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Kinetics of color development, pH decreasing, and anti-oxidative activity reduction of Maillard reaction in galactose/glycine model systems

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Abstract

Galactose/glycine model systems of sugar concentration 0.035, 0.069, 0.139, and 0.278 M were incubated at 60, 75, and 90 °C separately for studying the reaction kinetics of color development, pH change, and system anti-oxidative activity change in Maillard reaction. The results indicated that system color development followed first-ordered kinetics on galactose concentration; system pH went linearly down with a logarithm-ordered kinetics on galactose concentration; and anti-oxidative activity reduced linearly with a first-ordered kinetics on galactose concentration. The values of Q_{10} and activation energy ranged from 1.98 to 2.00 and from 68.8 to 69.5 kJ/mol, respectively, for these three properties.

Keywords: Maillard reaction; Reaction kinetics; Anti-oxidative activity

1. Introduction

Maillard reaction is one of the reactions that attract the very curiosities of food chemists and technologists. This is not only because that the reaction initiates with the consumption of two macronutrients common in foods and results in the formation of brown pigments and roasted aroma. But also, its outputs are so complicate that we can hardly define a real image whether or not the reaction occurring in foods is good for food quality or our health.

The anti-oxidative activity derived from Maillard reaction is one of such confusions that food scientists would want to explore. In the literatures pertaining to oxidative activity of Maillard reaction products (MRPs), some indicated that MRPs could act as antioxidants (Benjakul, Lertittikul, & Bauer, 2005; Osada & Shibamoto, 2006; Wagner, Derkits, Herr, Schuh, & Elmadfa, 2002); while others indicated MRPs were pro-oxidants (Anese, Manzocco, Nicoli, & Lerici, 1999; Odani et al., 1998; Puscasu & Birlouez-Aragon, 2002; Yen & Liao, 2002); and still others reported MRPs to exhibit both anti-oxidative and pro-oxidative activities (Calligaris, Manzocco, Anese, & Nicoli, 2004; Wijewickreme & Kitts, 1997; Yilmaz & Toledo, 2005). By reviewing these literatures, we can see such contradictory findings were differentiated from each other by the stages of Maillard reaction progresses. During the earlier stage, MRPs of smaller molecule such as glyoxal, methylglyoxal, some reductones, and other dicarbonyls are formed (Chen, Jin, & Chen, 2005; Hodge, 1953; Yaylayan & Haffenden, 2003). Since these compounds are high in oxidative potential and chemical activity, MRPs formed at this stage tend to be pro-oxidative. The high chemical activity of these compounds then drives Maillard reaction progress to the later stage forming products with high

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molecular weight and brown color through series of condensation and polymerization. Complex of MRPs at the later stage had been proved to be anti-oxidative (Wagner et al., 2002) and were named collectively as melanoidins. It is clear that the pro-oxidative MRPs are formed prior to the anti-oxidative ones in Maillard reaction. Consequently, it would be more healthful for any food processing dealing with Maillard reaction to take anti-oxidative activity into consideration. To reduce pro-oxidative activity and promote anti-oxidative activity in Maillard foods, food technologists need to know the reaction kinetics of Maillard reaction, i.e. the time and temperature required for foods to reach the optimal anti-oxidative activity.

Literatures concerning the reaction kinetics of Maillard reaction mainly focused on the reactant consumption (Chen et al., 2005), the color development (Ajandouz & Puigserver, 1999; Chen et al., 2005; Peterson, Tong, Ho, & Welt, 1994; Rapusas & Dricoll, 1995; Turkmen, Sari, Poyrazoglu, & Velioglu, 2006), and the formation of intermediate MRPs (Chen et al., 2005; Martins & van Boekel, 2005a, 2005b). However, because of its universal existence in foods, its critical role for food quality, its complexity in reaction mechanism, and its high diversity or reaction products, Maillard reaction, especially its reaction kinetics, has become quite a field worthy of far more exploration. In addition to the outputs mentioned above, there remains the reaction kinetics of still other resultant properties such as anti-oxidative activity, mutagenic activity, volatile formation, system pH, etc. to be investigated.

For Mallard reaction experiment, glucose/glycine model system was usually selected in many researches (Chawla, Chander, & Sharma, 2007; Göğüş, Bozkurt, & Eren, 1998; Martins & van Boekel, 2005a, 2005b; Schamberger & Labuza, 2007; van Boekel & Martins, 2002). Galactose is the major sugar in milk, which is wildly used as raw material in food processing. However, galactose/glycine model system was less adopted in pervious investigations (Chen et al., 2005). Therefore, in the current study, galactose/glycine model systems were used for constructing the kinetic parameters of color development, pH change, and anti-oxidative activity change in Maillard reaction.

