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TBARS predictive models of pork sausages stored at different temperatures

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ABSTRACT

2-Thiobarbituric acid reactive substances (TBARS) is an important quality index for pork sausages. To study this in pork sausages during storage, kinetic models were developed to predict TBARS content changes of pork sausages at different temperatures. The predictive models of TBARS content with respect to storage time and temperature were developed based on primary and Arrhenius equations. The regression coefficients ($R^2 > 0.95$) indicated the acceptability of the primary reaction and Arrhenius model for predicting TBARS content changes of pork sausages. The activation energy (E_A) of TBARS is 14.12 kJ mol^{-1}, and the corresponding rate constant (k_0) is 9.262×10^{10}. Relative errors between predicted and measured values of TBARS content are all within ±8%. Thus, the established model could effectively predict the TBARS content of pork sausages between 5 and 35 °C during storage.

1. Introduction

Pork sausages are one of the oldest processed meat products enjoyed by millions of consumers all over the world. Traditionally, pork sausages are made of pork meat and fat, which are chopped and mixed thoroughly with seasonings, such as pepper powder, spice paprika, salt, rice wine, sugar, monosodium glutamate and ginger. After stuffing the meat mixture in natural casings from the cleaned small intestine of pigs, the sausages are dried at room temperature (Sebranek, Sewalt, Robbins, & Houser, 2005; Qiu, Zhao, Sun, Zhou, & Cui, 2013).

Fat is an important constituent of processed pork sausage products because it affects tenderness and juiciness. A high fat content is traditionally associated with succulence and flavor (Vural, 2003). However, fat content is associated with a higher degree of lipid oxidation during storage, and consumers' acceptability of pork sausages declines due to the development of rancidity caused by lipid oxidation and/or microbial growth (Bradley et al., 2011). Therefore, oxidative rancidity is considered the major cause of reduced quality of pork sausages. Generally speaking, rancidity occurs through the reaction of unsaturated fats with oxygen, which is influenced by heat, light, and pro-oxidant compounds found in the ingredients, such as salt and sodium lactate (Cheng, Wang, & Ockerman, 2007; Sallam & Samejima, 2004).

TBARS content, which reflects the content of malonaldehyde, one of the degradation products of lipid hydro peroxides and peroxides formed during the oxidation of polyunsaturated fatty acids (Gomes, Silva, Nascimento, & Fukuma, 2003), is widely used as an indicator of the degree of lipid oxidation and is considered an important quality index for pork sausages (Tang, Sheehan, Buckley, Morrissey, & Kerry, 2001). Though the TBA assay is sensitive and widely used, it is not specific and in high oxidative conditions, TBA reacts with a number of components such as the decomposition products of aldehydes in volatile compounds, which are present in the pork sausage at the end of storage. There are a number of studies that investigate the various chemical changes that take place, including changes of TBARS content in pork sausages. However, studies on the predictive models for quality parameters of pork sausages are limited. In order to obtain useful information to optimize pork sausage storage management and enhance the safety of pork sausages, this study investigated the TBARS content changes of pork sausages at different temperatures. Primary and Arrhenius equations were combined to develop models to predict the TBARS content of pork sausages during storage.

2. Materials and methods

2.1. Sausage sample preparation

Fresh boneless pork hams and backfat were purchased from a local meat market. Lean tissue and pork backfat were ground through an 8–12 mm plate. Approximately 65% lean tissue and 35% pork backfat were mixed thoroughly with non-meat ingredients, 3% salt, 2% rice wine, 0.5% monosodium glutamate, 0.5% sugar, and 0.05% pepper powder. Then, the meat mixtures were stuffed into natural pork casings, previously soaked in water. Raw sausages were manually tied at approximately 15 cm-intervals, dried at 40 °C for 6 h, then

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stored at 5, 10, 15, 20, 25, 30 and 35 °C, respectively. Three sausage samples were taken randomly every 6 days for analysis of TBARS.

2.2. TBA analysis

TBARS content was determined colorimetrically by the method of Pokorny and Dieffenbacher (Kirk & Sawyer, 1991), which is based on the spectrophotometric determination of the pink complex formed after the reaction of one molecule of malondialdehyde (MDA) with two molecules of 2-thiobarbituric acid. TBARS was expressed as mg MDA/kg pork sausages. Samples (10 g) were homogenized in 20 ml of TBARS solution (prepared by dissolving 200 mg of 2-TBA in 100 ml 1-butanol, filtered, stored at 4 °C for not more than five days), and the mixture was heated for 10 min in boiling water (95 °C). After being cooled with running water, the absorbance (As) was measured at 530 nm against a water blank. A blank reagent was run and the absorbance (Ab) was recorded. The TBA value (mg of malonaldehyde per 100 g of tissue) was obtained by: TBA = 50 ∗ (As − Ab) / 200.

2.3. Statistical analysis

All analyses were run in triplicate. Data were analyzed using the general linear model (GLM) of Statistical Analysis System's Procedures (SAS Institute Inc., 1999). Duncan's multiple range tests were used to determine differences between means. Significance level was set at 5%.

