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Kinetics study of quality of Mee-Krob during storage and development of a shelf life model

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Abstract

The objective of the present work was to investigate the kinetic models of the effects of storage temperatures (4, 30 and 50°C) and different packaging, namely polypropylene bag under atmospheric condition, aluminium foil bag under atmospheric condition, and aluminium foil bag under modified atmospheric packaging (MAP) (99.99% N_2), on the qualities of Mee-Krob during storage of four to eight weeks. Peroxide value, colour parameters and consumers' acceptability were also investigated. During storage, Mee-Krob underwent lipid oxidation and colour changes, causing a lower consumer acceptance. The increase in peroxide formation and the deterioration of sensorial acceptance scores followed zero-order reaction kinetics. Variation of the rate constants for these reactions with temperature can be described by the Arrhenius and Eyring-Polanyi models. Based on packaging conditions, aluminium foil bag under MAP was the most effective treatment for improving visual colour and overall acceptability, and lowering peroxide value of Mee-Krob. Overall, at a reference storage temperature of 30°C, shelf life of Mee-Krob increased from 74 to 80 days or increased by 8% as compared to the control sample based on the sensorial evaluation criteria.

Introduction

Mee-Krob is a traditional Thai sweet and sour fried noodle or seasoned crispy rice vermicelli, produced from fried rice noodles tamarind sauce and/or tomato sauce, lime juice, palm sugar and bitter orange juice (TISI, 2003). At present, Mee-Krob is one of the food products in the One Tambon One Product (OTOP), and is a popular product in Thailand. In general, Mee-Krob is stored in polypropylene boxes at room temperature. It is thus exposed to oxygen and light, leading to quality deterioration from lipid oxidation. In addition, reaction rate of lipid oxidation is accelerated by heating (Wasowicz *et al*., 2004). Lipid oxidation is a complex series of reactions, which occurs in food products containing lipids. Oxidation reactions of unsaturated lipids with molecular oxygen result in the formation of hydroperoxides, which afterward break down to volatile off-flavour compounds such as aldehydes, ketones and hydrocarbons, or toxic compounds to health such as lipid peroxides (Liang, 2000; Wasowicz *et al*., 2004; Mohammadi *et al*., 2016). This will result in the reduction of sensorial characteristics and limits the shelf life of many products including Mee-Krob.

Previous studies suggested that the shelf life of food products can be extended by altering the environment, particularly the gas composition in which the food products are packaged (Bak *et al*., 1999; Ghayal *et al*., 2015; Jain *et al*., 2015). Oxygen plays a crucial factor in promoting deteriorative reactions such as lipid oxidation in foods during storage. Elimination or reduction of oxygen in environmental packaging results in slowing the rate of deteriorative reactions and enhancement of shelf life of food products (Tolstorebrov *et al*., 2014).

Modified atmospheric packaging (MAP) is an efficient prevention method for prolonging the shelf life and preservation of the quality of food products by decreasing the rate of lipid oxidation and the

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growth of spoilage microorganisms (Bak *et al*., 1999; Ghayal *et al*., 2015; Jain *et al*., 2015). Gases such as nitrogen (N_2) or carbon dioxide (CO_2) are mostly used in order to substitute oxygen in the package. Ghayal and Jha (2015) found that rabri packed with 100% N_2 in polyethylene bags was more stable in the chemical qualities including hydroxyl methyl furfural (HMF), thiobarbituric acid (TBA) and free fatty acids (FFA) concentration, and the number of microorganisms analysed by Total Plate Count, Yeast and Mould Count, and Coliform Count as compared to other gases such as atmospheric air and 50% CO_2:50% N_2.

To the best of our knowledge, no information on the effects of storage temperatures and packaging conditions on the quality and shelf life of Mee-Krob have been studied thus far. Lipid oxidation in Mee-Krob can be evaluated by determining the peroxide value (PV) in which 30 mEq. of O_2 per kg oil was considered as the threshold limit for oxidative rancidity in Mee-Krob (TCPS, 2003). In addition, sensorial consumer acceptance could also be regarded as the threshold limit for product in which 5-point hedonic scales of overall acceptability was used as the lower limit of consumer acceptance (Tsironi and Taoukis, 2010; Dermesonluoglu *et al*., 2015). Therefore, the purpose of the present work was to investigate the effects of storage conditions including temperatures and packaging conditions on quality attributes of Mee-Krob. Kinetic models were developed to estimate the changes in Mee-Krob qualities and further predict the product's shelf life based on excess the threshold values.