2. Materials and methods

2.1. Galactose/glycine model systems

Galactose and glycine stock solutions were prepared separately. For galactose stock solutions, 50.0 g of α-D(+)-galactose (Sigma Chemical Co., USA) was dissolved in distilled and deionized water to make a final volume of 1000 mL. A series of twofold diluting process was then made from this original solution, and stock galactose solutions of 0.56, 0.28, 0.14, and 0.07 M were obtained separately. For glycine stock solution, 50.0 g of L-glycine (Sigma Chemical Co., USA) was dissolved in distilled and deionized water to make a final volume of 1000 mL. This was equivalent to a molar concentration of 1.33 M.

In the beginning of experiments, equal volume of stock galactose solution and stock glycine solution at the same temperature were mixed, adjusted pH to 8.0 using 1.0 N NaOH and 1.0 N HCl solutions. The final concentrations of galactose and glycine in the mixtures would be half of the stock solutions. The mixtures were dispensed in glass tubes, screw capped, then incubated at 60, 75, or 90 °C water bath immediately. Values of pH, brown color, and anti-oxidative activity were determined at interval of half an hour to 24 h(s) by using the following methods.

2.2. Measurement of pH

A pH meter (Model SP-71, Suntex Inc., Taiwan) was used for the determination of systems' pH values.

2.3. Measurement of brown color

The brown color of model systems was determined using absorbance at wavelength 420 nm (A_{420}) as the indicator. Instrument for determining A_{420} was a spectrophotometer (U-2100, Hitachi, Japan).

2.4. Measurement of anti-oxidative activity

Inhibition on the autoxidation of linoleic acid (Lingnert, Vallentin, & Ericksson, 1979) was modified and used for the determination of systems' anti-oxidative activity. Emulsion of 20 mM linoleic acid was prepared by dispersing equal volumes of linoleic acid (Sigma Chemical Co., USA) and Tween 20 (Sigma Chemical Co., USA) in 0.2 M phosphate buffer solution of pH 6.6. The experimental samples were prepared by adding DMSO-diluted galactose/glycine solution to the linoleate emulsion by a volumetric ratio of 200 μL to 2.0 mL, vortexed, and then incubated still in a dark chamber at 37 °C for 15 h. The blank sample was prepared in the same procedure with the experimental sample except that distilled and deionized water was used to replace galactose/glycine solution. Spectrophotometric detection was performed before and after the incubation. For spectrophotometric detection, 0.2 mL of sample emulsion was mixed with 7.0 mL 80% methanol, vortexed then put into the Hitachi U-2100 spectrophotometer for determination of A_{234}, which was used as the relative quantity of conjugated di-enes formed during linoleate oxidation. To eliminate the interference rose from the continuous Maillard browning during incubation, the baseline of A_{234} was prepared as the following procedure: mixtures containing the same components except with distilled and deionized water in place of linoleic acid were incubate at same conditions, and determined the absorbance difference. The anti-oxidative activity (AOA) of the model system was determined by the following equation:

$$\mathrm{AOA} = (\Delta A_{234\mathrm{B}} - \Delta A_{234\mathrm{E}})/\Delta A_{234\mathrm{B}} \quad (1)$$

where ΔA_{234B} was the absorbance increment of blank samples after incubation; and ΔA_{234E} was that of the experimental samples minus baseline A_{234}.

2.5. Data analysis and statistical method

Rates of reaction including color development, pH change, and anti-oxidative activity change were calculated using Eq. (2) which was derived from Laidler (1987):

$$v = dP/dt = k[G]^n \quad (2)$$

where v was reaction rate, P was the intensity of response, $[G]$ was initial galactose concentration, t was time, k was reaction constant, and n was the order of reaction.

For figuring out the effects of temperature on the reaction, the temperature coefficient (Q_{10}) and activation energy (E_a) were calculated using Eqs. (3) and (4), respectively.

$$\log k = \log(Q_{10}) \times 10^{-1} T_C + C \quad (3)$$

$$\ln k = C + (E_a/R) T_K^{-1} \quad (4)$$

where T_C and T_K were temperatures in Celsius and Kelvins respectively, E_a was activation energy in kJ/mol, C's were constants, and R was gas constant, which was 8.31×10^{-3} kJ/K mol. Eq. (3) was derived from Eq. (5), which as widely used for calculating the reaction rate at different temperature by known temperature coefficient.

$$k_{T_1} = k_{T_0} * Q_{10}^{(T_1 - T_0)/10} \quad (5)$$

where k_{T_1} and k_{T_0} were the reaction rate constants at temperature T_1 and T_0, respectively. Eq. (4) was derived from Arrhenius equation (Eq. (6)) (Laidler, 1987) by taking natural logarithm on both sides, and the natural logarithm of frequency factor, $\ln A$, as the constant.

$$k = A * e^{-E_a/RT} \quad (6)$$

All experiments were done in triplicate. Stepwise simple linear regression analysis, on the basis of least sum of square of residuals and visual examination on distribution of residuals, was used to describe the reaction rate.

