

ANALYSIS OF THE THERMAL DECOMPOSITION OF COMMERCIAL VEGETABLE OILS IN AIR BY SIMULTANEOUS TG/DTA

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Abstract

This work presents a study of the thermal decomposition of commercial vegetable oils and of some of their thermal properties by termogravimetry (TG), derivative termogravimetry (DTG) and by differential thermal analysis (DTA). Canola, sunflower, corn, olive and soybean oils were studied. A simultaneous SDT 2960 TG/DTA from TA Instruments was used, with a heating rate of 10 K min⁻¹ from 30 to 700°C. A flow of 100 mL min⁻¹ of air as the purge gas was used in order to burnout the oils during analysis to estimate their heat of combustion. From the extrapolated decomposition onset temperatures obtained from TG curves, it can be seen that corn oil presents the highest thermal stability (306°C), followed by the sunflower one (304°C). Olive oil presents the lowest one (288°C). The heat of combustion of each oil was estimated from DTA curves, showing the highest value for the olive oil. Except for corn oil, which presents a significantly different thermal decomposition behavior than the other oils, a perfect linear correlation is observed, with negative slope, between the heat of combustion of an oil and its respective extrapolated onset temperature of decomposition in air.

Keywords: DTA, DTG, heat of combustion, stability, TG, thermal decomposition, vegetable oil

Introduction

Fats and vegetable oils, commonly called triglycerides, are triesters of glycerol usually made up by fatty acids molecules of 16 or more carbon atoms. Fats, as proteins and carbohydrates, are basic food substances and they are the highest source of energy in a diet, an important source of oil-soluble vitamins and of some essential unsaturated fatty acids [1].

Thermal analysis techniques has been used for edible oil and fat characterization by measuring several properties such as thermo-oxidative behavior and stability [2–4], specific heat [5], thermal decomposition activation energy [6], temperature and enthalpy of crystallization [7–10]; action of antioxidants in oil thermal stability [6, 11], unsaturation degree from melting and crystallization oil profile curves [12] and high-pressure oxidation induction time measurements [13].

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The higher is the onset temperature of decomposition of an edible oil, the higher is its thermal stability. This property is of great practical importance, specially when frying foods, to avoid the deterioration of the oils. On the other hand, their calorific power, which can be estimated from the heat of combustion, allows an evaluation of the corresponding calorific value during their metabolism in the human body. In this paper the thermal decomposition of commercial canola, sunflower, corn, olive and soybean oils was studied by simultaneous thermogravimetry (TG) and differential thermal analysis (DTA). Except for corn oil, which shows a different burnout behaviour, a very good correlation of experimental data indicates that the lower is the thermal stability of the oil the higher is its heat of combustion. Among the studied oils, the olive one presents the lowest decomposition onset temperature and the highest calorific value.

Materials and methods

The thermal decomposition of the following commercial vegetable oils was studied: canola, sunflower, corn, olive and soybean. The analyses were performed in a simultaneous DTA-TGA equipment, TA Instruments, model SDT 2960, with a 10 K min^{-1} constant heating rate from 30 to 700°C . Air was used as the purge gas at a 100 mL min^{-1} flow rate. About 10 mg of sample were used in platinum pans in each analysis. TG and DTA curves, as well as derivative thermogravimetric (DTG) curves were used in the study.

The heat of combustion was estimated from the total area of the exothermal DTA peaks of the thermal decomposition of each oil, which occurs during the analysis. The thermal stability was measured from the extrapolated onset temperature of the first step of thermal decomposition from respective TG curves, by using the beginning and the peak temperature of the respective DTG peak, as the temperature limits of the data analysis software of the instrument.

Results and discussion

Figure 1 shows the TG, DTG and DTA curves of the olive oil. As can be seen from TG curve and more precisely from the DTG curve, the first step of decomposition begins at 200 and ends at 350°C . The extrapolated onset temperature is 288°C and the first DTG and DTA peaks occur, respectively at 324 and 329°C . The second mass loss step occurs from 350 to 410°C , also presenting an exothermal DTA peak. The third mass loss step, which actually is composed by many sharp DTG and exothermal DTA peaks, occurs up to about 470°C and is followed by a final exothermal mass loss step, which ends at 580°C , due to the burnout of the residual carbonaceous material of the previous steps.