3. Results and discussion

3.1. Changes in TBA content of pork sausages during different storage temperatures

TBARS has been used to determine the degree of lipid oxidation, and the presence of TBA reactive substances is due to the second stage of auto-oxidation, during which peroxides are oxidized to aldehydes and ketones (Li et al., 2013). According to Connell (1990), a TBA value of 2 mg MDA/kg is the limit. The changes in TBARS of pork sausages at different temperatures are shown in Fig. 1. The initial TBARS of the sausages was 0.22 mg MDA/kg. This value is close to the 0.24 mg MDA/kg reported by Martínez, Djenane, Cilla, Beltrán, and Roncalés (2006) for Spanish fresh pork sausages but higher than the 0.17 mg MDA/kg reported by Kuo and Chu (2003) for Chinese pork sausages and lower than the 0.29 mg MDA/kg reported by Tan, Liao, Jhan, and Liu (2007) for Taiwanese pork sausages. Differences among the initial TBA content in pork sausages may be due to the type of seasoning, fat composition, as well as the type of pork muscles used in each type of sausage. TBARS for all sausages increased throughout storage, and the increase in TBARS may be attributed to the partial dehydration of the sausages and increased oxidation of unsaturated fatty acids (Mendes, Pestana, & Gonçalves, 2008). In addition, the increasing rate of TBARS during storage was higher as storage temperature increased. Low temperatures are known to inhibit the oxidation of lipids.

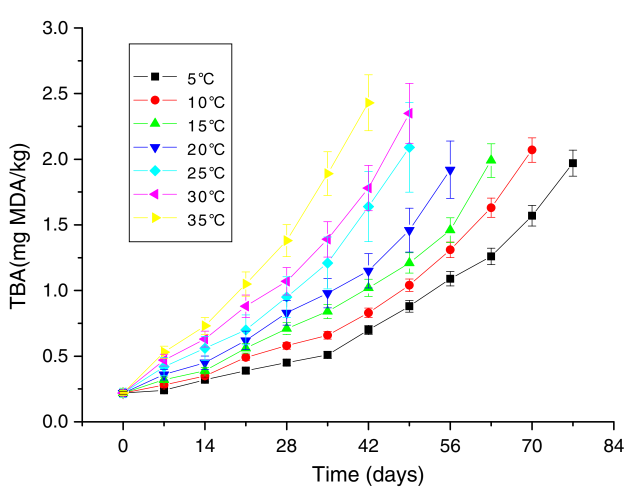

Fig. 1. Changes in TBARS content of pork sausages at different storage temperatures.

3.2. Determination of TBARS models

To validate the applicability of the models, TBARS changes of the sausage samples stored at 5, 15, 25, 30, and 35 °C were used to establish the predictive model, and the samples stored at 10 and 20 °C were treated as controls, verifying the application techniques as well as demonstrating the validity of the approach (Zhang, Li, Lu, Shen, & Luo, 2011). The TBARS data at constant temperature was first fitted by a conventional first-order kinetic model (Maskan, 2001).

First-order kinetic model:

$$B = B_0 e^{k_B t} \tag{1}$$

where B is the value of TBARS indicators, B_0 is the initial TBARS value, and k is the rate constant (day^{-1}) at a given temperature.

The TBARS values of sausages stored at different temperatures were analyzed to determine the reaction order. The values of k were obtained from the slope of regression of ln $[B / B_0]$ versus time. First-order equations for TBARS values of pork sausages at different temperatures are given in Table 1. Regression coefficients of the first-order kinetic equations for TBARS values of pork sausages at different temperatures are all higher than 0.95, the highest value being 0.9946. These high regression coefficient values indicate the acceptability of the first-order reaction.

The data was then applied to the Arrhenius model and integrated as described by Giannakourou and Taokis (2003).

Arrhenius equation:

$$K_B = K_0 \exp\left(-\frac{E_A}{RT}\right) \tag{2}$$

where K_0 is the frequency factor, E_A is the activation energy ($J\ mol^{-1}$), T is the absolute temperature (K), R is the gas constant (8.3144 $J\ (mol\ K)^{-1}$), and K_0 and E_A are constants related to the nature systems.

The modified Logistic Arrhenius equation is given by:

$$\ln K_B = \ln K_0\left(-\frac{E_A}{RT}\right). \tag{3}$$

In the calculated rate constants at different temperatures, the slope of the regression line ($-E_A / R$) was obtained through the use of ln K_B on the reciprocal (T^{-1}) plot. Activation energy (E_A) was obtained through the slope of the regression line, and K_0 was obtained through the intercept of the regression line. The temperature dependence of the rates on TBARS changes is described adequately by Arrhenius

Table 1
First-order kinetic equation for TBARS values of pork sausages at different temperatures.

Temperature (K)	First-order kinetic equation	R^2 (Regression coefficient)
278.15	$y = 0.2072e^{0.0288t}$	0.9946
288.15	$y = 0.2516e^{0.033t}$	0.9874
298.15	$y = 0.2745e^{0.0428t}$	0.9778
303.15	$y = 0.2999e^{0.0439t}$	0.9587
308.15	$y = 0.303e^{0.053t}$	0.9516