi were estimated to be 16.070kcal/mole for the zero order and 16.006kcal/mole for first order and, those of pH in Kimchi were 15.522kcal/mole for the zero order and 15.813kcal/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($F>31.77$). The levels of significance in regressions were $p<0.01$. For the acidity of Kimchi, the zero order had the highest correlation among three different method to estimate the kinetics parameters. While, for the pHs of Kimchi, the first order had the highest correlation. These activation values for acidity and pH using the non-linear regression method are similar to those of two step method, 16.215kcal/mole for acidity and 16.003kcal/mole for pH. Other literature results, the activation energies of acidity and pH were 18.99kcal/mole and 15.67kcal/mole respectively(16). The differences of activation energies resulted from salt concentration, formulation and soluble solid content differences(3,4).

Predicting the acidity and pH change

Fig. 3 shows the changes in acidity and pH of Kimchi and the predicted curves using a non-linear procedure at various fermentation temperatures. These curve patterns of acidity increase and pH decrease were related to the following reason. The bacteria that bring about the characteristic Kimchi fermentation act upon the fermentable sugars and break down to mainly lactic acid which dropped the pH in Kimchi. Increased rate

Table 3. Comparison of activation energy between zero order and first order using a non-linear regression procedure[1)]

Fermentation temp.(℃)	Acidity						pH					
	Zero order			First order			Zero order			First order		
	k_0	E_a[2)]	F[3)]	k_0	E_a	F	k_0	E_a	F	k_0	E_a	F
4	1.15E11	16.078	392.36	2.05E11	15.967	197.83	2.5E10	14.867	2651.09	1.3E10	15.419	2605.05
12	1.43E11	16.146	166.30	2.41E11	16.148	31.77	1.1E11	15.638	355.41	1.3E10	15.303	496.59
20	1.39E11	15.900	541.09	2.12E11	15.756	68.90	2.40E11	15.785	2275.36	8.0E10	16.077	4235.58
28	9.60E10	16.154	980.48	2.31E11	16.153	75.96	1.40E11	15.797	629.98	9.0E10	16.456	1058.114
Average		16.070			16.006			15.522			15.813	

1) Using modified Gauss-Newton method in SAS, 2) Unit of activation energy is kcal/mole, 3) $F(0.001, 1, 6)=35.50$

Table 4. Shelf-life of Kimchi based on the 1.0% of acidity at various fermentation temperatures

Fermentation temp.(°C)	Shelf-life(day)
4	33.1
12	9.4
20	4.1
28	2.8

of acidity was almost constant or dropped gradually as fermentation time increased between 12°C and 28°C. On the other hand, the acidity slowly increased the first 14 days of fermentation and then increased rapidly until 28 days of fermentation at 4°C.

The pH of Kimchi sharply dropped the first 3 days of fermentation from 6.07 to 4.12 and then decreased slowly at 28°C. The curve pattern of pH reduction at 20°C was almost similar to fermentation at 28°C. While the pH was slowly decreased the first 14 days of fermentation and then decreased rapidly until 28 days of fermentation at 4°C. This phenomenon is supported by other literature(1).

For the prediction of acidity and pH during Kimchi fermentation, the non-linear procedure was better for fitting equations to experimental data than the traditional two-step method based on the comparison of levels of significance in regressions and also calculated E_a without determining individual rate constant values. The non-linear form of the zero order and first order reactions were used to predict the acidity and pH changes during Kimchi fermentation, respectively.

Estimating the shelf-life

Table 4 shows the shelf-life of Kimchi based on the time to reach the 1.0% of acidity at various fermentation temperatures. The shelf-life of a food product is the period before microbiological, physicochemical or sensory qualities deteriorate beyond a set limit. Fermentation temperatures significantly affected the shelf-life of Kimchi as shown on Table 4. At 4°C, the shelf-life was extended to 33.1 day. While, the shelf-life was only 2.8 day at 28°C.

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