Materials and methods

Sample storage

Mee-Krob was acquired from a local market in Chachoengsao province, Thailand. The ratio of its various ingredients and the manufacturing process were not available. Next, 50 g Mee-Krob was stored in different packaging conditions including polypropylene bag under atmospheric package (PP-Air), aluminium foil bag under atmospheric package (AF-Air) and aluminium foil bag flushed with 99.99% N_2 (AF-MAP). The size of the polypropylene bag was 8 × 11 inches with a thickness of 40 µm. The oxygen transmission rate at 23°C and 0% relative humidity was 2,057 cm^3/m^2.day, while the water vapour transmission rate at 38°C and 90% relative humidity was 5.71 g/m^2.day. Aluminium foil bags were made from plastic bags laminated with oriented polypropylene (OPP), polyethylene (PE) and aluminium foil. The size of the aluminium foil bag was 5 × 8 inches with a thickness of 80 µm. The oxygen transmission rate at 23°C and 0% relative humidity was 0.06 cm^3/m^2.day, while the water vapour transmission rate at 38°C and 90% relative humidity was 0.06 g/m^2.day.

Under atmospheric conditions, bags were sealed using a hand sealer, while for MAP packaging, 99.99% gaseous nitrogen was flushed into the aluminium foil bags using an Ultra Vac packaging machine (UV-420T, Pascal Intertech, Thailand). Samples were stored at 4 and 30°C for eight weeks, and 50°C for four weeks in incubators (4°C: refrigerator, Toshiba, Japan; 30 and 50°C: incubator Model 600, Memmert, Germany). The temperature inside incubators was monitored using thermometers (TH-03, Digicon, Japan). During storage, samples were taken every week to analyse the peroxide value, colour parameters and sensorial characteristics. Moisture content and water activity (a_w) of samples were also quantified (AOAC, 2000). The experiment was carried out in two replications.

Extraction of oil

Oil from the samples was extracted by the solvent extraction-gravimetric method (AOAC, 2000) with some modifications. Samples (3 g) were transferred to a separatory funnel with petroleum ether (30 mL), vigorously shaken for 30 min and extracted repeatedly until no more oil left. The solvent was evaporated from the solvent-oil mixture at 50°C and the vessel containing residual solvent was dried at 105°C for 1 h in an oven (Model 100-800, Memmert, Germany). The oil was weighed and immediately analysed for peroxide.

Determination of peroxide value (PV)

Lipid oxidation of Mee-Krob, an expression of rancidity, is indicated by peroxide value, which was measured in the present work by the iodometric method (AOCS, 2007). The peroxide value [miliequivalent peroxide (mEq. of O_2) per kilogram (kg) oil sample] was calculated using Equation (1):

$$PV = \frac{1000 \times (S\text{-}B) \times N)}{W} \qquad \text{(Equation 1)}$$

where S = titre volume of sodium thiosulfate for the sample (mL), B = titre volume of sodium thiosulfate for the blank (mL), N = normality of the sodium thiosulfate solution, and W = weight of oil in the sample (g).

Colour parameter measurements

Visual colour was measured with a Hunter colorimeter (Minican XP Plus, Hunter Associates

Laboratory, USA). The L^* value corresponds to lightness and varies from 0 for black to 100 for perfect white. The a^* value measures the red-green colour; positive indicates redness, zero indicates greyness and negative indicates greenness. The b^* value measures the yellow-blue colour; positive indicates yellowness, zero indicates greyness and negative indicates blueness. The instrument was calibrated with black and white reference tiles. The total colour difference (ΔE^*) between fresh and aged Mee-Krob can be expressed using the Hunter-Scotfield Equation (Equation 2):

$$\Delta E^* = \sqrt{(L_0^* - L^*)^2 + (a_0^* - a^*)^2 + (b_0^* - b^*)^2} \quad \text{(Equation 2)}$$

where L_0^*, a_0^* and b_0^* = values at the initial time, and L^*, a^* and b^* = values at any time of storage.

Sensory evaluation

Sensory evaluation of Mee-Krob was performed by 30 untrained panellists from the Faculty of Science, Burapha University, Thailand. Samples were taken from their packages and separately provided in white plastic cups, which were coded with different random 3-digit numbers. All samples were served at room temperature. Panellists were asked to evaluate appearance, colour, crumbliness, texture, flavour and overall acceptability using a 9-point hedonic test (1 = extremely dislike to 9 = extremely like). In addition, the intensity of off-odour or rancidity smell was evaluated by 10 trained volunteers using quantitative descriptive analysis (QDA) (10-cm linear rating scale from none to strong rancidity odour).

