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EVOLVED GAS ANALYSIS (COUPLED TG-DSC-FT-IR) APPLIED IN THE STUDY OF FRUCTOOLIGOSACCHARIDES FROM CHICORY

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ABSTRACT

EGA (Evolved Gas Analysis) is a group of coupled techniques (in this case TG-DSC and FT-IR) that was used to provide information about the thermal and calorimetric behavior of standard fructooligosaccharides (FOS) from chicory. These FOS are found in several foods (tuber, roots, fruits, leaves, cereals, etc.) and have been the subject of several studies. In the present study thermogravimetry (TG) allowed the characterization of FOS a standard (Sigma-Aldrich), in which the weight loss can be observed in three stages (Δm 7.56, 55.53 and 36.53%, respectively). The simultaneous use of DSC showed endo and exothermic events in temperature characteristics and in agreement with TG curves. The enthalpies of the main stages of decomposition were calculated: ΔH_{dehydr} 260 J g^{-1} and ΔH_{dec} 410 J g^{-1}. From the FT-IR spectrum of the volatiles was possible to characterize the main bands, which confirmed CO and CO_2 as a result of thermal decomposition.

Keywords: FOS, thermal analysis, FT-IR, enthalpy

INTRODUCTION

According to the literature (**Palacio, Etcheverría, Manrigue, 2013**), the growing awareness of consumers about the relationships between food and health has led to an increasing demand for nutritional foods.

Among the various substances which contain nutraceuticals, fructooligosaccharides (FOS) are present in the form of plant storage reserve carbohydrates, and they occur naturally in many tuberous roots such as chicory (*Cichorium intybus*), artichoke (*Cynara scolymus*), yacon (*Smallanthus sonchifolius*) and are also present in many others, in different quantities. FOS are fructose oligosaccharides joined by β-(2$\rightarrow$1) or β-(2$\rightarrow$6) linkages and terminated with a glucose molecule linked to fructose by an α-(1$\rightarrow$2) bond (**Fernández *et al*, 2013; Campbell *et al*., 1997**).

Due to their relatively high amount of FOS, these tuberous have received special attention from the scientific community because these substances have a beneficial effect on human health (**Santana, Cardoso, 2008**).

FOS exhibit prebiotic function is to stimulate the growth and / or activity of one or a limited number of bacteria in the colon that can improve the health of the host health (**Gibson, Roberfroid, 1995**).

Foods containing FOS are considered nutraceuticals, which can be defined as foods that provide physiological benefits to consumers. They are low caloric foods, which promote immune response and enhance resistance to pathogens that stimulate the growth of bifidobacteria in the human colon and reduce cholesterol levels in the serum (**Delgado *et al*., 2013; Valentová *et al*., 2006; Campbell *et al*., 1997**).

Chicory (*Cichorium intybus*) is a perennial plant from the *Asteraceae* or *Compositae* family that has its origins in Europe, western Asia and central Russia. Nowadays, it is cultivated in a number of temperate regions around the world (**Koch *et al*, 1999**).

In Brazil, chicory is cultivated for the production of its leaves and consumed in salad. In other countries, the roots are used roasted and mixed with coffee seeds for the preparation of coffee powder. Belgium has been active in processing the root for the production of inulin (fructose polymer) and its hydrolysis products such as oligofructose and fructose (**Figueira *et al*., 2004**; **Zhang *et al*., 2003**).

EGA analysis consists of the following coupled techniques: thermogravimetry (TG), differential scanning calorimetry (DSC) and Fourier transform infra-red spectrophotometry (FT-IR), which are widely used to evaluate the thermal behavior of solid compounds, as well as to investigate the volatile compounds that are generated. In the present study, a standard sample of FOS obtained from chicory was acquired from Sigma-Aldrich and the study was performed with the aim of assessing thermal behaviour as well as the evolved gas analysis (EGA) employing simultaneous TG-DSC-FT-IR techniques.

MATERIAL AND METHODS

The standard samples of FOS used in this study were acquired from Sigma-Aldrich Co; the FOS was from chicory (*Cichorium intybus* L).

Simultaneous Thermogravimetry and Differential Scanning Calorimetry (TG-DSC)

The curves were obtained by using a TGA-DSC 1star^{e} system from Mettler Toledo Co. The purge gas had an air flow of 50 mL.min^{-1}, and a heating rate of 10 ºC.min^{-1} was adopted, with samples weighing about 20 mg. Open alumina crucibles were used for recording the TG-DSC curves. The instrument was calibrated (standard mass, monohydrate calcium oxalate) according to the literature (**Alberton *et al*., 2014; Andrade *et al*., 2014**) and the manufacturer's instructions.

