International Food Research Journal 23(1): 30-33 (2016)
Journal homepage: *http://www.ifrj.upm.edu.my*

Modelling the thermal decomposition of 3,4,5-trihydroxybenzoic acid using ordinary least square regression

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Article history

Received: 26 May 2015
Received in revised form: 19 June 2015
Accepted: 27 June 2015

Keywords

Phenolic compounds
TG
DSC
Kinetics
Regression

Abstract

Thermalgravimetric analysis and differential thermal analysis were employed to study the thermal behavior of gallic acid using regression models. Data were subjected to ordinary least square regression models and results showed that thermal decomposition occurred in three main steps with two endothermic peaks and two exothermic peaks due to oxidation process. The dehydration started at 74°C in a single step until 107°C. After that, the anhydrous compound was stable until 210°C, when the decomposition of organic matter occurred in two consecutive steps. Regression models based on a first-order kinetic of gallic acid decomposition were proposed and equations were deemed statistically significant ($p<0.05$) and explained suitably the phenomenon. Differential scanning calorimetry (DSC) allowed the determination of the enthalpy of the main events and the Flynn-Wall-Ozawa non-isothermal method was used to investigate the activation energy of decomposition process that was found to be 150.31 kJ.mol^{-1}.

Introduction

Several phenolic compounds are found in fruits and vegetables and have been described in the literature (Vita, 2005). They can exert various health-promoting functions such as: reducing the risk of different types of cancer, protecting against some non-transmissible degenerative diseases, and reducing the risks of heart diseases (Vita, 2005; Kaur and Kapoor, 2001). Other beneficial effects that have already been reported include neuroprotection (Mandel and Youdim, 2004), hypoglycemic and antihyperglycemic activities (Abeywickrama *et al*., 2011) as well as *in vitro* and *in vivo* antioxidant activity (Morais *et al*., 2009; Macedo *et al*., 2013; Alezandro *et al*., 2013). In the plant kingdom, gallic acid (3,4,5-trihydroxybenzoic acid) is a phenolic acid that can be found in several fruits, such as grapes, pomegranates, blackberries and in processed food and beverages as prunes, wines, juices, teas, etc. (Amakura *et al*., 2000; Bakkalbaşı *et al*., 2005; Dias *et al*., 2013; Zielinski *et al*., 2014).

Based on the fact that temperature is one important factor that can ultimately affects the antioxidant activity of phenolic acids and thus its mechanism of action (Réblová, 2012), the information about stability and behavior of gallic acid subjected to thermal analysis would facilitate the understanding on how this phenolic compound would behave during a food processing, for example. In a preliminary study, this work aims to investigate the thermal behavior of gallic acid and its decomposition kinetics using the following thermoanalytical techniques: thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC) as well as X-ray diffractometry (XRD) and infrared spectroscopy (FT-IR).

Material and Methods

Reagent

Gallic acid monohydrate (≥99%, HPLC grade; Sigma-Aldrich) was kept in a desiccator containing anhydrous calcium chloride until constant mass and then analyzed.

Thermonalytical behaviour of gallic acid

The simultaneous TG-DTA was performed on a SDT 2960 (TA-Instr., USA) calibrated according to the manufacturer's recommendation. Under synthetic air flow of 100 mL.min^{-1}; mass around 5 mg of the gallic acid, heating from 30 to 600°C at a heating rate

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of 10°C min^{-1} in an open alumina crucible.

The DSC curves were obtained using a DSC-Q200 (TA-Instr. Co., USA) calibrated according to the manufacturer's recommendation. Approximately 5 mg of the gallic acid were placed in an aluminum crucible with perforated cover and then heated from 30 to 300°C at a rate of 10°C min^{-1}. The analysis was performed under air flow of 100 $mL.min^{-1}$. The Universal Analysis software was used to determine all percentages of mass losses (TG-DTA) and the main endo or exothermic peaks and enthalpy values (DSC).

The non-isothermal kinetic study was performed on thermal analysis system TGA-50 (Shimadzu, Japan) calibrated according to the manufacturer's recommendation. Using the Flynn-Wall-Ozawa method (Flynn, 1966; Ozawa, 1965) where samples (5 mg) were heated from 25 to 400°C at heating rates of 10, 15, 20, and 25°C min^{-1} under air atmosphere with a flow of 150 $mL.min^{-1}$. All the instruments were calibrated prior to the analysis. Experimental data were fit using a linear approximation based on the integral calculus from the Arrhenius equation (first-order kinetics). Prior to the regression analysis, normality was formally checked by the Anderson-Darling test and Box-Cox transformation was applied when data did not follow the normal distribution. Then, results were adjusted to a first-order model by Equation 1:

$$C = C0e^{kt} \qquad \text{(Equation 1)}$$

Where C the mass in a certain point of the analysis and C_0 represent the initial mass and k is a rate constant. Then, regression analysis based on the ordinary least square method was performed aiming to characterize the degradation of gallic acid at different heating rates. The regression terms were calculated and their significance was assessed by analysis of variances taking on a probability level of 5%. In order to assess the statistical quality of the proposed model, also known as goodness-of-fitting, the determination coefficient (R^2), adjusted R^2, the probability value (p-value) of the regression and the correlation coefficient (r-value) were also calculated (Granato *et al*., 2014). Prediction intervals for all regression models were calculated as considering a normal distribution of data with means (μ) and standard deviation (σ).