Kinetics study

The reaction rates of peroxide formation and loss of overall acceptability of Mee-Krob during storage were expressed using Equations 3 and 4, respectively:

$$\frac{dC}{dt} = kC^n \quad \text{(Equation 3)}$$

$$\frac{dC}{dt} = -kC^n \quad \text{(Equation 4)}$$

where C = peroxide value (mEq. of O_2/kg oil) or sensory score for overall acceptability, t = time (weeks), k = reaction rate constant, and n = kinetic order of the reaction (Maskan and Karatas, 1999; Horia, 2006; Jirasatid *et al*., 2013).

A kinetic model was proposed and described to a mathematical model by deriving a differential equation using zero-, first- and second-order kinetics. The differential equation was solved concurrently by numerical integration and fitted with the experimental data (Jirasatid *et al*., 2013). The best fitted data was determined from the correlation coefficient (R^2) and root mean square percent (RMS, %) (Singh *et al*., 2009; Jha and Patel, 2012). Thus, the order and rate constants were determined.

The temperature dependence of rate of peroxide formation and/or loss in score for overall acceptability was determined using the Arrhenius equation (Equation 5):

$$k = k_0 \exp\left[\frac{-E_a}{RT}\right] \quad \text{(Equation 5)}$$

where k = rate constant, k_0 = Arrhenius constant, R = gas constant (8.314 J/mol.K), T = absolute temperature (K), and E_a = activation energy (J/mol), which were calculated on the basis of the regression slope in plots of ln k against 1/T (Bunkar *et al*., 2014; Nambi *et al*., 2016).

The half-life time ($t_{1/2}$) is the time required for peroxide formation, or loss in overall acceptability scoring to reach 50%. The half-life time of the zero-order kinetic reaction was calculated using Equation 6:

$$t_{1/2} = \frac{C_0}{2k} \quad \text{(Equation 6)}$$

where C_0 = initial content of peroxide value (mEq. of O_2/kg oil), or initial sensory score for overall acceptability (Horia, 2006).

Thermodynamic functions of activation such as free energy (ΔG, J/mol), enthalpy (ΔH, J/mol) and entropy (ΔS, J/mol.K) for peroxide formation and loss in overall acceptability score at experimental temperatures were obtained from the regression analysis of ln ($k.h/kB.T$) on 1/T according to the Eyring-Polanyi model (Equation 7) based on transition state theory (Van Boekel, 2009). The free energy of activation (ΔG) was then obtained from the relationship described by Equation 8:

$$k = \frac{k_B T}{h} \exp\left(\frac{-\Delta G}{RT}\right) = \left(\frac{k_B T}{h}\right) \exp\left(\frac{-\Delta H - T \cdot \Delta S}{RT}\right) \quad \text{(Equation 7)}$$

$$\Delta G = \Delta H - T \cdot \Delta S \quad \text{(Equation 8)}$$

where k_B = Boltzmann's constant (1.381×10^{-23} J/K), h = Plank's constant (6.626×10^{-34} J·s), T = absolute temperature (*K*), and *R* = gas constant (8.314 J/mol.K) (Cisse *et al*., 2009; Kechinski *et al*., 2010).

Development of shelf life modelling

Mathematical shelf life models were developed from the Arrhenius kinetic model (Calligaris *et al*., 2007; Tsironi and Taoukis, 2010; Dermesonluoglu *et al*., 2015). The shelf life of Mee-Krob was predicted based on excess the threshold values of peroxide value and overall consumer acceptability.

Statistical analysis and model evaluation

The fitness of the models to experimental data was determined using the coefficients of determination (R^2) and root mean square percent [(RMS, %) (Equation (9)]. The highest R^2 values and lowest RMS values were accepted as the best fit to the experimental data.

$$\mathrm{RMS\%} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{P_{obs}-P_{pred}}{P_{obs}}\right)^2} \times 100 \qquad \text{(Equation 9)}$$

where P_{obs} = observed parametric value, P_{pred} = predicted parametric value, and n = number of observations (Singh *et al*., 2009; Jha and Patel, 2012).

Statistical analysis was performed by analysis of variance (ANOVA). The difference of the mean values was determined according to Duncan's multiple range tests and was considered as significant at a confidence level above 95%.