3. Results and discussion

3.1. Color development

The progress of color development in Maillard browning, by using absorbance at 420 nm (A_{420}) as the indicator, could be divided into three linear stages. The first linear stage was at the beginning of browning reaction, during which change of A_{420} was not so apparent and was named the induction stage. This was followed by a sharp linearly increasing browning, namely the zero-ordered stage. After that, the change in A_{420} slowed down which might because that the system came gradually to saturation of brown color or the sedimentation of brown pigment, and that was the third linear stage. It was the zero-ordered stage that most researchers concerned about. The linear slope of A_{420} by time during the zero-ordered stage had been used as the browning rate in most studies. Consequently, the same parameter was employed as the reaction rate of color development in the current study.

Standard deviation of each data point ranged between 0.001 and 0.008 and is indicated as error bar in Fig 1. The rate of color development in galactose/glycine model systems, as shown in Fig. 1, was dependent not only on temperature but also on galactose concentration. Table 1 summarizes the linear regression parameters of systems' browning at the zero-ordered stage as shown in Fig. 1. Browning rates of the model systems (v_B), as shown in Table 1, ranged 0.11–0.67 $\times 10^{-4}$, 0.70–3.14 $\times 10^{-4}$, and 0.91–5.13 $\times 10^{-4}$ ΔA_{420}/s at temperature 60, 75, and 90 °C separately, depending on galactose concentration. Fig. 2 shows the correlation between browning rate and initial galactose concentration and revealed a first-ordered empirical equation of color development on galactose concentration:

$$v_B = C_1 + k_B[G]^1 \quad (7)$$

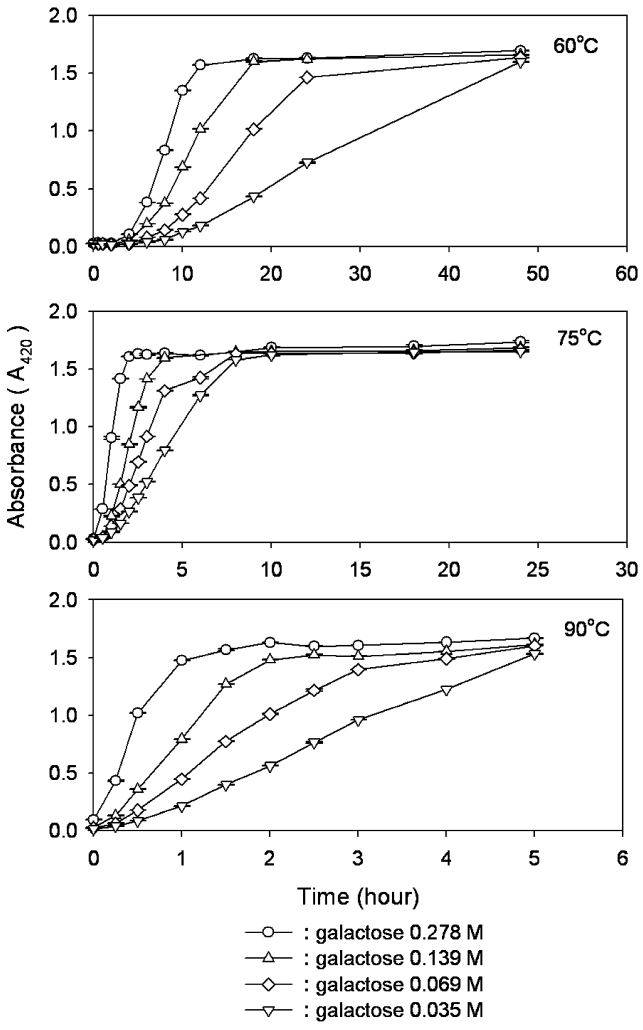

Fig. 1. Changes of the absorbance at 420 nm in galactose/glycine model systems incubated at 60, 75, and 90 °C.

Table 1
Linear regression parameters of browning reaction in galactose/glycine model systems using A_{420} as indicators

Galactose (M)	v_B ($\times 10^{-4}$ ΔA_{420}/s)			Intercept (A_{420})			R^2			Interval of regression (h)		
	90 °C	75 °C	60 °C	90 °C	75 °C	60 °C	90 °C	75 °C	60 °C	90 °C	75 °C	60 °C
0.035	0.91	0.70	0.11	−0.005	−0.012	−0.014	0.996	0.999	0.997	0.5–5	1.5–6	10–48
0.069	1.47	1.11	0.24	−0.004	−0.016	−0.031	0.996	0.998	0.996	0.25–2.5	1–4	8–24
0.139	2.51	1.69	0.33	−0.005	−0.022	−0.029	0.998	0.997	0.988	0.25–1.5	1–3	6–18
0.278	5.13	3.14	0.67	0.003	−0.014	−0.060	0.976	0.997	0.999	0–0.5	0.5–1.5	6–10

