Food Chemistry 194 (2016) 601–607

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Differential scanning calorimetry study—Assessing the influence of composition of vegetable oils on oxidation

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ARTICLE INFO

Article history:
Received 9 February 2015
Received in revised form 30 July 2015
Accepted 31 July 2015
Available online 6 August 2015

Keywords:
Differential scanning calorimetry
Vegetable oil
Fatty acid
Triacylglycerol
Lipid oxidation
Kinetic analysis

ABSTRACT

The thermal oxidation of eight different vegetable oils was studied using differential scanning calorimetry (DSC) under non-isothermal conditions at five different heating rates (5, 7.5, 10, 12.5, and 15 °C/min), in a temperature range of 100–400 °C. For all oils, the activation energy (E_a) values at T_p were smaller than that at T_s and T_{on}. Among all the oils, refined palm oil (RPO) exhibited the highest E_a values, 126.06 kJ/mol at T_s, 134.7 kJ/mol at T_{on}, and 91.88 kJ/mol at T_p. The E_a and reaction rate constant (k) values at T_s, T_{on}, and T_p were further correlated with oil compositions (fatty acids and triacylglycerols) using Pearson correlation analysis. The rate constant (k) and E_a of all oils exhibited varying correlations with FAs and TAGs, indicating that the thermal oxidation behaviors were affected by oil compositions.

1. Introduction

Vegetable oils play an important role in the human diet due to their nutritional and sensory properties. They are also one of the main ingredients in a wide range of food products, such as ice cream, sausages, and margarine (Shahidi & Zhong, 2010). However, oils are susceptible to oxidation reactions during food processing and subsequent storage of food products. The oxidation of oils leads to the development of off-flavor compounds and undesirable chemical changes of foods, resulting in decreased nutritional value of foods and potential food safety problems (Choe & Min, 2006; Dijkstra & Segrers, 2007).

Differential scanning calorimetry (DSC), which belongs to the family of thermal analysis, has been applied for the last 50 years in the field of fats and oils for various purposes (Tan & Nehdi, 2014). In particular, DSC evaluates the thermal oxidation behaviors of oils through precise recording of heat flow into and out of an oil sample. The heat flow is reported as a function of either time or temperature and plotted on the DSC thermograms, in which each peak is associated with a specific physical or chemical process (Vecchio Ciprioti & Chiavaro, 2014). As a very well-established method, DSC has been widely applied in lipid studies. Cerretani et al. (2012) investigated the effect of fatty acid composition and phenol contents on the stability of extra virgin olive oil under accelerated oxidative test using DSC. Caponio et al. (2013) applied DSC in the evaluation of cooling and heating curves as well as thermal attributes of olive oil during refining process. Cerretani, Maggio, Barnaba, Toschi, and Chiavaro (2011) quantified the fatty acid in olive oils using a novel DSC-PLS (partial least square) method. Maggio, Barnaba, Cerretani, Paciulli, and Chiavaro (2014) developed a faster analytical method based on DSC, named high-pressure liquid chromatography–differential scanning calorimetry–partial least square (HPLC–DSC–PLS), to investigate the DSC cooling curves of extra virgin olive oil affected by triacylglycerol composition.

Oil oxidation is a complex reaction involving several simultaneous reactions. The different oxidation behaviors among oils may be affected by the various oil compositions. To the best of our knowledge, only one study conducted by Vecchio, Cerretani, Bendini, and Chiavaro (2009) investigated the relationship between oil composition and thermal oxidation properties. They reported that the onset temperatures of the thermal decomposition transition, the maximum heat flow temperatures, and as well as the sum of enthalpy were found to significantly correlate with the components of twelve different extra virgin olive oils. However, no study was found to address the relationship between oil composition and

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http://dx.doi.org/10.1016/j.foodchem.2015.07.148
0308-8146/

thermal oxidation properties for other vegetable oils, such as soybean oil, corn oil, and sunflower oil.

Therefore, the aim of this study was to evaluate the thermal oxidation properties of vegetable oils using DSC, and further investigate the relationships between oil compositions and thermal oxidation properties.

2. Materials and methods

2.1. Materials

Eight different vegetable oils, namely refined palm oil (RPO), olive oil (OeO), grapeseed oil (GsO), sunflower oil (SuO), corn oil (CnO), soybean oil (SoO), safflower oil (SaO), and sesame oil (SeO), were purchased from a local market. Fatty acid methyl esters (FAME) standards were purchased from Sigma–Aldrich (St. Louis, MO, USA). All other chemicals and reagents used were of analytical grade.

2.2. Analysis of fatty acid (FA) by GC–MS

The gas chromatography–mass spectrometry (GC–MS) analysis of fatty acid composition was performed using an Agilent GC–MS instrument (7890A-MSD5975C, Agilent Technologies, Palo Alto, CA, USA) equipped with a quadrupole selective mass detector. A CP-Sil 88 capillary column (100 m × 0.25 mm i.d., 0.2 μm film thickness, Chrompack, Bridgewater, NJ, USA) was used in the analysis. The fatty-acid methyl esters (FAMEs) were prepared according to (ISO, 1990) method 5508. The injection volume of FAMEs was 1 ml. Helium was used as the carrier gas at a flow rate of 0.8 ml/min. Split ratio was 1:30. The injection temperature was 260 °C, and detector temperature was 280 °C. The GC oven program was as follows: first held at 70 °C for 1 min, and then increased to 100 °C at 5 °C/min and held for 2 min; then increased to 175 °C at 10 °C/min and held for 40 min; and finally increased to 220 °C at 15 °C/min and kept for 30 min. The individual fatty acids were identified and quantified by comparing their retention times with external standards.