Results and discussion

Initial values of water activity (a_w) and moisture content in Mee-Krob samples (PP-Air, AF-Air and AF-MAP at 4-50°C) were 0.21 ± 0.10 a_w and 3.45 ± 0.16% (wet basis), respectively. During storage, a_w and moisture content of all samples varied within the range of 0.17-0.40 a_w and 3.45-7.98%, respectively. The a_w of all samples was less than 0.4, which did not exceed the threshold limit ($a_w \leq 0.4$) for Mee-Krob (TCPS, 2003).

Peroxide formation in Mee-Krob

The effects of storage temperatures and conditions in packaging on peroxide value are presented in Figure 1. The initial content of peroxide value in Mee-Krob was 3.02 ± 0.05 mEq. of O_2/kg oil. A significant increase in peroxide value were observed on storage up to four to eight weeks ($p < 0.05$), indicating that hydroperoxides were continuously generated. This suggested that the rancidity in Mee-Krob tended to increase throughout the entire storage duration. The same observation was reported by Maskan and Karatas (1999) in whole-split pistachio nuts during storage at 10-30°C, Gotoh *et al*. (2007) for instant noodles under storage at 40 to 60°C, and Ahlawat *et al*. (2017) for noodles and noodles incorporated with okara powder during storage at 28°C for 45 days.

The temperature, oxygen and light negatively

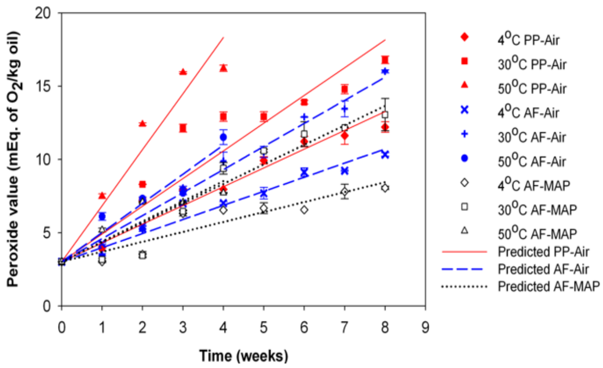

Figure 1 Fit of the zero-order kinetics models to the experimental data for peroxide formation during storage of Mee-Krob. Simulation data and experimental data are lines and symbols, respectively.

influenced lipid oxidation. Peroxide value in Mee-Krob packed in AF-MAP was significantly lower than in AF-Air and PP-Air, respectively at the same storage temperature and time. This result indicated that hydroperoxides accumulated rapidly in Mee-Krob stored under atmospheric air, particularly for the samples packed in PP bags, while those packed in MAP condition (99.99% N_2) combined with AF bags, the increase of peroxide was greatly retarded.

The highest increase in peroxide value occurred after eight weeks of storage under packaging condition of PP-Air at 30°C and was about 5.6 times of the initial value, while the smallest increase was about 2.7 times of AF-MAP packaging at 4°C demonstrating the great impact of combination of AF bags and MAP on lipid oxidation of Mee-Krob during storage.

Non-linear regression analysis confirmed that the formation of peroxides in Mee-Krob followed zero-order kinetics with high R^2 and low RMS values of 0.858-0.983 and 7.04-25.71%, respectively (Figure 1 and Table 1), while lower R^2 and higher RSM were obtained using a first-order model (R^2 = 0.733-0.922, RSM = 14.19-27.67%) or a second-order model (R^2 = 0.548-0.864, RSM = 18.53-41.68%). In the case of zero-order kinetics, it can be explained that the reaction rate did not depend on the substrate concentration because substrate including polyunsaturated lipid and oxygen were in excess for lipid oxidation under PP-Air and AF-Air. However, under AF-MAP, only lipid was in excess.

Table 1 Kinetic parameters of peroxide formation in Mee-Krob during storage at different temperatures and different package conditions.

Package condition	Temperature (°C)	k (mEq. of O_2/kg oil. week)	R^2	RMS (%)	$t_{1/2}$ (weeks)	E_a (kJ/mol)	k_0 (mEq. of O_2/kg oil.week)	R^2	ΔH (kJ/mol)	ΔS(J/mol.K)	ΔG (kJ/mol)	R^2
	4	1.281	0.948	9.83	1.2							
PP-Air	30	1.892	0.970	15.70	0.8	17.12	2016	0.923	14.65	-190	71.86	0.899
	50	3.826	0.878	10.17	0.4							
	4	0.961	0.890	7.04	1.6							
AF-Air	30	1.573	0.983	12.75	1.0	11.92	172	0.993	9.44	-210	72.82	0.988
	50	1.992	0.941	11.34	0.8							
	4	0.678	0.937	13.78	2.2							
AF-MAP	30	1.329	0.920	25.71	1.1	11.98	131	0.874	9.50	-213	73.56	0.810
	50	1.375	0.858	11.72	1.1							

k: reaction rate constant; R^2: correlation coefficient; RMS: root mean square percent; $t_{1/2}$: half-life time; E_a: activation energy; k_0: Arrhenius constant;ΔH: activation enthalpy; ΔS: activation entropy; ΔG: free energy of activation