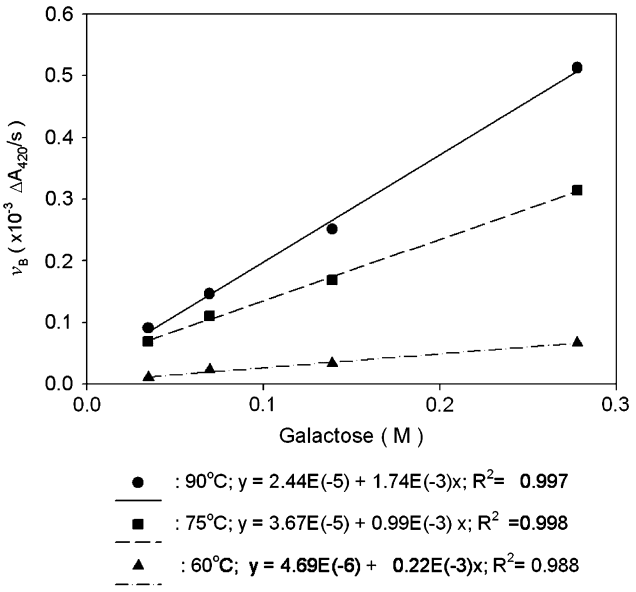

Fig. 2. Correlations of galactose concentration to the rate of color development in galactose/glycine model system at 60, 75, and 90 °C.

where C_1 was the constant, v_B was browning rate in ΔA_{420}/s, the slope k_B was rate constant of browning, which was 0.04, 0.20, and 0.35 ΔA_{420}/s M for systems at 60, 75, and 90 °C in sequence. The coefficients of determination (R^2) for Eq. (7) were all no less than 0.98 (Fig. 2). That justified the first-ordered kinetics of browning reaction in galactose/glycine model systems.

The effect of temperature on color development was figured out by taking linear regression according to Eqs. (3) and (4) and concluded with Eqs. (8) and (9):

$$\log k_B = 2.96 \times 10^{-2} T_C - 5.36 \quad (8)$$

$$\ln(k_B) = 17 - 8302 T_K^{-1} \quad (9)$$

Slope of Eq. (8) was equivalent to a Q_{10} of 1.98 for the reaction of color development in galactose/glycine model systems at temperature range between 60 and 90 °C. Slope of Eq. (9) was equivalent to activation energy 69.0 kJ/mol for the reaction of color development in the galactose/glycine model systems.

Reaction kinetics of color development in Maillard reaction had been reported to be zero- or pseudo-zero-ordered previously (Ajandouz & Puigserver, 1999; Chen et al., 2005; Peterson et al., 1994; Rapusas & Dricoll, 1995; Turkmen et al., 2006). If it were so, according to Eq. (2), the browning rates among different sugar concentrations at the same temperature, pH, and other conditions should have had no significant difference. However, in the studies of Peterson et al. (1994), Rapusas and Dricoll (1995), Ajandouz and Puigserver (1999), and Turkmen et al. (2006), only one single set of reactant concentration each was performed. It was very difficult to figure out the rate constant of color development from a single reactant concentration. The results of Chen et al. (2005) showed that the browning rate constant depended on the sugar concentration in galactose/glycine and glucose/glycine model systems. These rate constants reported in the above literatures seem more likely to be the browning rate. There was possibility that browning rate had been mistaken for browning rate constant. That led to the conclusion of "zero-ordered reaction kinetics of browning rate". In the current study, however, we found that color development in Maillard reaction was dependent upon galactose concentration as shown in Fig. 2 and Eq. (7). We thought that it would be much more suitable to define the kinetics of the color development in Maillard reaction to be first-ordered instead of zero- or pseudo-zero-ordered.

The activation energy and reaction Q_{10} had been the important and widely used parameters for predicting the effect of temperature on any specific reaction. There were literatures concerning the activation energy and reaction Q_{10} of Maillard browning in real food systems, including: Rapusas and Dricoll (1995) figured out the activation energy of Maillard browning in onion slices between 121 and 139 kJ/mol and Q_{10} value between 4 and 5 and Turkmen et al. (2006) indicated that the activation energy of zero-ordered formation of Maillard brown pigment in heat-treated honey between 50 and 70 °C was 122 kJ/mol. The employment of real food systems could be much practical for specific food environments. On the other hand, using model galactose/glycine systems as the subject in the current study could provide a much more fundamental model for understanding the reaction mechanism.

