산업식품공학
Food Engineering Progress

Review

Kinetic Data for Texture Changes of Foods During Thermal Processing

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Abstract

To automate cooking processes, quantitative descriptions are needed on how quality parameters, such as texture change during heating. Understanding mechanical property changes in foods during thermal treatment due to changes in chemical composition or physical structure is important in the context of engineering models and in precise control of quality in general. Texture degradation of food materials has been studied widely and softening kinetic parameters have been reported in many studies. For a better understanding of kinetic parameters, applied kinetic models were investigated, then rate constants at 100°C and activation energy from previous kinetic studies were compared. The food materials are hardly classified into similar softening kinetics. The range of parameters is wide regardless of food types due to the complexity of food material, different testing methods, sample size, and geometry. Kinetic parameters are essential for optimal process design. For broad and reliable applications, kinetic parameters should be generated by a more consistent manner so that those of foods could be compared or grouped.

Key words: thermal processing, texture, softening, kinetics

Introduction

Texture is one of the most important characteristics of foods and quantifying changes in texture is quite useful to product and process and equipment design (Lund, 1982). For producers, postharvest handlers, processors, marketers and consumer, knowledge of texture properties is crucial because texture measurement is the most common techniques and procedures (Chen & Opara, 2013).

Understanding of pattern and mechanism of the texture changes is necessary to control, improve and predict the quality of heat processed foods. Many researchers have examined thermal softening of food materials and applied chemical reaction kinetic models to quantify a quality attribute. Foods are unstable in the thermodymic sense and tend to be stable kinetically; therefore, the models describing quality changes are kinetic models (Van Boekel, 2008). Real foods are complex biological system. Various reactions such as chemical oxidation, microbial growth, biochemical denaturation and physical changes occur in series or in parallel during thermal processing. Final food quality is decided by interacting and complex reactions rather than a single reaction (Ling et al.,

2015). Due to the complexity, modeled foods are normally regarded as a simple system.

To predict quality change during a simple cooking process, heat transfer and texture kinetic models should be considered simultaneously, and parameters for the both are required to simulate time-temperature history inside foods (Lee et al., 2007). It might be necessary to obtain objective and compatible texture kinetic parameters for precise quality prediction.

For the better understanding of texture kinetic parameters, published texture softening data, mainly vegetables, were investigated. Temperature of reaction rate constants was set to 100°C for reasonable comparison. Recently, Ling et al. (2015) reviewed kinetics of food quality changes during thermal processing and presented published kinetic parameters of different food product for color, nutrient content, and texture. However, they showed rate constants at different temperature condition.

This review describes 1) quantifying textural quality, 2) kinetic models on thermal softening of foods, and 3) previous studies on kinetic parameters for future texture kinetic studies. The better understanding of thermal softening kinetic parameters would lead to better process control.

Quantifying Textural Quality

The textural quality of foods changes as a result of physico-chemical changes during thermal processing (Rao & Lund, 1986) and the quality is perceived by various sensory inputs,

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interactions between foods and consumers before and during consumption; so, sensory evaluation is a method for expressing texture. However, sensory analysis is difficult to be conducted during each processing step (Jack et al., 1995). Therefore, mechanical properties of foods by instrumental measurements have been used as indices of texture for predicting effect of processing. Wide range of texture measurement instrument from simple hand-held device to instron machine and texture analyzer are adopted for objective tests (Chen & Opara, 2013).

Human perception to foods is based on several interacting factors while instrumental measurements measure one factor (Sawyer, 1971); therefore, instrumental measurements could not reflect exact sensory perception by consumers. However, both measurement methods are associated with a certain property. For softening, instrumental and sensory results are reported (Rao & Lund, 1986) to be linearly related in studies on green beans, corns, peas, and asparaguses (Hayakawa et al., 1977), black beans (Silva et al., 1981b), and shrimps (Ma et al., 1983). In addition, Collison et al. (1980) showed significant correlation between rupture load and taste panel score of potatoes during cooking. Böhler et al. (1986, 1987) examined the quality of cooked potatoes using both sensory and instrumental methods and coupled texture properties with appropriate instrumental methods.

Instrumental measurements are practical methods to quantify, collect, and generalize texture changes of foods to predict effects of processing conditions even though it is impossible to thoroughly replace sensory measurements with instrumental measurements.