Reaction rate constants (k) for peroxide formation in PP-Air, AF-Air and AF-MAP samples increased directly with storage temperature from 4-50°C (Table 1). Moreover, at the same storage temperature, the highest k value occurred in sample stored under PP-Air packaging system, followed by those from AF-Air and AF-MAP packaging systems, respectively (Table 1). These findings clearly demonstrated that lower peroxide values were achieved at lower storage temperatures and packaging systems void of oxygen and light.

The dependence of the rate constants on temperature was modelled using the Arrhenius equation (Equation 5). The activation energies for peroxide formation in Mee-Krob stored under PP-Air, AF-Air and AF-MAP systems varied from 11.92-17.21 kJ/mol (Table 1). In an earlier study, Hosseini *et al*. (2014) found activation energies for peroxide formation in whole walnut and walnut kernels during storage at 62-82°C to be 79.57 and 74.01 kJ/mol, respectively. This indicated that the peroxide formation in Mee-Krob was less susceptible to change in the temperature than that in whole walnut and walnut kernels.

The half-life time for peroxide formation varied from 0.4 to 1.2, 0.8 to 1.6 and 1.1 to 2.2 weeks under PP-Air, AF-Air and AF-MAP systems, respectively (Table 1). An increase of storage temperature led to a decrease in the half-life time in all samples (PP-Air, AF-Air and AF-MAP). Additionally, the AF-MAP packaging system provided Mee-Krob a longer storage half-life than either of the other systems at the same storage temperature. For instance, the half-life time of a sample packed in the AF-MAP system was approximately 1.4-2.8 and 1.2-1.4 times longer than for those in both PP-Air and AF-Air systems, respectively at 4-50°C.

Activation enthalpy (ΔH), activation entropy (ΔS) and free energy of activation (ΔG) for peroxide formation in Mee-Krob stored at 4-50°C varied with packaging conditions (Table 1). ΔG represents the difference between an activated state and the reactants, thus it must have a positive sign. The similar factors influenced peroxide formation of Mee-Krob in three packaging systems is indicated by the resemblance of ΔG values. The positive sign of ΔH showed that the reaction between the activated complex and reactant was endothermic, which led to the increase of peroxide value with increasing temperature. The relatively high value of ΔS indicated the high significance of this thermodynamic function, while its negative sign implies that change of disorder after the new molecules of lipid oxidation were forming in the system (Al-Zubaidy and Khalil, 2007; Kechinski *et al*., 2009; Van Borkel, 2009).

Colour parameters

The L^* value of Mee-Krob slightly decreased with increasing storage time and temperature (data not shown). The falling L^* value indicates a browning of the sample (Ibarz *et al*., 1999). After storage at 50°C for four weeks, L^* values were about 91, 95, and 93% of the initial value in samples packed under PP-Air, AF-Air and AF-MAP, respectively. However, at 4°C, the brightness of sample in all package systems was maintained approximately 98-99% of the initial value.

The colorimetric $+a^*$ (redness) parameter tended to decline with storage time (data not shown). The conditions in packages and the storage temperatures affected the a^* value. The highest reduction in a^* value was observed in the sample stored at 50°C for four weeks with the percentage decrease of *a** values being 88, 86 and 93% under PP-Air, AF-Air, and AF-MAP, respectively. It was obvious that the remaining of *a** value in AF-MAP sample was higher than the other storages (PP-Air and AF-Air). The decrease in *a** parameter could possibly be due to the destruction of natural pigments, such as lycopene, in Mee-Krob by higher temperatures and the presence of oxygen. Previous studies suggested that oxygen causes oxidation of carotenoids thereby producing colourless products. Pigment stability was facilitated by the addition of nitrogen in packaging which impairs oxidation (Bonnie and Choo, 1999; Cisse *et al*., 2009).