3.2. Rate of pH changes

Acidity of model systems increased throughout the experiments. Fig. 3 shows that the pH values in all model systems decreased linearly with time except those with higher galactose concentrations incubated at 90 °C. In the 90 °C systems, rate of pH also decreased linearly with a higher rate during the first 5 h then turned into a second

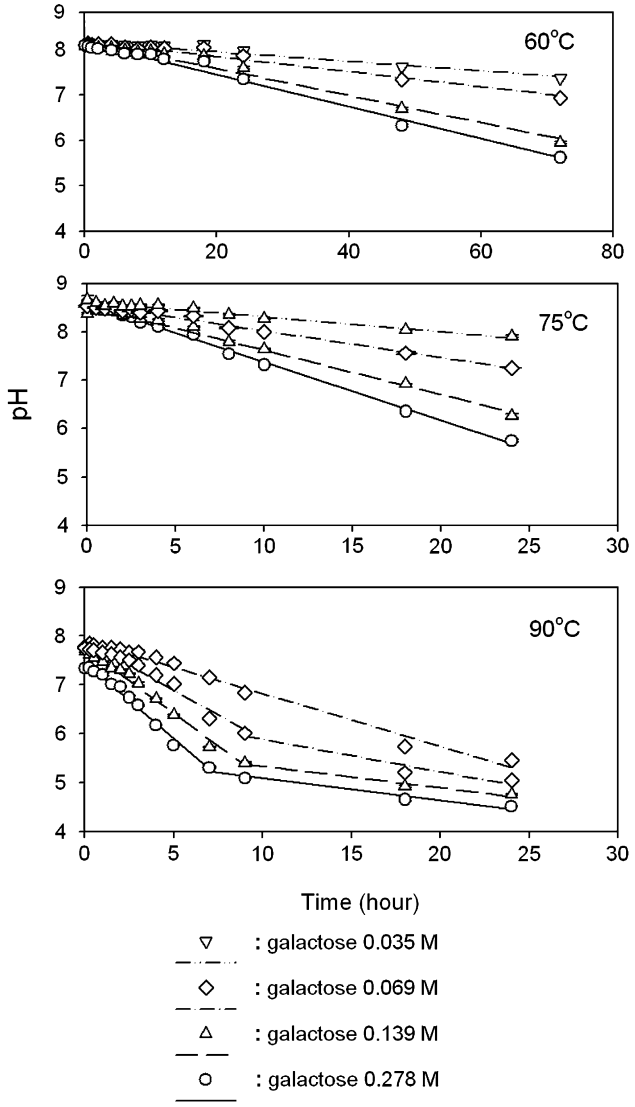

Fig. 3. Changes of pH in galactose/glycine model system incubated at 60, 75, and 90 °C.

linear stage with lower rate at hour between 5 and 10. These initial pH decreasing trends could be figure out with a linear empirical equation:

$$A_p = v_p t + C_2 \quad (10)$$

where A_p was acidity in pH, C_2 was the constant, t was time in s, and v_p was the decreasing rate of pH in ΔpH/s. All the linear parameters in Fig. 3 are shown in Table 2, in which decreasing rate of pH for model systems incubated at 60, 75, and 90 °C ranged −0.29 to -0.89×10^{-5}, −0.86 to -3.35×10^{-5}, and −3.00 to -8.67×10^{-5} ΔpH/s in order. The R^2 values of these regression lines were not less than 0.94. That verified the predictability of these empirical equations. Data in Table 2 also revealed that the rates of pH decreasing were dependent on initial galactose concentration and are illustrated in Fig. 4. Correlation between initial galactose concentration and pH decreasing rate followed logarithm-ordered reaction kinetics as the following equation:

$$V_p = C_3 - k_p \ln[G] \quad (11)$$

where C_3 was the constant, and k_p indicated the rate constant of pH decreasing which was 0.15×10^{-4}, 0.49×10^{-4}, and 1.24×10^{-4} ΔpH/s M for systems incubated at 60, 75 and 90 °C separately. The effect of temperature on pH decreasing rate were further calculated and concluded with Eqs. (12) and (13).

$$\log k_p = 2.96 \times 10^{-2} T_C - 7.20 \quad (12)$$

$$\ln(k_p) = 12 - 8273(1/T_K) \quad (13)$$

Slope of Eq. (12) was equivalent to a Q_{10} of 1.98 at the range of temperature between 60 and 90 °C. And slope of Eq. (13) was equivalent to an activation energy 69 kJ/mol for pH decreasing in the galactose/glycine model systems.