Kinetic Models on Thermal Softening of Foods

First order kinetics

Most published texture studies express thermal softening as simple first order kinetic models. The first order kinetic model is simple and useful approach to express the degree of softening of foods (Rao & Lund, 1986). First order kinetic model for a texture property, P, is given by (equation 1) and the temperature dependence of softening rate, k, is described by the Arrhenius relationship (equation 2). Texture degradation of vegetables follows a first order kinetic model and the kinetic parameters are valuable for optimizing product quality (Rizvi & Tong, 1997). Even though the first order kinetic model can not express all of the data for extended thermal process times, it is still useful if the desired final texture value is within the range which the simple model describes.

$$\frac{dP}{dt} = -k \cdot P \tag{1}$$

$$k = k_o \cdot \exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

Dual mechanism first order kinetics

Huang & Bourne (1983) studied kinetics of thermal softening of vegetables for extended process times and proposed a dual mechanism first order kinetic model. They examined the rate of softening in several canned vegetables; beans, peas, beets and carrots during retort process at 100-121°C during which the softening was consistent with two simultaneous first order kinetic mechanisms. They hypothesized that there were two substrates 'a' and 'b' contributing to the firmness A and B and the sum of two was the total texture property at any time (equation 3). Both degradation of A and B could be expressed by first order kinetics. The rate constants for mechanism 1 (equation 4) acting on substrate 'a' is greater than those for mechanism 2 (equation 5) acting on substrate 'b', and temperature dependent rate constants in both mechanisms are expressed by Arrhenius equation (equation 2). A few assumptions have been made to explain the dual mechanisms thermal softening although there was no complete explanation for the mechanisms of two substrates. Huang & Bourne (1983) reported that the first rapid decrease is attributed to pectic changes in the interlamella layer but the mechanism of the following slow decrease is unknown. Alvarez et al. (2001) observed that the thermal softening kinetics of potato tissue is composed of two simultaneous pseudo first order reactions at 70 and 80°C while it is one pseudo first order kinetic mechanism at 50, 90 and 100°C, and presumes that the fast decreasing in the beginning of cooking time at 70 and 80°C is due to both starch gelatinization and slight changes of pectic substances, and the following slow decreasing is mainly affected by the pectic changes.

The dual mechanism first order kinetic model describes well the texture softening of vegetables but it needs further explanation for mechanisms of two substrates and abnormal kinetic parameters such as negative activation energy for second mechanism of green beans (Huang & Bourne, 1983).

Total property $P = A + B \tag{3}$

Mechanism 1 $\dfrac{dA}{dt} = -k_A \cdot A \tag{4}$

Mechanism 2 $\dfrac{dB}{dt} = -k_B \cdot B \tag{5}$

The two simultaneous first order kinetic models by Huang

& Bourne (1983) need rigorous mathematical treatment to obtain behavior of mechanism 1 and 2, which are effective whole cooking time. Feng et al. (1989) and Nourian & Ramaswamy (2003) showed two separate first order kinetic models for fast and slow degradation, respectively. It is easier to obtain kinetic parameters of two separate models than two simultaneous models. However, there is no clue to define the time when the first mechanism ends and the second, slower mechanism begins during cooking at different temperatures.

Fractional conversion technique

Foods lose their firmness completely after prolonged cooking in the simple first order kinetic and dual mechanism model but foods have nonzero maximum retainable texture property even after prolonged heating. Rizvi & Tong (1997) reexamined published texture softening data described by dual mechanism model and confirmed that the kinetics of softening of vegetables could be expressed well by a simple first order kinetic model when nonzero equilibrium texture property was considered. The fractional conversion factor, f, is defined as the ratio what has reacted in specified time to what must be reacted for completion (equation 6), and the change of (1-f) follows a simple first order reaction kinetics (equation 7). The rate constants in fractional conversion technique follow Arrhenius relationship (equation 2).