The visual +*b** values (yellowness) of all packed Mee-Krob were almost constant throughout the entire storage (data not shown). The *b** values of samples stored at 4-50°C varied within the ranges of 30.9-35.8, 30.5-33.4, and 29.9-34.9 under PP-Air, AF-Air, and AF-MAP systems, respectively.

A good parameter to illustrate the visual colour variation of foods is the total colour difference (ΔE*) due to the combination of *L**, *a** and *b** parameters. Total colour difference of Mee-Krob increased during storage. The storage temperatures influenced on total colour difference as well as packaging conditions (data not shown). Colour change was particularly noticeable at 50°C. Samples stored at 50°C for four weeks under PP-Air packaging displayed a maximum total colour difference of 6.02 in contrast to a minimum total colour difference of 1.59 at 4°C for eight weeks in AF-MAP packaging.

Sensory evaluation

Initially, all samples had crumbly texture, and a sweet and sour taste. Initial sensorial scores of all samples for appearance, colour, crumbliness, texture, flavour and overall acceptability were described within the range of very much like to extremely like (data not shown). During storage, the scores of all sensorial attributes continuously diminished with storage period ($p < 0.05$), resulting in a sticky texture and a strong rancid flavour in the Mee-Krob. However, for the same storage time, there was insignificant difference in scores of such attributes in PP-Air, AF-Air, and AF-MAP ($p > 0.05$).

The rancidity in all samples was developed during storage. The increase in rancidity intensity scores were higher in samples stored at higher temperature. For instance, rancidity intensity of samples packed in PP-Air, AF-Air and AF-MAP at 50°C for four weeks varied at 6.4-7.6 scores, while 1.6-3.3 scores were observed in sample stored at 4°C for eight weeks. Moreover, at the same storage temperature, the rancidity intensity scores were the highest in samples packed in PP-Air followed by AF-Air and AF-MAP. The rancidity intensity scores of samples packed in PP-Air, AF-Air and AF-MAP at 30°C for eight weeks were 4.2, 2.4 and 1.8, respectively. This result is in agreement with that of Bak *et al*. (1999) who reported that the rancidity score of frozen shrimps packed under atmospheric air was significantly higher than those packed under MAP.

The overall acceptability is commonly used to represent all sensorial attributes in predicting the shelf life of food products (Tsironi and Taoukis, 2010; Jha and Patel, 2014; Dermesonluoglu *et al*. 2015). Therefore, the kinetics of changes to the overall acceptability scores in Mee-Krob during storage was analysed. Non-regression analysis demonstrated that changes of overall acceptability scores in Mee-Krob followed zero-order kinetic reaction with higher R^2 (0.959-0.975) and lower RMS intervals (1.00-3.27%) (Figure 2a-c and Table 2) as compared with first-order (R^2 = 0.947-0.974, RMS = 0.92-3.63%) and second-order kinetic models (R^2 = 0.929-0.976, RMS = 0.87-4.44%). The values of k increased slightly as the storage temperature increased (Table 2), indicating that the deterioration rate of overall acceptability in Mee-Krob increased as storage temperature increased. In addition, the deterioration rate of overall acceptability in Mee-Krob stored under AF-MAP was slightly lower than those under AF-Air and PP-Air, respectively as shown by lower k values when compared at the same storage temperature.

The temperature dependence of the rate constant for quality loss in the overall acceptability attributes was further modelled using the Arrhenius equation (Equation 5). The Arrhenius plots showed straight lines with high R^2 value (0.873-1.000) (figure not shown). Activation energies for the deterioration of overall acceptability attributes in Mee-Krob ranged from 0.87-1.43 kJ/mol and the Arrhenius constant ranged from 0.415-0.529 scores/week (Table 2).

The half-life values of overall acceptability scores using zero-order kinetics were calculated using Equation 6, and is given in Table 2. The half-life time of each sample generally decreased with the increasing storage temperature. AF-MAP helps to prolong the half-life time of overall acceptability in Mee-Krob during storage compared to AF-Air and PP-Air as indicated by higher half-life time at the same storage temperature (Table 2). The highest half-life time of 15.1 weeks was found under AF-MAP at a storage temperature of 4°C.