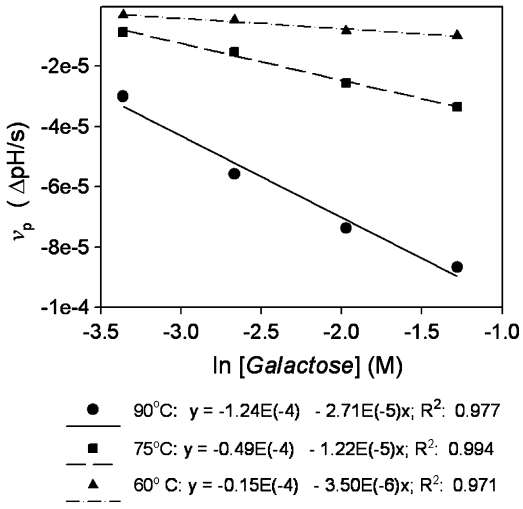

Fig. 4. Correlation of galactose concentration to the rates of pH decreasing in galactose/glycine model system at temperature 60, 75, and 90 °C.

Table 2
Linear regression parameters of pH changes in galactose/glycine model systems

Galactose (M)	v_p ($\times 10^{-5}$ ΔpH/s)			Intercept (pH)			R^2		
	90 °C	75 °C	60 °C	90 °C	75 °C	60 °C	90 °C	75 °C	60 °C
0.035	−3.00	−0.86	−0.29	7.90	8.62	8.17	0.9840	0.9749	0.9429
0.069	−5.57*	−1.52	−0.46	7.89*	8.57	8.18	0.9622	0.9872	0.9641
0.139	−7.38*	−2.54	−0.83	7.75*	8.53	8.18	0.9878	0.9892	0.9772
0.278	−8.67*	−3.35	−0.98	7.46*	8.58	8.16	0.9864	0.9969	0.9851

Note: *Data were obtained from the first linear stage of Fig. 4.

The initial pH value of the reaction system was considered to affect Maillard reaction significantly. In alkaline condition, schiff-base formed easily and promoted the Maillard reaction further. Consumption of the amino group by Maillard reaction could shift systems into more acidic condition and lowered the browning reaction (DeMan, 1999). In addition, some acidic compounds with buffering capacities including formic acid, acetic acid, methylglyoxal, glyoxal, etc. (Chen et al., 2005; Martins, Marcelis, & van Boekel, 2003) had been reported to present in the intermediate MRPs, whereas none of any basic intermediate MRPs had yet been found during the earlier stage. Consequently, the consumption of amino group, together with formation of acids, could be the mechanism of pH decreasing tendency in the galactose/glycine model systems in the current study.

For the phenomenon of second and slower linear decreasing rates of pH in systems at 90 °C as shown in Fig. 4, there could be two mechanisms: (1) the higher reaction rates of higher galactose concentration and temperature drove pH lower enough to slow down the reaction during the experimental period and (2) the high activities of intermediate MRPs transformed these acids into other products and cut down the increasing rate of acids concentration.

The interaction as both influencing factor and resultant product of pH on Maillard reaction had been discussed in literatures. Despite the report by Reyes, Poocharoen, and Wrolstad (1982) who indicated that no apparent pH changes were observed in the Maillard reaction of sugar/glycine model systems at 60 °C, DeMan (1999) stated that pH would decrease in Maillard reaction on the consumption of amino acids. Chen et al. (2005) displayed a descriptive pH fluctuation model in model systems. Yet there still were not enough data for developing any inferential model until the current study. The logarithm-ordered reaction model of initial galactose concentration on pH decreasing developed here (Fig. 4 and Eq. (11)) provided a systematic method for understanding the interaction between Maillard reaction and the pH of system.

3.3. Anti-oxidative activity

The values of systems' oxidative activity went linearly down throughout the experiments as shown in Fig. 5. That revealed the systems' anti-oxidative condition were continuously decreasing throughout the experimental period. Standard deviation of each data point ranged between 0.001 and 0.061 and is indicated as error bar in Fig. 5. The statistical parameters of regression lines in Fig. 5 are listed in Table 3, and could be indicated by an empirical equation:

$$A_o = v_o t + C_4 \tag{14}$$

where A_o was the anti-oxidative activity, C_4 was the constant, and v_o was the rate of anti-oxidative activity reduction which ranged -0.19×10^{-5} to -0.67×10^{-5}, -0.70×10^{-5} to -3.41×10^{-5}, and -0.91×10^{-5} to -5.13×10^{-5} ΔAOA/s for systems incubated at 60, 75, and 90 °C, in sequence. The magnitudes of v_o increased as temperature and initial galactose concentration increased (Table 3). Fig. 6 shows the effects of initial galactose concentration on the reduction rate of systems' v_o, that followed a first-ordered kinetics as the empirical equation:

$$v_o = C_5 - k_o[G]^{-1} \tag{15}$$

where the rate constants of anti-oxidative activity decreasing, k_o, were 2.7×10^{-5}, 6.5×10^{-5}, and 2.2×10^{-4} ΔAOA/s M for systems incubated at 60, 75, and 90 °C, respectively.