They showed that fractional conversion technique provided more reasonable and reliable texture kinetic parameters than the dual mechanism model. The simple kinetic model using a fractional conversion technique explained well even the thermal softening data of green beans having the negative activation energy (Huang & Bourne, 1983) that the materials softened primarily during the early stage of the reaction and slowly reached to a nonzero equilibrium texture property at a higher temperature.

$$f = \frac{P_o - P_t}{P_o - P_\infty} \tag{6}$$

$$\frac{d(1-f)}{dt} = -k \cdot (1-f) \tag{7}$$

Previous Studies on Kinetic Parameters

Thermal softening of foods could be quantified and generalized using kinetic models, and the model parameters such as rate constant and activation energy make possible to predict and control product quality. Ling et al. (2015), Rao & Lund (1986) and Villota & Hawkes (1986) reviewed softening

kinetics of foods and summarized published kinetic parameters. Available kinetic parameters on softening of foods from these and other studies are summarized in Table 1 where the reaction rate constants at $100^{\circ}C$ are calculated from the activation energies which are given or derived from the experiment results. The calculated rate constants do not always fit to experiment results well but the confidence interval issue is beyond the scope of this study. In most of the previous kinetic studies, vegetables were selected as a subject, deformation force or stress was measured as an index texture parameter, and the changes of texture properties were expressed by simple first order kinetic model. Unusually, Mansfield (1974) and Silva et al. (1981a) used the time to reach a certain texture property as an index texture parameter.

Lund (1982) reviewed that activation energies of muscle tissues were over 209 kJ/mol and those of plant tissues were 63-167 kJ/mol. Salmon (Kong et al., 2007), beef (Bertola et al., 1994) and canned shrimp (Ma et al., 1983) showed toughening and softening during cooking; so it is hard to compare with kinetics parameters from plant foods. In order to compare muscle foods with plant foods, more kinetic studies are needed.

Previous studies show wide ranges of kinetic parameters even among the same material. Texture indices are affected by not only testing methods such as instrument types and deformation methods but also sample geometry and size; therefore, it is hard to explain clearly the reason for the variation. Remarkably, the rate constants are similar in each study regardless of testing parameters though magnitude of the values is quite different among the studies. After measuring different texture properties of potatoes, both Alvarez et al. (2001) and Nourian & Ramaswamy (2003) obtained narrow ranges of rate constants, 0.059-0.098 and 0.127-0.169 /min, respectively. Harada et al. (1985) tested maximum shear force of three varieties of potatoes and found 0.279-0.396 /min of rate constants. For carrots, Verlinden et al. (1996) showed 0.161-0.660 /min of rate constants after measuring different texture properties whereas Paulus & Saguy (1980) obtained 0.041-0.069 /min from three different sizes and varieties of carrots.

Stoneham et al. (2000) pointed out that the variance of range of rate constants was due to not only testing parameters but also kinetic data reduction procedure on softening kinetics; so, insisted that the inconsistency of kinetic parameters could be overcome by using the fractional conversion technique because this data reduction procedure normalizes experimental parameters on the basis of total texture changes with nonzero final property. They showed that when the texture degradation

Table 1. Published texture kinetic parameters of foods

Subject		Kinetic model	Property	k, k_I or k_A at 100°C (/min)	Ea (kJ/mol)	Reference
Apricot (canned)		S	Maximum force	0.269	146.2	Mallidis & Katsaboxakis (2002)
Asparagus		S	Maximum force	0.106	79.5	Rodrigo et al. (1997)
		S		0.120	83.7	
		S		0.078	96.2	
		S		0.134	76.6	
		S		0.089	87.4	
		S		0.056	100.4	
		S	Maximum shear force	0.128	76.9	Rodrigo et al. (1998)
	(butt)	S	Maximum shear stress	0.065	102.5	Lau et al. (2000)
	(bud)	S		0.103	98.3	
Bean		S	Time to be acceptable product	0.144	171.5	Mansfield (1974)
	(canned)	S	Time to reach 150 g	0.023	131	Silva et al. (1981a)
	(canned)	S	of puncture force	0.015	79.9	
	(canned)	S		0.082	162.8	
	(canned)	D_1	Peak extrusion force	0.040	Ea_A=104.2, Ea_B=54.0	Huang & Bourne (1983)
	(canned)	D_1		0.107	Ea_A = 82.8, Ea_B = -136.8	
Beef		C	Maximum force	-	604.6 (net, <65°C), 362.4 (hardening, 65°C<)	Bertola et al. (1994)
Beet		S	Time to be acceptable product	0.115	142.3	Mansfield (1974)
	(canned)	D_1	Peak extrusion force	0.088	Ea_A = 94.6, Ea_B = 54.0	Huang & Bourne (1983)
	(canned)	D_1	Peak extrusion force	0.084	Ea_A = 113.4, Ea_B = 77.0	Huang & Bourne (1983)
		D_2	Maximum force	2.960	Ea_1 =82, Ea_2= 118 (<70°C), 17 (70°C<)	Feng et al. (1989)
		D_2		5.930	Ea_1 = 105, Ea_2 = 188 (<70°C), 47 (70°C<)	
Broccoli		S	Time to be acceptable product	0.217	54.4	Mansfield (1974)
Cabbage		S	Maximum shearing force	0.146	71.4	Jaiswal et al. (2012)
Carrot		S	Time to be acceptable product	0.126	159	Mansfield (1974)
		S	Rupture stress	0.049	92.05	Paulus & Saguy (1980)
		S		0.052	112.97	
		S		0.069	117.15	
		S		0.047	112.97	
	(canned)	D_1	Peak extrusion force	0.083	Ea_A = 63.6, Ea_B = 21.3	Huang & Bourne (1983)