As can be seen in Fig. 2, corn oil presents a different behavior during its second thermal decomposition step, which occurs from 375 to about 425°C , with a significantly higher DTG peak than in the same decomposition step of the other oils, probably because of its fatty acid composition. Thus, the first three steps present a more homogeneous mass loss rate behavior than the other oils, as can be seen in the DTG

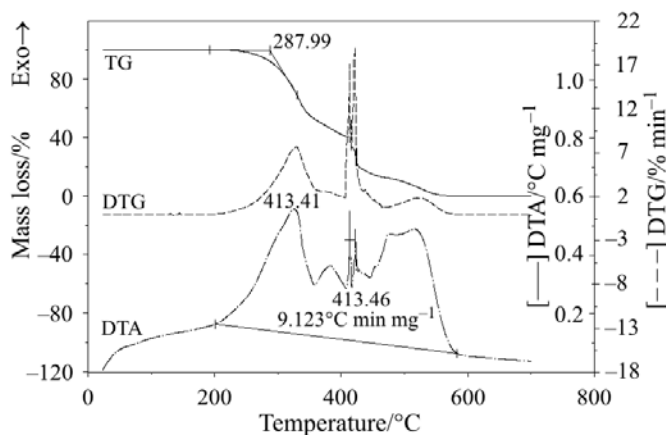


Fig. 1 TG, DTG and DTA curves of olive oil in air

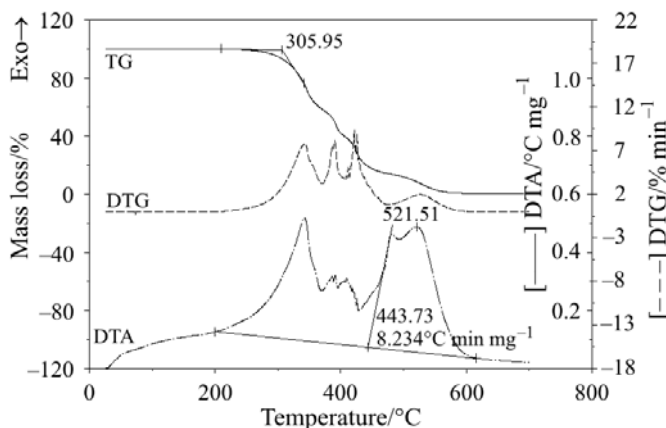


Fig. 2 TG, DTG and DTA curve of corn oil in air

curve. The last step, when the combustion of the carbonaceous residue occurs, has similar behavior to the other ones.

The thermal decomposition behavior of canola, sunflower and soybean oils is similar to the olive oil one as shown in Figs 3 to 5, which respectively compare TG, DTG and DTA curves of these oils. As can be seen in Fig. 3, practically there is no significant residue after 600°C for almost all the oils in the oxidative ambient of air flow. The final step of mass loss, due to the burning of the carbonaceous residues, present similar mass loss rates for all oils as can be seen in Fig. 4.

On the other hand, as can be seen in Fig. 5, the heat released in each decomposition/combustion step depends on the oil, probably because of the different respective initial fatty acid compositions [1]. The same occurs for the final step, where probably different residual carbonaceous materials are formed from the previous steps [14].