The effects of temperature on v_o, as expressed by Q_{10} and activation energy, followed the following equations, respectively:

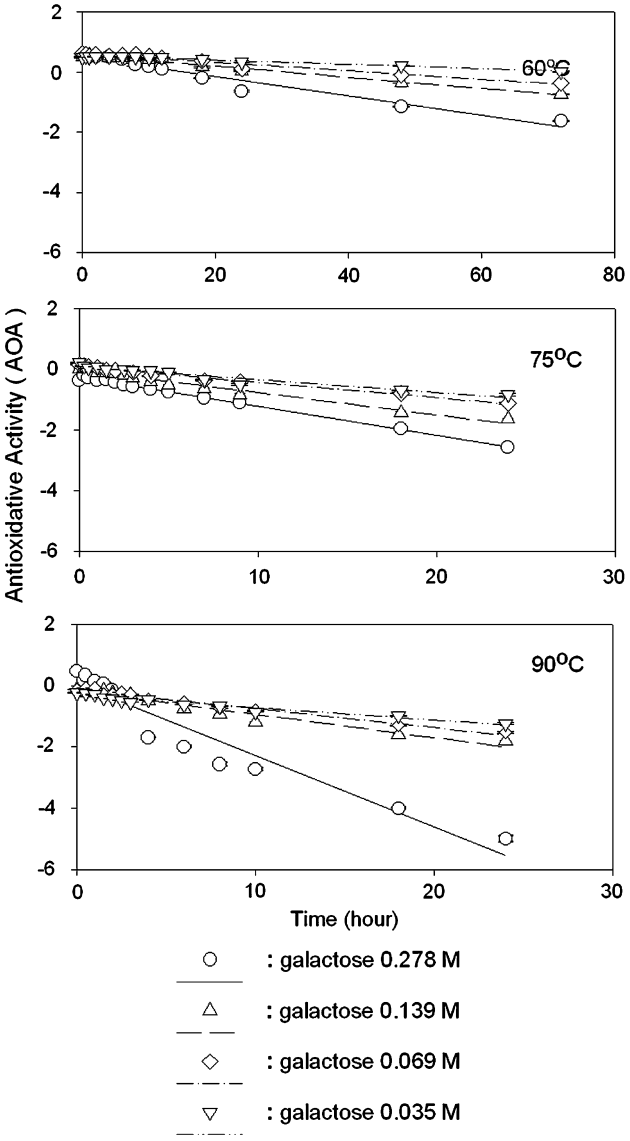

Fig. 5. Changes of anti-oxidative activities in galactose/glycine model systems incubated at 60, 75, and 90 °C.

Table 3
Linear regression parameters of anti-oxidative activity changes in galactose/glycine model systems

Galactose (M)	v_o ($\times 10^{-5}$ ΔAOA/s)			Intercept (AOA)			R^2		
	90 °C	75 °C	60 °C	90 °C	75 °C	60 °C	90 °C	75 °C	60 °C
0.035	−1.11	−1.19	−0.19	−0.32	0.08	0.54	0.9401	0.9299	0.9662
0.069	−1.74	−1.41	−0.39	−0.13	0.07	0.61	0.9753	0.9809	0.9576
0.139	−2.13	−2.04	−0.52	−0.17	−0.04	0.57	0.9496	0.9716	0.9791
0.278	−6.48	−2.67	−0.90	0.05	−0.26	0.51	0.9223	0.9951	0.9589

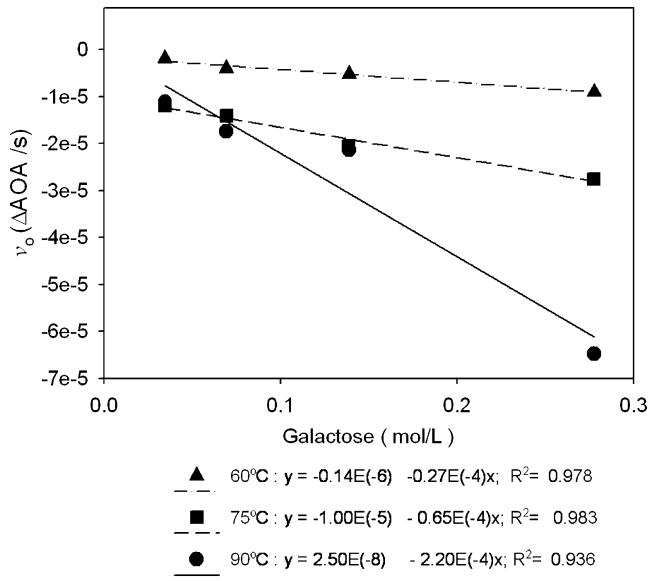

Fig. 6. Correlation of galactose concentration to the rate of anti-oxidative activity reduction in galactose/glycine model systems incubated at 60, 75, and 90 °C.

$$\log(k_o) = 3.02 \times 10^{-2} T_C + 6.40 \quad (16)$$

$$\ln(k_o) = 14 - 8367 T_K^{-1} \quad (17)$$

The slope of Eq. (16) was equivalent to a Q_{10} value of 2.00, and that of Eq. (17) was equivalent to an activation energy 70 kJ/mol for the reaction of anti-oxidative activity decreasing.