Table 1. Published texture kinetic parameters of foods (continued)

Subject	Kinetic model	Property	k, k_1 or k_A at 100°C (/min)	Ea (kJ/mol)	Reference
	C	E-modulus	0.161	138	Verlinden et al. (1996)
	C	Rupture work	0.660	156	
	C	Rupture deformation	0.500	162	
	C	Rupture stress	0.381	143	
	C	Rupture stress	-	$Ea_C = 149$, $Ea_R = 26.9$, $Ea_D = 360$	Verlinden & De Baerdemaeker (1997)
	F	Peak force of the first compression	0.222	117.56	Vu et al. (2004)
	F	Maximum compression force to 70% of initial thickness	0.296	152.12	De Roeck et al. (2010)
Corn	S	Time to be acceptable product	0.325	66.9	Mansfield (1974)
Litchi	S	Peak compression force	0.008	59.13	Yu et al. (2011)
	F	Peak compression force	0.027	79.70	
Mushroom	D_2	Compression force to 50% of initial thickness	0.269	$Ea_1 = 15.22$, $Ea_2 = 10.32$	Ko et al. (2007)
Pea	S	Time to be acceptable product	0.439	81.6	Mansfield (1974)
	S		0.246	81.6	
(canned)	S	Extrusion tests	0.071	77.3	Rao et al. (1981)
(canned)	D_1	Peak extrusion force	0.080	$Ea_A = 113.4$, $Ea_B = 102.1$	Huang & Bourne (1983)
(canned)	D_1		0.101	$Ea_A = 146.4$, $Ea_B = 92.5$	
Potato	S	Time to be acceptable product	0.298	115.1	Mansfield (1974)
	S	Compression work	0.702	117.2	Loh & Breene (1981)
	S	Maximum shear force	0.396	133.3	Harada et al. (1985)
	S		0.279	140.2	
	S		0.387	145	
	S	Force resisting probe	0.224	70.91	Nisha et al. (2006)
	D_2	Peak force	0.781	$Ea_1 = 165.6$, $Ea_2 = 127.0$	Kozempel (1988)
	C	Rupture force	-	$Ea_F = 103$, $Ea_G = 820$ (<67.5°C), 244 (67.5°C<)	Verlinden et al. (1995)
	S		0.720	102	
	D_2 (70-80°C)	Rupture force	0.098	104.4	Alvarez et al. (2001)
	D_2 (70-80°C)	Apparent modulus	0.067	88.2	
	D_2 (70-80°C)	Shear force	0.081	117.4	

Table 1. Published texture kinetic parameters of foods (continued)

Subject	Kinetic model	Property	k, k_1 or k_A at 100°C (/min)	Ea (kJ/mol)	Reference
Potato	D_2 (70-80°C)	Apparent modulus (shear)	0.059	100.5	Alvarez et al. (2001)
	D_2 (70-80°C)	Tension force	0.095	97.5	
	D_2	Hardness	0.169	$Ea_1 = 107.5$, $Ea_2 = 79$	Nourian & Ramaswamy (2003)
	D_2	Stiffness	0.167	$Ea_1 = 107.0$, $Ea_2 = 80$	
	D_2	Firmness	0.127	$Ea_1 = 103.6$, $Ea_2 = 70$	
	S	Tangent modulus (Axial)	0.069	51.1	Solomon & Jindal (2003a)
	S	Tangent modulus (Radial)	0.290	84.5	
	F	Tangent modulus (Axial)	0.078	18.1	Solomon & Jindal (2003b)
	F	Tangent modulus (Radial)	0.152	26.9	
Rice	F	Deformation ratio	0.230	79.5 (75-100°C), 36.8 (110-150°C)	Suzuki et al. (1976)
Salmon	S	Shear force	0.004	100.47 (second phase)	Kong et al. (2007)
Shrimp (canned)	S	Shear force	0.007	100.4	Ma et al. (1983)
Squash	S	Time to be acceptable product	0.282	104.6	Mansfield (1974)

