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Inverse method to estimate anthocyanin degradation kinetic parameters in cherry pomace during non-isothermal heating

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ABSTRACT

Cherry pomace, a by-product of juice production, is rich in health beneficial anthocyanins (ACY). This study aimed to determine ACY retention in 25, 41, and 70% moisture content (MC) pomace at elevated temperatures. Pomace was heated in sealed metal cans at 105 °C and 127 °C in a steam retort up to 125 min. ACY levels were measured by the pH-differential method. A first-order degradation model with an Arrhenius dependence for the rate constant was used for modeling ACY levels. The rate constant and activation energy for the pomace at each moisture level were estimated by two inverse methods. For 70% MC, $k_{115.8°C} = 0.0129\ min^{-1}$ and Ea = 75.7 kJ/mol. MC had no significant effect on the parameter estimates. Sequential estimation showed that the experiment had to be run to ≤25% ACY retention to obtain accurate parameter estimates. The estimation methods presented will be helpful for designing dynamic processes.

1. Introduction

Cherry (*Prunus cerasus* L.) pomace is the solid waste or by-product of cherry juice processing consisting of cherry skin and seeds. It accounts for over 90% of dry matter with high quantities of lignin, cellulose, and dry fiber components (Nawirska and Kwaśniewska, 2005). Cherries are known to contain substantial quantities of anthocyanins (Wang et al., 1999), which are mainly concentrated in the skins (Chaovanalikit and Wrolstad, 2004; Tomas-Barberan et al., 2001).

Anthocyanin stability of black carrots was studied at various solid contents and pH levels during both heating, 70–90 °C, and storage at 4–37 °C. Degradation of monomeric anthocyanins was shown to increase with increasing solid content during heating, while it decreased during storage (Ahmed et al., 2004; Kirca et al., 2007). The degradation kinetics of anthocyanins in blood orange juice was studied (Kirca and Cemeroglu, 2003). The activation energies for solid content of 11.2–69 °Brix were found to be 73.2–89.5 kJ/mol. Lai et al. (2009) investigated thermal and moisture effects on grape anthocyanin degradation using solid media to simulate processing at temperatures above 100 °C. Anthocyanin degradation followed a pseudo first-order reaction that was moisture-dependent and anthocyanins degraded more rapidly with increasing temperature and moisture. The thermal degradation of anthocyanins has been studied in red cabbage (Dyrby et al., 2001), raspberries (Ochoa et al., 1999), pomegranate, grapes (Marti et al., 2002), plum puree (Ahmed et al., 2004), blackberries (Wang and Xu, 2007), purple corn cob (Yang et al., 2008) and blueberry (Kechinski et al., 2010).

Kinetic studies on ACY are needed to minimize undesired degradation and to optimize quality of foods. ACY degradation under isothermal heating (50–90 °C) is reported to follow first order kinetics (Ahmed et al., 2004; Markakis et al., 1957). Degradation of ACY in strawberry paste during high-temperature (80–130 °C) and high-pressure (up to 700 MPa) treatments showed that ACY degradation is accelerated by both temperature and pressure, with the temperature effect being more pronounced (Verbeyst et al., 2010). The effect of water activity on ACY degradation was studied under non-isothermal heating (100–140 °C), results showed an increase in reaction rate constant as water activity decreased (Jimenez et al., 2012).

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The Arrhenius equation describes temperature dependence of reaction rate. a higher activation energy implies that a smaller temperature change is needed to degrade a specific compound more rapidly (Cemeroglu et al., 1994). Studies on ACY extracts from purple-flesh potato and grape showed significantly lower stabilities than ACY in red-flesh potato and purple carrot extracts at 98 °C (Reyes and Cisneros-Zevallos, 2007). Several studies suggested the reparameterization of the Arrhenius equation by applying the reference temperature (T_r) in the model (Himmelblau, 1970; Pritchard and Bacon, 1978). Another parameter estimation study established a new approach that was more effective than the standard experimental design criteria in both reducing the uncertainty regions of the parameters and improving the consistency of the estimates (Franceschini and Macchietto, 2008).

Accurate parameter estimates are needed for any food process design and optimization, such as designing drying, extrusion, and other thermal processes for baked goods, confectionaries, breakfast cereals, and other foods containing ACY-rich ingredients, such as cherry pomace. These processes are typically non-isothermal and require nonlinear modeling and estimation of all the parameters simultaneously. Estimating the parameters using all the data simultaneously in a one-step regression has been shown to provide better accuracy than estimating the parameters from the same data using two-step regression (Jewell, 2012).