Evolved Gas Analysis

The measurements of the gaseous products were carried out using the TG-DSC Mettler Toledo coupled to a FT-IR spectrophotometer, from Nicolet Co., with gas cell and DTGS detector. The furnace and the heated gas cell (250 ºC) were coupled through a heated (225 ºC) 120 cm stainless steel line transfer, with a diameter of 3.0 mm; both purged with dry air (50 mL.min^{-1}). The FT-IR spectra were recorded with 16 scans per spectrum at a resolution of 4 cm^{-1}. The methodology used was according to the literature (**Souza *et al*, 2014; Locatelli *et al*., 2014**) and it provided information about the volatile products generated during the thermal decomposition process.

Differential Scanning Calorimetry (DSC)

For the determination of enthalpy values, the DSC curves were obtained using a DSC-Q200 (TA-Instruments, USA) instrument, which was calibrated with standard indium 99.99% purity, m.p. = 156.6ºC, ΔH = 28.56 J g^{-1} (**Andrade *et***

***al*., 2014; Oliveira *et al*, 2014**). The samples were heated from -60 to 300 ºC, by using a platinum crucible with a perforated pierce lid (orifice with 1.0 mm). The mass sample was around 5 mg and an air flow of 50 mL min^{-1} was employed at a heating rate of 10 ºC min^{-1}.

RESULTS AND DISCUSSION

The simultaneous TG-DSC curves of the standard samples of FOS from chicory showed the profile that can be seen in Figure 1. In the TG curve (solid line) three main stages of mass loss can be seen; the first stage occurred between 30 and 122 ºC due to dehydration, with a loss of 7.56% of initial mass, followed by stability from 122-207 ºC. The second stage occurred between 207 and 321 ºC with a mass loss of 55.53%, and was due to the decomposition of the FOS. This was followed, in a consecutive reaction, by the third stage of decomposition of the FOS from 321-598 ºC with a mass loss of 36.53%, which was attributed to oxidation of the organic matter and the formation of ash, which was 0.38% of initial mass.
The simultaneous DSC curve (dash line) was in agreement with the TG curve and showed an endothermic reaction at a temperature of 122-207 ºC (peak temperature, T_p at 82 ºC) due to the dehydration process, with stability of the FOS sample up to 207 ºC. During the second stage, the profile of the DSC curve showed an endothermic reaction (T_p at 241 ºC), followed by consecutive exothermic reactions during the third stage (with shoulder, T_p at 362 ºC followed by exothermic reactions, T_p at 526 and 588 ºC). In order to identifying steps the mass loss of the FOS sample, the first derivative of the thermogravimetric curve was used, i.e. derivative thermogravimetric analysis (DTG).

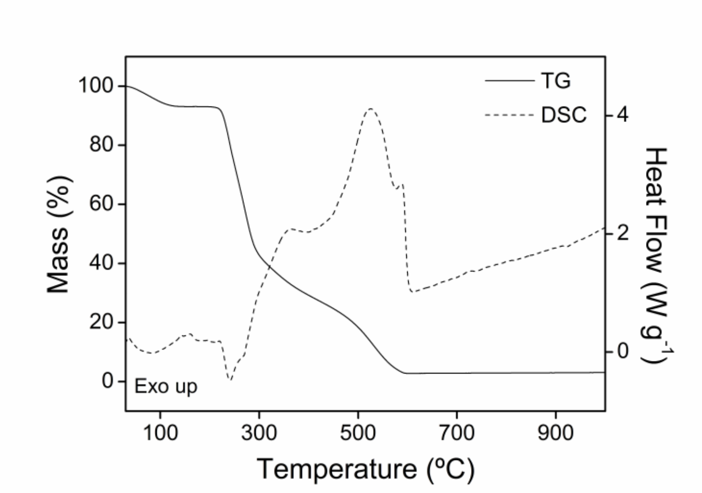

Figure 1 Simultaneous TG-DSC curves of fructooligosaccharides

In order to assess the main calorimetric properties of the FOS, the DSC curve was obtained using a DSC Q-200 instrument (TA-Instruments). The DSC curve is depicted in Figure 2 and it was performed from -60 to 300 ºC. It was possible to investigate the *onset* temperature (T_o), the *peak* temperature (T_p), and the *endset* or *conclusion* temperature (T_c), as well as to calculate the dehydration enthalpy (ΔH_{dehydr}), and the first decomposition enthalpy (ΔH_{dec}). The differences between the DSC curves in Figures 1 and 2 are due to the calorimetric sensibility of the instruments and the thermal condutivity of the crucibles (open alumina and platinum with perforated lid, respectively).