Results and Discussion

Figure 1 shows the thermal behavior of gallic acid (TG-DTA and DSC) from 25°C (room temperature) up to 600°C. As it can be observed, the compound is stable up to 74°C when occurs the first mass loss (9.1%) up to 107°C due to hydration water (endothermic peak at 92°C) that correspond to one mol. Above this temperature until 210°C gallic acid is stable with no mass loss and no endo or exothermal events. The second mass loss (78.8%) occurs between 210-264°C with an endothermic peak (256°C) observed in the DTA curve. Imediatelly occurs the third mass loss (10.5%) with the oxidation of the organic matter and two corresponding exothermic peaks (at 410 and 431°C), respectively. The final residue of decomposition of gallic acid was 1.6% of the total initial mass (carbon residue). All the thermal decomposition steps (25, 150, 250 and 300°C) were evaluated by FTIR and X-Ray Diffraction Powder Patterns (XRD).

The dehydration water peak occurs as an endothermic phenomenon with the onset, conclusion, peak temperatures as well as enthalpy, respectively T_o = 67°C, T_p = 97.5°C, T_c = 116°C and ΔH = 265J g^{-1}. In the same way, the values for the second peak were To = 252°C, T_p = 265°C and T_c = 295°C, respectively. The melting enthalpy was not calculated because the melting point occurs together the second mass loss.

The FTIR spectra with KBr pellets of gallic acid at the temperatures of 25, 150, 250 and 300°C were realized and the main bands can be observed, 25°C the ν (-OH) at 3,770 and ν (C=O) at 1,720 cm^{-1}were assigned to the monohydrate compound. At 150°C all the main bands of gallic acid were characteristic with some slight shift in the peak positions due to the anhydrous compound due the decrease of hydrogen bonds with water after dehydration. At temperatures above 300°C was observed decrease in the main absorption peaks indicating that the final product is carbon. These results are in agreement with the literature (Rao and Reddy, 1981).

In the same way the X-ray Powder Patterns Diffractometry, show what the main diffraction peaks are: (a) at 25°C, 2θ= 8.2, 16.2, 19.0, 25.4, 27.8 and 32.6; the intensity 1439, 4267, 1335, 352, 352, 425 cps, respectively; (b) at 150°C, 2θ = 14.3, 16.4, 23.2, 25.4, 27.6, the intensity 342, 970, 256, 1380, and 1008 cps, respectively; (c) at 250°C, 2θ = 14.5, 15.6, 16.4, 23.4, 25.3, 27.6 and 32.0 the intensity 338, 313, 1080, 304, 1472, 1139 and 235 cps, respectively; (d) at 300°C, 2θ = 14.5, 15.5, 16.8, 25.1, 26.9 and 27.6 the intensity 213, 532, 409, 721, 594 and 509 cps, respectively. The XRD results are in agreement with those found in the literature (Bhagat *et al*., 2015; Liu *et al*., 2014). After dehydration crystallinity of Gallic acid practically no changes (Figure 3 a-c). After heating at 350°C and cooling occurs recrystallization

Table 1. Statistical parameters of the kinetic values obtained from thermal decomposition of gallic acid

Heating rate	Data points	Regression Equation	Standard error of estimate	R^2 (%)	Adjusted R^2 (%)	F-value	p-value
10 °C min^{-1}	898	y = 2.678,16*1/K - 4.91	0.0740	95.16	95.15	17.617,36	<0.00001
15 °C min^{-1}	598	y = 2.304,36*1/K - 4.20	0.0770	93.10	93.08	8.038,20	<0.00001
20 °C min^{-1}	448	y = 1.767,86*1/K - 3.21	0.0674	91.21	91.19	4.627,46	<0.00001
25 °C min^{-1}	357	y = 6.86*1/K - 0.01	0.0007	55.68	55.56	446.05	<0.00001