2.3. Identification and quantification of triacylglycerol

The triacylglycerol (TAG) analysis was conducted on an Eksigent high performance liquid chromatography (HPLC) system (AB SCIEX, CA, USA) equipped with a tandem quadrupole mass spectrometer (TripleTOF 4600, AB SCIEX, CA, USA) and a 250 × 4.6 mm C18 column (Waters, Milford, MA, USA). Gradient elution was performed using n-hexane and dichloromethane (1:1, v/v) as mobile phase A and acetone and acetonitrile (5:95, v/v) as mobile phase B at a flow rate of 0.6 ml/min. The elution program used was as follows: from 0 to 20 min, held at 20% A; from 20 to 35 min, increased to 80% A; from 35 to 45 min, decreased back to 20% A. The column temperature was set at 40 °C. TAGs were identified according to their mass spectra data in literatures (Cunha & Oliveira, 2006; Holcapek, Lisa, Jandera, & Kabatova, 2005; Lerma-Garcia et al., 2011; Zeb, 2012). The amount of each TAG was normalized and expressed as a percentage of the total peak area (%). According to the types of fatty acids bonded to glycerol skeleton, the TAG were further grouped as trisaturated (TSTAG), disaturated (DSTAG), monosaturated (MSTAG), and triunsaturated triacylglycerol (TUTAG).

2.4. Differential scanning calorimetry analysis

The DSC analysis was conducted on a STA449 F3 simultaneous thermoanalyzer (Netzsch, Bavaria, Germany) using oxygen (99.99%, 80 ml/min) as the purge gas and nitrogen (99.99%, 20 ml/min) as the protective gas. An oil sample of 2.7–3.6 mg was weighed into an aluminum pan and hermetically sealed with a pinhole lip, which can allow for constant interaction between the sample and the oxygen streamoxygen stream. The system was equilibrated at 30 °C for 5 min and then heated linearly to 400 °C at 5, 7.5, 10, 12.5, and 15 °C/min to generate the oxidative profile

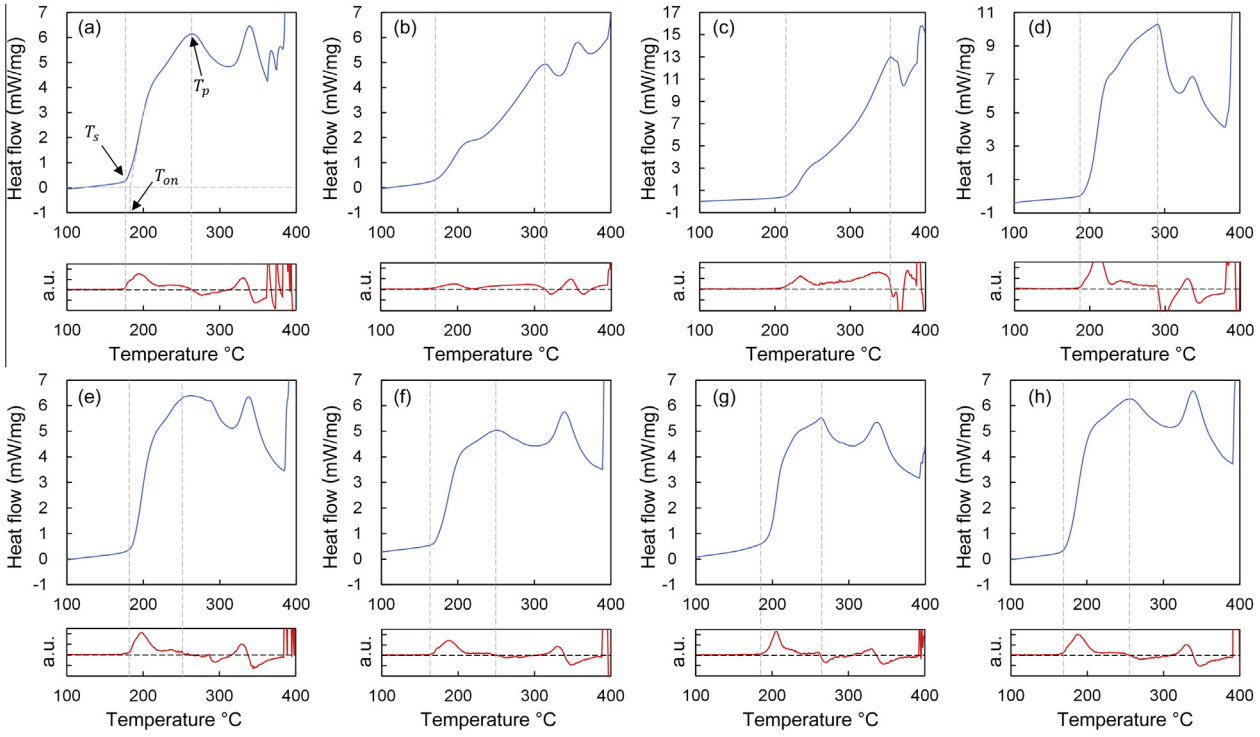

Fig. 1. DSC oxidation curve of the eight different oils at the heating rate of 10 °C/min. (a) Sunflower oil; (b) soybean oil; (c) refined palm oil; (d) olive oil; (e) corn oil; (f) safflower oil; (g) sesame oil; (h) grapeseed oil. Top large plots: DSC oxidation curve. Bottom small charts: first derivative of DSC oxidation curve.