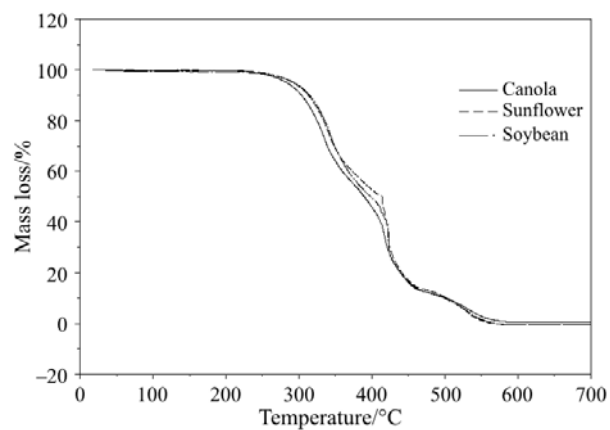


Fig. 3 TG curves of canola, sunflower and soybean oil in air

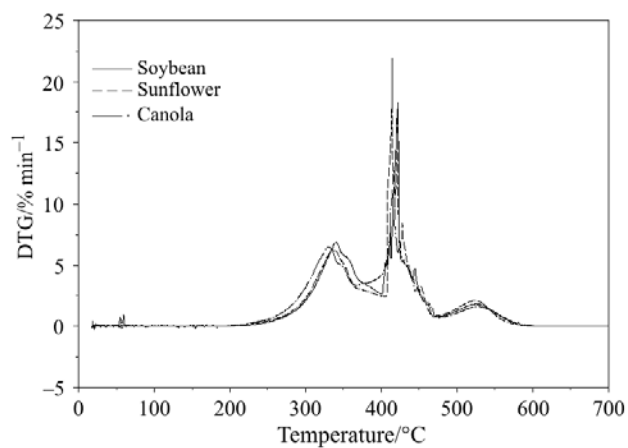


Fig. 4 DTG curves of canola, sunflower and soybean oil in air

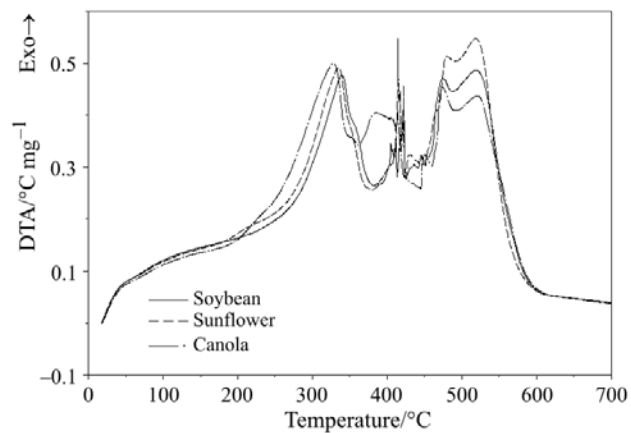


Fig. 5 DTA curves of canola, sunflower and soybean oil in air

The total energy per unit mass released during combustion, which is the heat of combustion (ΔH_c), is directly proportional to the total area of the respective DTA peaks and is calculated by the software of the instrument, in $^{\circ}\text{C min mg}^{-1}$ units, as shown in Figs 1 and 2. To estimate the value of the DTA peak area in kJ kg^{-1} , a pro-analysis calcium hydroxide sample was analyzed by DTA and by DSC in the same heating rate and air flow than the used for the oils, using aluminum pans and heating from ambient temperature to 600°C instead. It was used a TA Instrument, DSC model 2010, which was previously calibrated with indium. The area of the calcium dehydroxylation peak, which occurs between 400 and 550°C , was measured from three runs, obtaining a mean conversion factor of $5.0788 \text{ kJ kg}^{-1}$ per $^{\circ}\text{C min mg}^{-1}$. This value was used to estimate the ΔH_c of the oils from their respective combustion DTA peak areas. The standard deviation of the three determinations was about 2% of the mean value, which is the estimated experimental error of the procedure. As an example of comparison with other methods, the estimated heat of combustion of the analyzed soybean oil was 40885 kJ kg^{-1} . Considering the experimental error, it is in good agreement with values obtained in the literature from conventional calorimetric methods for other soybean oil samples, such as 39417 [15] and 40810 kJ kg^{-1} [16].

Figure 6 shows a plot of the estimated heats of combustion of olive, canola, sunflower and soybean oils as a function of their respective extrapolated onset decomposition temperature. It can be seen for these oils that, the higher is the onset temperature, the lower is the heat of combustion. As it can be noticed, the correlation coefficient is almost one. This indicates a perfect linear correlation between stability and calorific power for the studied oils except for corn oil, which does not follows this behavior.

Analyzing typical compositions of the studied oils [1] it is interesting to note that only olive oil is made up of saturated fatty acids molecules of 14 carbon atoms (1–3 mass%), with the highest content of those with 16 atoms of carbon (7–16 mass%), what may explain its lowest decomposition onset temperature. On the other hand, as

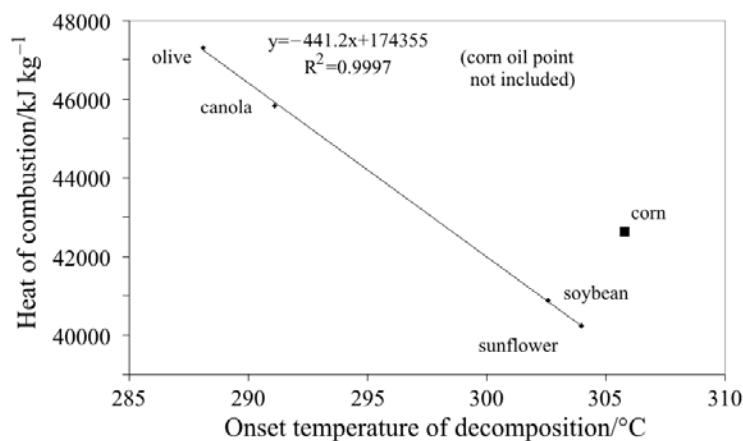


Fig. 6 Estimated heat of combustion of the oils as a function of the respective decomposition onset temperature

corn oil is made up by the highest content of unsaturated fatty acid molecules with 18 atoms of carbon it shows the highest thermal stability among the oils.

The lower is the molecular mass and number of double bonds of a hydrocarbon, the higher is the carbon/hydrogen (C/H) mass ratio and the higher is its heat of combustion [17]. The mean iodine value of olive oil is significantly lower than the other analyzed oils [1]. That means that its C/H mass ratio is the highest one among the studied oils and consequently, this fact explains its highest heat of combustion.

Conclusions

On the base of the respective decomposition onset temperatures obtained from respective TG curves in air, corn oil presents the highest thermal stability, followed in decreasing stability order by sunflower, soybean, canola and olive oils.

The combustion heat of the oils, estimated from the total area of their several burnout DTA peaks, decreases in the following order: olive, canola, corn, soybean and sunflower.

Except for corn oil, which presents a thermal decomposition behavior significantly different from the other oils, a very good correlation of experimental data for the other oils indicates that the lower is the thermal stability of the oil the higher is its heat of combustion.

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