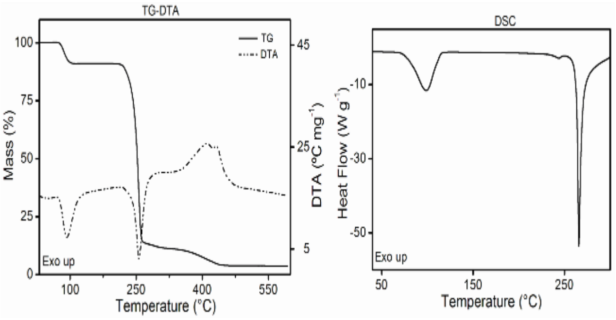

Figure 1. Simultaneous TG-DTA curves (left) and DSC curve (right) of gallic acid

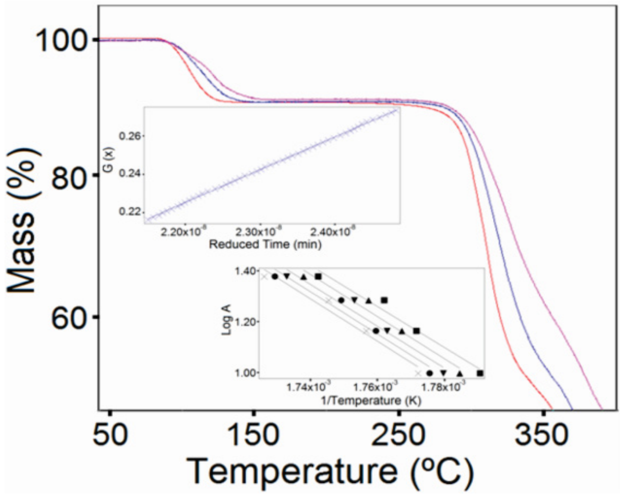

Figure 2. TG curves on kinetic values in the thermal decomposition of gallic acid at heating rates of 10, 15, 20 and 25°C min^{-1}

of the compound, small displacement in XRD peaks (Figure 3 d) suggest that the compound is recrystallized from a different crystalline form of the initial.

The data obtained from thermogravimetric analyses under four heating rates were used to propose first-order mathematical models of decomposition kinetics of gallic acid and the curves are depicted in Figure 2.

The multiple regression analysis showed that the decomposition models for heating rates of 10, 15 and 20°C min^{-1} were highly significant ($p<0.00001$) and they were able to explain more than 90% of all variance in experimental raw data. Thus, the regression equations that described the decomposition of gallic acid for heating rates of 10 and 15°C.min^{-1} can be used to explain adequaly the phenomenon. Conversely, the mathematical model obtained at 25°C min^{-1} explained only 55% of the data and thus should not be used to predict the kinetics of decomposition. In Table 1 are gathered these obtained results and Figure 3 shows the trend for gallic acid decomposition at different heating rates.

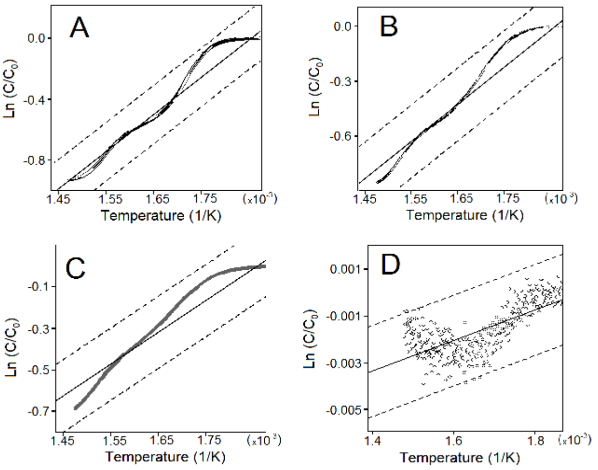

Figure 3. Regression equation of gallic acid decomposition at 10°C/min (A), 15°C/min (B), 20°C/min (C), and 25°C/min (D)

Thermogravimetric analysis under different heating rates can be used to determination of Arrhenius parameters as reported in literature (Vyazovkin *et al.*, 2014). This decomposition of gallic acid followed first-order reaction (n= 1), and the activation energy (Ea) was found to be 150.31 kJ.mol^{-1}, when the Arrehnius frequency factor was 1.712 x 10^7 min^{-1}.

Conclusion

Thermal analysis (TG-DTA and DSC) was proved to be suitable techniques for evaluating the thermal behavior of gallic acid and allowed to calculate dehydration and fusion enthalpies. The decomposition models proposed could explain more than 90% of all variance in data and regression equations were statistically significant. The non-isothermal interconversion kinetic method describes the complexity of the decomposition process and allowed to obtain the kinetic (Ea) parameters of gallic acid decomposition.

Acknowledgements

The authors acknowledge CAPES/PNPD (D. Granato), CNPq and the Araucaria Foundation, Brazil, for the financial support.

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