Nasri et al. (1993) estimated the kinetic parameters for thiamin destruction in pea puree in unsteady-state heating in cans in a steam retort at six constant retort temperatures ranging from 103 to 116 °C. They used a finite-difference scheme (Nasri, 1990) to approximate the heat-diffusion partial differential equation (PDE) solution for the temperature within the pea puree. Parameters were estimated using ordinary least squares and nonlinear regression. Welt et al. (1997) estimated kinetic parameters for *B. stearothermophilus* spores in pea puree in cans heated at three retort temperatures from 110 to 125 °C, also using a finite-difference computer program. They used a custom-built method to estimate the parameters. The similarities between these two studies and the present study were: 1) heating a food product inside cans in a retort; 2) using a computer program to compute the temperatures in the can (the present study used a finite-element program); and 3) using a nonlinear-regression routine to estimate the parameters via ordinary least squares. The strength of the present study was that it did not assume that kinetic parameters could be estimated, but rather used the concept of scaled sensitivity coefficients a) to prove which parameters could be estimated and which were more accurate; and b) to design the second experimental retort temperature used in the study such that the parameters could be estimated accurately. Other differences included that the present study used sequential estimation to show how the parameters changed during the experiment; and the present study did not assume thermal properties, but used previously measure temperature-dependent properties.

In light of the need for continued advancement of parameter estimation methods, the objectives of this study were to estimate the kinetic parameters for ACY in cherry pomace at three constant moisture contents and different time-temperature combinations under non-isothermal processing.

2. Materials and methods

2.1. Pomace sample preparation

Montmorency cherry pomace was obtained from Cherry Growers Inc., (Grawn, Michigan, U.S.A.). The moisture content (MC) of the samples was measured using a Sartorius MA30 Moisture Analyzer (Sartorius AG, Goettingen, Germany). The initial MC of cherry pomace was 70% (wet basis, control or MC-70). Two additional samples with MC of 41% (MC-41 and 25% MC-25) were prepared using a pilot-scale cabinet dryer (Proctor and Schwartz Inc., Philadelphia, Penn, U.S.A.) at 50 ± 2 °C. Each of the three cherry pomace sample was filled and sealed under vacuum (20-mm Hg) in 202 × 214 steel cans (54-mm diameter and 73-mm height) and heated at 127 °C for 0, 25, 40, 60 and 90 min and at 105 °C for 100 and 125 min using a rotary steam retort (FMC Steritort Laboratory Sterilizer, Madera, Calif, U.S.A.). The parameter estimation results of the first retort temperature test (127 °C) were used to plot scaled sensitivity coefficients (SSCs) at several different constant retort temperatures and design the best temperature for the second set of tests (@ 105 °C). The details of the SSCs are explained under "Results and Discussion." The steam retort was used to simulate dynamic conditions at process temperatures above 100 °C, while the container prevented moisture loss or gain to the pomace. Each can was pre-fitted with a needle thermocouple (Ecklund-Harrison Technologies Inc., Fort Myers, Florida, U.S.A.) to measure the can center temperature. The time-temperature profile of retorting process (samples and retort) is shown in Fig. 1.

2.2. Anthocyanins extraction

ACY from pomace were extracted using the method of Chaovanalikit and Wrolstad (2004) with some modification. Briefly, fresh and heat-treated samples of cherry pomace were dried (41 °C) and then ground using a coffee grinder (Krups, Medford, Mass, U.S.A.) to a coarse particle size powder. Ground pomace (20 g) was suspended in 80 mL of acetone stock solution (70% aqueous acetone, 0.01% hydrochloric acid, and 30% distilled water). The pomace slurry was stored overnight (−20 °C) in sealed glass bottles that were wrapped in aluminum foil to protect the sample from light, to achieve an equilibrium state. The slurry was filtered through Whatman number 4 filter paper (Whatman Inc., Clifton, New Jersey, U.S.A.) using a Buchner funnel (under vacuum), followed by a wash with 50 mL stock buffer. The filtrate was mixed with 40 mL of chloroform and stored overnight. The supernatant was collected and used for the determination of monomeric ACY content.

2.3. Monomeric anthocyanin content determination

Total monomeric ACY were determined using the pH differential assay Rodriguez-Saona et al. (1999). Specific volume of the supernatant was dissolved in potassium chloride buffer (0.025 M, pH 1.0) and sodium acetate (0.4 M, pH 4.5) and allowed to equilibrate, with a predetermined dilution factor. The absorbance of each equilibrated sample of extracted ACY was then measured at 510 nm and 700 nm for haze correction, using a Genesys 5 spectrophotometer (Spectronic Instruments, Rochester, NY, U.S.A.) and 1-cm pathlength cells were used for spectral measurements. ACY contents were calculated as cyanidin 3-glucoside equivalent (Lee et al., 2005) and reported as mg kg^{-1} (dry-basis).

2.4. Mathematical modeling

2.4.1. Estimation of the kinetic parameters

The heating was assumed to be axisymmetric in the can. Gauss-Legendre quadrature was used to choose a total of 15 points in half of the can (Fig. 2). Gauss-Legendre quadrature was chosen as the integration method because it is the most accurate of all numerical integration techniques for a given number of points Chapra (2011). The point locations were normalized with r/R′, z/H, where R′ and H were the can's radius and height, respectively. COMSOL was used to compute T(r, t, z) at the 15 points, using the can dimensions based