S: Simple first order kinetic model
D_1: Dual mechanism model; two simultaneous first order kinetics
D_2: Dual mechanism model; two separate first order kinetics
C: Compartment model
F: First order kinetic model using the fractional conversion technique

of potatoes was measured at 80°C in different instrument types, cross-head speeds, sample sizes, and texture parameters, the rate constants for in the fractional conversion technique were independent of experimental conditions even though the values of texture properties were affected significantly by the testing parameters. There have been only few kinetic studies providing both rate constants and activation energy for texture degradation using the fractional conversion technique. Solomon & Jindal (2003b) used the fractional conversion technique to describe texture changes of potatoes in various testing methods. In order to validate whether the change of conversion factor is certainly independent of testing parameters, further studies are required. Furthermore, the effects of testing protocols and temperatures on initial and equilibrium texture properties should be investigated.

Calculated rate constants at 100°C from Loh & Breene (1981), Feng et al. (1989), and Verlinden et al. (1995) were higher than others. They measured very beginning of cooking time and obtained the rate constants, which are only effective for 6 minutes, 15 seconds, and 5 minutes, respectively. Fast loss of turgor pressure at the initial cooking time might be one of the main reasons of the higher rate constants. Later, Verlinden et al. (1996) and Verlinden & De Baerdemaeker (1997) proposed compartment models to describe texture changes of carrots in which the mechanical properties were expressed by sum of components and the mechanical property contributed by turgor pressure, one of the components, was treated as a step function because it disappeared at the beginning of cooking. Kozempel (1988) suggested two separate first order kinetics for potatoes after measuring softening of potatoes at 74-85.5°C and explained that the initial faster softening was caused by starch gelatinization. The predicted rate constant for the fast softening at 100°C is very high as 0.781 /min but it is unknown how long the fast degradation lasts and how much the gelatinization process affects on the softening of potatoes at 100°C. Alvarez et al. (2001) observed similar biphasic degradation of potatoes only at 70 and 80°C. They concluded that the contribution of gelatinization to thermal softening was limited even though the initial fast softening mechanism was influenced by the gelatinization process, and the softening was mainly affected by solubilization of pectic material in cell wall and middle lamella after starch was gelatinized.

Conclusions

Kinetic parameters strongly depend on measurement methods and cooking conditions, and influence of physico-chemical changes on texture is quite complex. Rao & Lund (1986) emphasized that it is impossible to quantify all the changes of foods on account of thermal processing, and thermal lag effect must be considered in studies on softening because it depends on both size of the container and investigation methods.

The better prediction model could be obtained from the better understanding of kinetic parameters, and more reliable process control would be possible as kinetic parameters are generated in more consistent manner. Furthermore, the sensory perception during consumption has not been related to an objective engineering parameter. The relationship between sensory perception by large deformation during chewing and engineering parameters should be defined in future work.

List of Symbols

A: Texture property due to substrate a
B: Texture property due to substrate b
C: Compartment model
D_1: Dual mechanism model; two simultaneous first order kinetics
D_2: Dual mechanism model; two separate first order kinetics
Ea: Activation energy (kJ/mol)
Ea_A: Activation energy for texture property A (kJ/mol)
Ea_B: Activation energy for texture property B (kJ/mol)
Ea_1: Activation energy for fast process (kJ/mol)
Ea_2: Activation energy for slow process (kJ/mol)
f: The ratio what has reacted in specified time to what must be reacted for completion
F: First order kinetic model using the fractional conversion technique
k: Reaction rate constant at temperature T (/min)
k_A: Reaction rate constant for texture property A (/min)
k_B: Reaction rate constant for texture property B (/min)
k_o: Reaction rate constant at $T=\infty$ (/min)
k_1: Reaction rate constant for fast process (/min)
k_2: Reaction rate constant for slow process (/min)
P_t: Texture property at time t
P_o: Texture property at time $= 0$
P_∞: Maximum retainable texture property at time $= \infty$
R: Gas constant (8.314 J/mol·K)
S: Simple first order kinetic model
T: Absolute temperature (K)

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