The thermodynamic functions such as activation enthalpy (ΔH), activation entropy (ΔS) and free energy of activation (ΔG) for the deterioration of

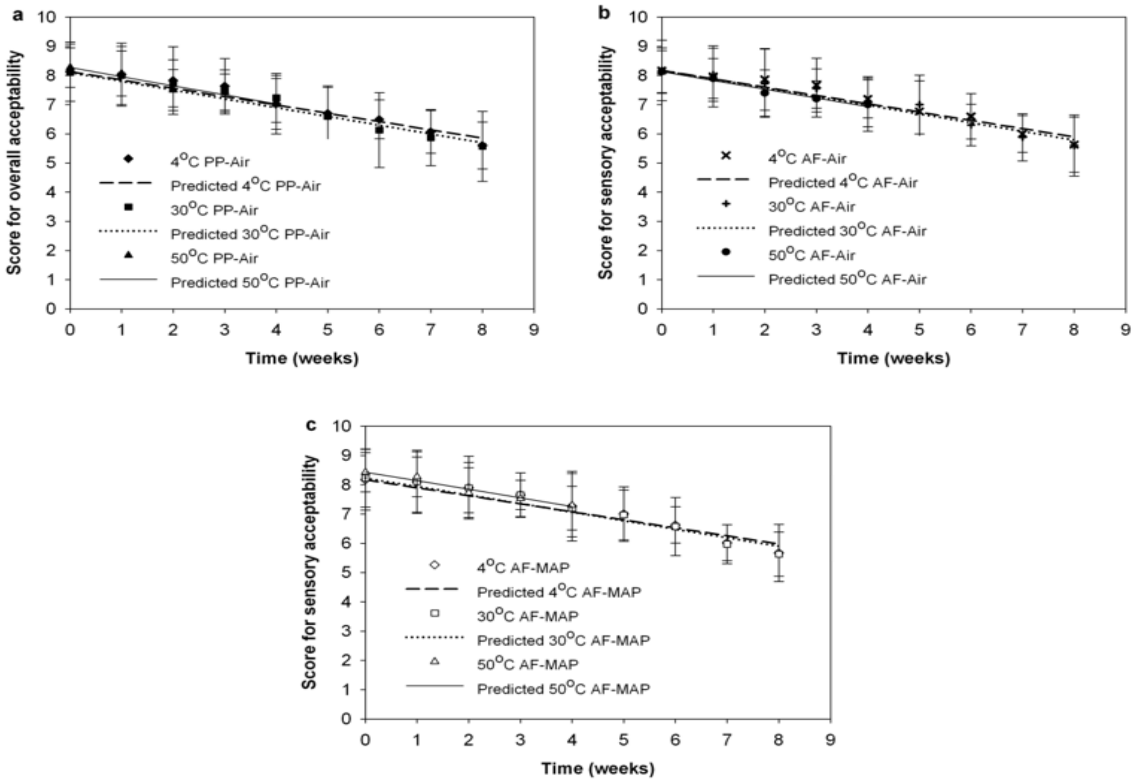

Figure 2 Fit of the zero-order kinetics models to the experimental data for loss of sensory scores for overall acceptability during storage of Mee-Krob. Simulation data and experimental data are lines and symbols, respectively.

Table 2 Kinetic parameters for deterioration of sensory scores used for overall acceptability in Mee-Krob during storage at different temperatures and different packaging conditions.

Package condition	Temperature (°C)	*k* (scores/ week)	R^2	RMS (%)	$t_{1/2}$ (weeks)	E_a (kJ/ mol)	k_0 (scores/ week)	R^2	ΔH (kJ/ mol)	ΔS (J/ mol.K)	ΔG (kJ/ mol)	R^2
	4	0.285	0.975	2.62	14.3							
PP-Air	30	0.301	0.974	2.71	13.6	1.43	0.529	1.000	-1.05	-259	76.81	0.995
	50	0.311	0.959	1.22	13.1							
	4	0.285	0.967	2.87	14.3							
AF-Air	30	0.298	0.971	2.78	13.7	0.87	0.415	0.917	-1.61	-261	76.85	0.963
	50	0.300	0.969	1.00	13.6							
	4	0.274	0.964	3.27	15.1							
AF-MAP	30	0.292	0.971	2.95	14.2	1.11	0.447	0.873	-1.37	-260	76.92	0.891
	50	0.293	0.966	1.02	14.2							

k: reaction rate constant; R^2: correlation coefficient; RMS: root mean square percent; $t_{1/2}$: half-life time; E_a: activation energy; k_0: Arrhenius constant; ΔH: activation enthalpy; ΔS: activation entropy; ΔG: free energy

overall acceptability in Mee-Krob are listed in Table 2. It was found that similar factors affected the deterioration rate of overall acceptability in Mee-Krob stored under PP-Air, AF-Air, and AF-MAP as indicated by the similar values of ΔG. The negative sign of ΔH showed that the reaction between the activated complex and reactant was exothermic. The deterioration rate of overall acceptability scores in Mee-Krob showed lower values of ΔH than those for peroxide formation (Table 1 and 2), indicating that the *k* values from the deterioration rate of overall acceptability was less influenced by storage temperature.