The findings that MRPs possessed either or both anti-oxidative and pro-oxidative activities with the latter presented at earlier stage and the former at later stage had been widely investigated in vitro, in foods, and by using model systems (Anese et al., 1999; Benjakul et al., 2005; Calligaris et al., 2004; Nicoli, Anese, Papinel, Franceschi, & Lerici, 1997; Odani et al., 1998; Osada & Shibamoto, 2006; Puscasu & Birlouez-Aragon, 2002; Turkmen et al., 2006; Wagner et al., 2002; Wijewickreme & Kitts, 1997; Yen & Liao, 2002; Yilmaz & Toledo, 2005). Although the pro-oxidative activity presented in Maillard foods might be due to thermal or oxidative destruction of naturally existing antioxidants (Anese et al., 1999; Nicoli et al., 1997) studies employing model system had justified the even more significant role of the intermediate MRPs with lower molecular weight such as some reductones, α-dicarbonyls, and pyrazinium cation (Chen et al., 2005; Hayashi & Namiki, 1981; Hofmann, Bors, & Stettmaier, 1999; Puscasu & Birlouez-Aragon, 2002; Wagner et al., 2002; Yilmaz & Toledo, 2005). There arose, consequently, the questions how and when the pro-oxidative activity converted into anti-oxidative activity. To solve the former question, understanding the whole mechanisms of Maillard reaction was necessary. If the inversion time of anti-oxidative activities was known, the condition of food processing could be optimized. Accordingly, the information of reaction kinetics should be explored. In studying the effect of thermal processing on milk, Calligaris et al. (2004) had plotted the decreasing-then-increasing trend of anti-oxidative activity of heated milk. Since no further statistical processing was performed, the plots completed by Calligaris et al. (2004) implied information much more descriptively than inferentially. Göğüş et al. (1998) indicated that reaction rate of 5-hydroxymethyl furfural (HMF) accumulation and brown pigment formation in the Maillard reaction of boiled grape juice followed an order of 0.5, which could be a useful model for constructing the reaction kinetics of MRPs significant in system anti-oxidative activity. In studying the formation of pyruvaldehyde in model systems, Chen et al. (2005) developed a third-ordered empirical equation for predicting its concentration. In other studies, a multiresponse modeling method employed by Martins, Jongen, and van Boekel (2001), Martins et al. (2003), and Martins and van Boekel (2005a, 2005b) had made available the formation rate constants of individual MRP like some di-carbonyls, melanoidins, etc. This method could be helpful for fundamentally predicting the trends of anti-oxidative activity change when the rate constants of all the MRPs were collected. However, since Maillard reaction pathways were so complicate that there remained still much more unknown MRPs influential on anti-oxidative activity to be identified. That would require a much longer way for the multiresponse modeling method to be used in anti-oxidative activity prediction.

The results that system anti-oxidative activities were continuously decreasing throughout the experimental period indicated that a thermal processing condition of 90 °C for 24 h would not be enough for the systems to develop enough anti-oxidative activity. This condition was much more severe than most of the thermal processing including pasteurization and blanching. In addition, the activity of glycine and galactose in Maillard reaction had been proved to be higher than most amino acids and glucose (Chen et al., 2005; DeMan, 1999). We therefore postu-

lated that some thermal-processed foods such as pasteurized milk or precooked meats were under pro-oxidative condition if there were not any other anti-oxidative factors. And that might also partially explain the quick development of warmed-over off-flavor of precooked meat during cold storage.

4. Conclusion

The study found that the rate of color development in Maillard reaction followed first-ordered kinetic that was a much more reasonable model than the previously suggested zero-ordered kinetic. Because the former model was used to describe a concentration-dependent reaction and the latter revealed no correlation between the reactant concentration and the reaction rate.

MRPs formed at the earlier stage of Maillard reaction tended to be small molecule and possess pro-oxidative activity. These MRPs would then polymerize and convert into higher molecular weight compounds with anti-oxidative activity. Therefore, it would be important to explore the mechanism and kinetics of this conversion for food processing. The kinetic parameters obtained in the current study had quantified the effects of galactose concentration and temperature on the anti-oxidative activity of Maillard reaction throughout the experimental period. However, to understand the conversion time of systems from pro-oxidative to anti-oxidative activity completely will need further investigations for higher temperature and/or longer experimental periods in the future works.

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