

## Quantitative analysis of overlapping processes in the non-isothermal decomposition of chlorogenic acid by peak fitting

Samuel K. Owusu-Ware, Babur Z. Chowdhry, Stephen A. Leharne, Milan D. Antonijević\*

School of Science, University of Greenwich at Medway, Chatham Maritime, Kent ME4 4TB, UK

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### ABSTRACT

The decomposition behaviour of chlorogenic acid (CGA) was studied under inert (nitrogen) and oxidative (air) atmospheres by thermogravimetric analysis (TGA). Thermal decomposition was found to be faster under an air atmosphere with a total weight change of  $97 \pm 1\%$  compared to  $61 \pm 1\%$  under a nitrogen atmosphere. At least 3 or 4 processes were observed for decomposition under air and nitrogen atmospheres, respectively. Furthermore, the 1st process, which follows a melt-crystallisation, was found not to be influenced by the different atmospheric conditions. Peak fitting of the CGA decomposition profile, in the form of a derivative thermogram (DTG), under a nitrogen atmosphere, revealed the presence of five complete decomposition processes and the first half of a sixth process between 160 and 500 °C. A comparison is made between the peak fitting and dynamic High-Res™ TGA experiments to demonstrate the reliability of the peak fitting approach. The predictions were then converted into discrete thermogravimetric (TG) curves with a single-step weight change. Since this approach provides baseline separation between overlapping processes, it has been possible to reliably determine the fractional weight change and the activation energy dependence on the reaction progression for the discrete TGA decomposition processes. The fractional weight change associated with processes 1–5 is:  $5.3 \pm 0.7$ ,  $2.0 \pm 0.4$ ,  $16.4 \pm 0.9$ ,  $30.9 \pm 1.6$  and  $5.5 \pm 0.5\%$ . Catechol was found to be the major decomposition product. The average activation energies of the 5 processes were calculated to be  $176 \pm 34$ ,  $185 \pm 4$ ,  $223 \pm 19$ ,  $245 \pm 47$ ,  $295 \pm 80$  kJ/mol when an integral method (Kissinger–Akahiro–Sunose) is used and  $120 \pm 25$ ,  $169 \pm 18$ ,  $191 \pm 12$ ,  $284 \pm 64$ ,  $245 \pm 46$  kJ/mol when a differential method (Friedman) is used for processes 1–5, respectively

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### 1. Introduction

Thermal gravimetric analysis (TGA) is a well-established method for characterising the decomposition behaviour of materials. However, extracting accurate quantitative data from TGA is difficult when the thermogram exhibits overlapping weight change profiles. In such situations there are several experimental methods that are generally employed in an attempt to resolve the complex TGA output. The simplest approach is the use of lower heating rates. However, this increases experimental time and may not necessarily resolve the overlapping processes. Another approach is the use of sample controlled methods, in which the heating programme is altered in response to changes in sample weight [1,2]. A limitation of this approach, however, is the inability to accurately assess the kinetic parameters of the decomposition processes, due to the inconsistent variation in the heating rate and temperature anomalies during experiments. Furthermore, baseline resolution is not

always achieved using high resolution/sample controlled methods and a greater level of operator expertise is required to optimise the method(s). Curve fitting is an alternative approach that can be used to resolve overlapping TGA outputs [3–5]. To our knowledge, the peak fitting approach has – hitherto – only been employed to obtain qualitative information about the decomposition behaviour of a sample from TGA data.

Chlorogenic acid (CGA; Fig. 1) is a member of the naturally occurring group of polyphenolic compounds found in many plants.

CGA is known to be a major component of commercially important products i.e. coffee beverages and tobacco. Whilst research has demonstrated the potential therapeutic benefits of CGA [6,7], its decomposition products are considered to be undesirable in coffee beverages [8,9] and potentially harmful in cigarette smoke [10,11]. Therefore, understanding the decomposition behaviour of CGA is extremely important.

Previous thermal decomposition studies [12] have demonstrated that CGA exhibits complex decomposition behaviour in non-isothermal TGA experiments for which the TGA outputs could not be resolved. Hence, the purpose of this study is to contribute data pertaining to the thermally induced decomposition of CGA

\* Corresponding author. Tel.: +44 0 20 8331 9841; fax: +44 0 208 331 9805.

E-mail address: [M.Antonijevic@gre.ac.uk](mailto:M.Antonijevic@gre.ac.uk) (M.D. Antonijević).

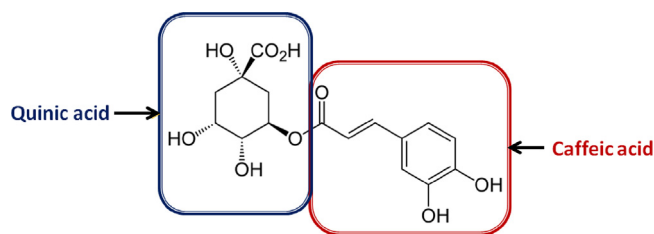


Fig. 1. Schematic of the chemical structure of chlorogenic acid (CGA).

by mathematically resolving the signals obtained for complex decomposition processes and exploring the capability of the “peak fitting approach” to provide quantitative information on overlapping decomposition processes examined via TGA experiments.

## 2. Materials and methods

### 2.1. Reagents

Chlorogenic acid hemihydrate (>98%) was purchased from Sigma–Aldrich and characterised, both qualitatively and quantitatively, using FTIR, NMR and elemental analysis. The samples were ground using a pestle and mortar and dehydrated in the TGA or DSC furnace before heating at a controlled rate.