Shelf life prediction models

The shelf life of Mee-Krob is on the time acquiring a peroxide value of 30 mEq. of O_2/kg oil (TCPS, 2003). In addition, a hedonic score of 5 for overall acceptability was used as the lower limit of consumer acceptance based on the response by panellists

(Tsironi and Taoukis, 2010; Dermesonluoglu *et al*., 2015). These indicators of quality for shelf life prediction using a zero-order kinetics reaction can be expressed by Equations 10 and 11.

$$t_{SL} = \frac{PV_1 - PV_0}{k_0 \exp\left[\frac{-E_a}{RT}\right]}$$ Equation 10 **based on peroxide value*

$$t_{SL} = \frac{S_0 - S_1}{(k_0 \exp\left[\frac{-E_a}{RT}\right]}$$ Equation 11**based on sensory score*

where t_{SL} = shelf life of Mee-Krob (weeks), PV_1 = limiting peroxide value (30 mEq. of O_2/kg oil), PV_0 = initial peroxide value (3.02 mEq. of O_2/kg oil), S1 and S_0 = limiting (s_1 = 5) and initial average sensory scores for overall acceptability, respectively, k_0 = rate constant of change in each index (Table 1 and 2), E_a = activation energy of each index (Table 1 and 2) and R = gas constant (Tsironi and Taoukis, 2010; Dermesonluoglu *et al*., 2015) .

Table 3 shows the predicted shelf life values of samples stored at 4°C and 30°C, which are the frequently used temperatures for storage of Mee-Krob. The predicted shelf life of Mee-Krob reflected significant differences between the calculated values based on the peroxide value and sensorial evaluation (Table 3). The predicted shelf life values based on the sensorial evaluation were shorter than that those calculated by the kinetic modelling of peroxide. In this case, the evaluation in shelf life of Mee-Krob should be decided from the sensorial evaluation criteria as consumer acceptability is more relevant quality index than the peroxide concentration criteria. The data show that the potential shelf life of Mee-Krob under AF-MAP, AF-Air and PP-Air conditions at the reference temperature of 30°C to be 80, 75 and 74 days, respectively (Table 3). The results clearly indicated that although AF-MAP significantly inhibited rancidity in Mee-Krob, there was little effect on sensorial attributes. It might be possible that samples had sticky texture resulting from the high presence of sugar.

Validation of the accuracy of the kinetic models in predicting the experimental data for the change of peroxide value and overall acceptability scores were also tested. The result showed that the Arrhenius models fitted reasonably well with the experimental data for peroxide value with high R^2 and low RMS values within the ranges of 0.858-0.983 and 6.92-23.48%, respectively. Similar correlation was found for overall acceptability scores with high R^2 and low RMS within the range of 0.959-0.975 and 1.00-2.96%, respectively. In addition, the fitting Eyring models with experimental results of peroxide value yielded high R^2 and low RMS intervals of 0.858-0.983 and 6.92-23.48%, respectively. Eyring models also adequately described the experimental data for overall acceptability scores with high R^2 of 0.959-0.975, and low RMS of 0.97-2.86%.

Table 3 Shelf life (t_{SL},days) calculation of Mee-Krob based on different quality indices (30 mEq. of O_2/kg oil, score for overall acceptability 5/9 during sensory evaluation).

Package condition	Temperature (°C)	PV, t_{SL} (days)	Sensory, t_{SL} (days)
PP-Air	4	158	77
	30	84	74
AF-Air	4	194	78
	30	124	75
AF-MAP	4	261	83
	30	167	80

PV: peroxide value

Conclusions

Storage of Mee-Krob in a AF-MAP (99.99% N_2) packaging system provided greater stability for visual colour and peroxide formation as compared to AF-Air and PP-Air systems. In addition, there was slight improvement in sensorial attributes and shelf life based on sensorial evaluation criteria (80 days as compared to 74 days for the control sample at 30°C). The formation of peroxide and the deterioration of overall acceptability attributes followed zero-order reaction kinetics. Temperature dependence of the rate constants for peroxide formation and/or the loss of overall acceptability scores can be described using the Arrhenius and Eyring equations. This information on optimum packaging and storage temperature with respect to product quality is of benefit for the commercial production of Mee-Krob.

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