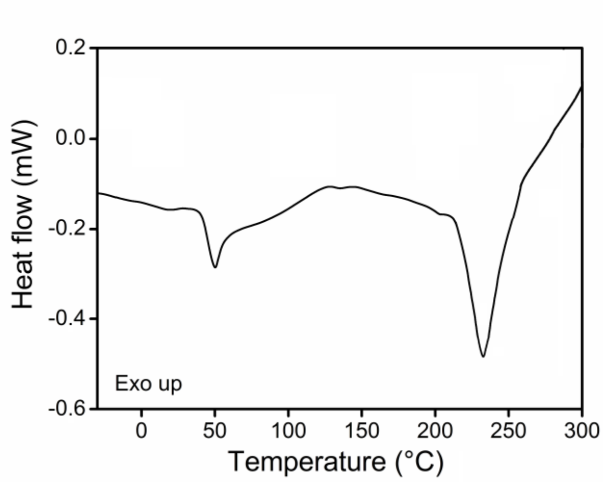

Figure 2 DSC curve of fructooligosaccharides from chicory

The first endothermic peak observed in the DSC curve, which occurred with T_o at 46.2 ºC, T_p at 50.2 ºC and and T_c at 57.4 ºC, respectively; was due to the dehydration process, where ΔH_{dehydr} was 260 J $^{g-1}$. The second endothermic peak of the FOS occurred with T_o at 219.2 ºC, T_p at 240.5 ºC, and and T_c at 260.9 ºC, respectively. The decomposition enthalpy ΔH_{dec} was 410 J g^{-1} and this event was associated with the second stage of decomposition, which was observed in the TG curve. The temperatures and enthalpy obtained using the DSC technique in this second stage were attributed to the decomposition and the caramelisation of the FOS, with the release of volatile compounds.
Separately, in an open glass flask on a hot plate with controlled heating, containing a small quantity of FOS, the decomposition of the material was observed, with dehydration in the first stage and decomposition, with caramelisation and browning, during the second mass loss.
In terms of the analysis of volatile compounds, Figures 3 (A) and 3 (B) show the 3D and 2D spectra collected at 500 °C FT-IR analysis, respectively.

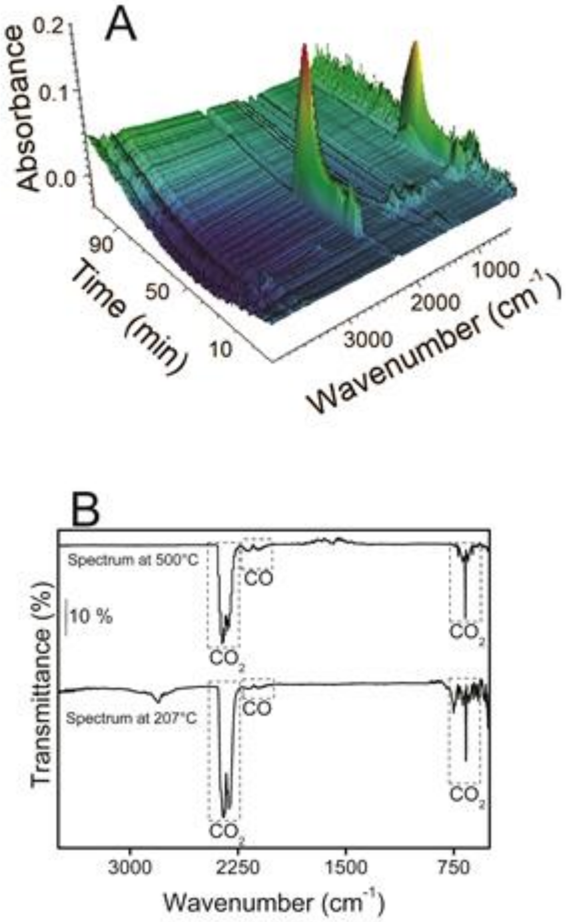

Figure 3 (A) - 3D infrared spectrum of the gases evolved from the thermal decomposition of fructooligosaccharides; (**B)** - infrared spectrum of gas collected at 500 °C from fructooligosaccharides.

The FT-IR spectra showed an absorption band between 3700-3500 cm^{-1} due to -OH groups (dehydration) and showed that in the temperature of the second mass loss, as observed in the TG-DSC curves, the main absorption bands occurred between 620-730 cm^{-1}, 2030-2250 cm^{-1} and 2250-2400 cm^{-1}, which were characteristic and were attributed to CO_2, CO and CO_2, respectively.

CONCLUSION

The TG-DSC curves supplied information about the thermal stability and thermal decomposition of the FOS from chicory, which occurred in three stages. The DSC technique allowed us to determine the dehydration enthalpy and the decomposition enthalpy (260.0 J $g^{-1}$and 410.0 J g^{-1}), respectively. Using the coupled FT-IR spectra it was possible to establish that the release of CO_2 and CO gases occurred when the FOS were heated above 207 ºC.

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