### 2.2. TGA experiments

Degradation experiments were conducted using a TGA 2950 (TA Instruments) under nitrogen and air atmospheres at a flow rate of 50 mL/min; 4.0 ± 0.5 mg of sample was heated from 160 °C to 500 °C at different heating rates (1 °C/min, 3 °C/min and 5 °C/min) using 40 μL aluminium crucibles. High-resolution experiments were performed on Q5000 thermogravimetric analyzer (TA Instruments) under a nitrogen atmosphere at a flow rate of 25 mL/min with sample mass of 2.0 ± 0.1 mg. The dynamic High-Res™ mode was employed with varying R (resolution) values (3–8) and an S (sensitivity) value of 1 (which is the recommended setting for this technique), while the maximum heating rate was 20 °C/min.

### 2.3. DSC studies

DSC studies were performed using a DSC823 instrument (Mettler Toledo) under a nitrogen atmosphere at a flow-rate of 50 mL/min with the samples placed in 40 μL aluminium pans with a pin hole in the lid. 2.5 ± 0.4 mg of sample was heated to 500 °C at different heating rates (1 °C/min, 3 °C/min and 5 °C/min).

## 3. Results and discussion

### 3.1. Comparison of CGA decomposition under inert and oxidative conditions

There are significant differences in the mass loss profiles of CGA when the compound is heated under atmospheres of nitrogen or air (Fig. 2) in TGA experiments. The fractional weight change observed in the temperature range 160 to 500 °C, under a nitrogen atmosphere, is 61 ± 1% at all heating rates. This behaviour is similar to that reported in a previous study using an inert (helium) atmosphere [12]. Greater levels of decomposition were observed under an air atmosphere, with a fractional weight change of 97 ± 1% in the temperature range 160–500 °C, indicating that decomposition under oxidative conditions is ~33% greater than that observed for CGA under inert conditions.

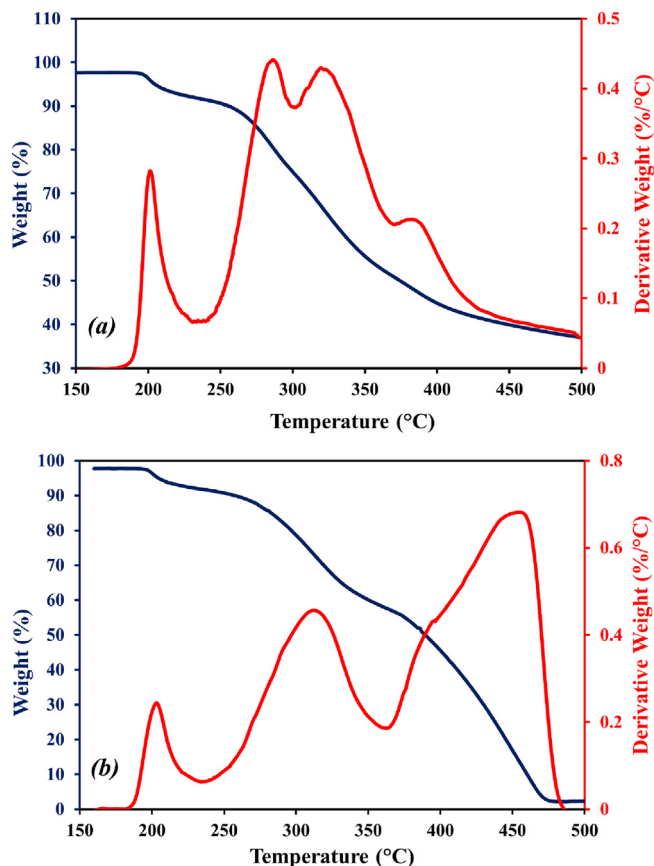


Fig. 2. TG-DTG output for the decomposition of CGA under (a) inert (nitrogen), and (b) oxidative (air) conditions obtained at a heating rate of 1 °C/min.

The derivative TGA curves in Fig. 2 show that the decomposition of CGA under both atmospheres in the temperature range analysed involves at least four decomposition processes, which have not been previously reported. The first decomposition process, at 201 ± 1 °C, under both atmospheric conditions, is identical with similar fractional weight changes (6.3 ± 0.6% and 6.6 ± 0.6% in nitrogen and air, respectively). This shows that the first decomposition process observed for CGA is not influenced by the atmospheric composition; indicating that the process is pyrolytic not oxidative. The second decomposition process in air has a peak temperature at 310 ± 3 °C, which is located between the second and third processes observed under a nitrogen atmosphere (peak temperatures 283 ± 2 °C and 327 ± 2 °C, respectively). Several hypotheses can be suggested to explain these observations. Firstly it is possible that under oxidative conditions the second and third processes observed under an inert atmosphere occur simultaneously i.e. the second process at 310 °C under an air atmosphere is composed of the second and third processes observed under a nitrogen atmosphere. This conclusion is supported by the similarities in the fractional weight change observed in the temperature region (250–375 °C) under both atmospheric conditions (42.7 ± 1.7% under nitrogen and 37.8 ± 2.7% in air). The foregoing data indicate that the decomposition processes occurring between 250 and 375 °C are strongly influenced by the atmosphere in which CGA is heated. Furthermore, the use of a nitrogen atmosphere provides better separation of the decomposition processes in the non-isothermal heating of CGA. Another implication of this observation is that under an atmosphere of air the second decomposition process proceeds via oxidative reactions, which results in the evolution of different product/products with a similar weight change in this temperature region. Thirdly, the second process observed

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