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Biosensors for monitoring the isothermal breakdown kinetics of peanut oil heated at 180 °C. Comparison with results obtained for extra virgin olive oil

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ABSTRACT

The present research was devoted to studying the kinetics of the artificial rancidification of peanut oil (PO) when a sample of this oil was isothermally heated at 180 °C in an air stream. The formation of radical species due to heating was evaluated using a radical index whose value was determined using a biosensor method based on a superoxide dismutase (SOD), while the increasing toxicity was monitored using a suitable toxicity measuring probe based on the Clark electrode and immobilized yeast cells.

An extra virgin olive oil was isothermally rancidified under the same experimental conditions and the corresponding data were used for the purpose of comparison.

Both the so-called "model-fitting" and the classical kinetic methods were applied to the isothermal process biosensor data in order to obtain the kinetic constant rate value at 180 °C.

1. Introduction

In recent years, in-depth research was carried out in our laboratory on the isothermal rancidification of extra-virgin olive oil (EVOO) performed at 98 °C (Tomassetti, Vecchio, & Campanella, 2011) in an air stream, using the classical A.O.M. method (AOCS, 1964). The kinetic rate of this process was also computed. A thermal decomposition study of monovarietal EVOO samples was also performed and a relation between the kinetic parameter of decomposition and the chemical composition of the samples was established (Vecchio, Cerretani, Bendini, & Chiavaro, 2009).

The aim of the present research was instead to study the kinetic rancidification of peanut oil (PO) when a sample of this oil was artificially rancidified isothermally at 180 °C in air; in practice the oil sample was heated to a high temperature, in order to determine the constant rate value and therefore the time span over which the product can effectively and safely be used for cooking and frying. However, as reported in literature (Buzás, Simon, & Holló, 1979; Campanella, Dragone, Fisco, & Tomassetti, 2004; Lorusso & Zelinotti, 1985; Tan & Che Man, 2000), the process of heating the oil samples (Carrasco-Pancorbo et al., 2007; Chiavaro et al., 2007; Kiritsakis & Markakis, 1987; Vazquez Roncero, Janer Del Valle, & Janer Del Valle, 1973) leads to chemical changes and causes the formation of radical species, which results in an appreciable increase in oil toxicity. In the present study, radical species formation due to heating was evaluated using a radical index. This was detected using a biosensor method (Amati et al., 2008; Campanella, De Luca, Favero, Persi, & Tomassetti, 2001a) based on a superoxide dismutase (SOD) obtained by coupling an amperometric Clark-type electrode with immobilised SOD enzyme operating in dimethylsulphoxide (DMSO), while the increasing toxicity was monitored using a suitable toxicity measuring probe (Campanella et al., 2004) consisting of an oxygen sensor + yeast immobilised cells.

Two different kinetic methods for processing data derived from biosensor measurements exploited during the isothermal breakdown of peanut oil at 180 °C were used. The corresponding data for a dephenolized extra-virgin olive oil were used for the purpose of comparison. Lastly, to complete the information regarding the principal decomposition processes affecting the triglycerides during the heating of the two food oils tested, the latter were subjected to thermal analysis: thermogravimetry (TG) and first-order derivative thermogravimetry (DTG). The data obtained, processed according to the Kissinger method (Vecchio, Campanella, Nuccilli, & Tomassetti, 2008), enabled the activation energy of the thermoxidation processes occurring in the triglycerides present to be assessed.

2. Materials and methods

2.1. Chemicals

Superoxide dismutase (SOD) (EC 1.15.1.1) from bovine erythrocytes, 7000 Units mg^{-1}, dimethyl sulphoxide (DMSO), potassium

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superoxide, silicon oil 350 Cps Crual srl, the internal solution of the Clark electrode, namely phosphate buffer solution 0.067 mol L^{-1}, pH = 7.5, were supplied by Sigma–Aldrich. Kappa-carrageenan was supplied by Fluka, while Yellow Springs supplied the gas PTFE permeable membrane (YSI model 5775). Monobasic and dibasic potassium phosphates RPE were supplied by Carlo Erba Reagents; potassium chloride was supplied by Riedel-de Haën (Seelze, Germany).

The cells used belonged to a *Saccharomyces cerevisiae*, wild-type W303-1a diploid strain, kindly made available by the Rome Botanical Gardens. The following reagents were used for the culture medium: yeast extract for microbiology, universal peptone for microbiology M66, D-glucose for microbiology, all of analytical grade, and high purity agar agar were all supplied by Merck, Darmstadt (Germany). The dialysis membrane (art. D-9777) was supplied by Sigma, St. Louis, MO (USA); Hepes buffer, was supplied by Fluka AG, Buchs (Switzerland).

2.2. Samples

Both the commercial peanut and extra-virgin olive oil samples analyzed (denoted as PO and EVOO, respectively), stored in sealed dark glass bottles, were purchased from a local shop and are marketed by a single supplier operating in Central Italy.

As the polyphenolic compounds contained in the EVOO can react with the superoxide radicals, which are introduced into the measurement solution as described in the SOD biosensor method for the radical determination, a decrease in the superoxide radical concentration in solution occurs, thus interfering with the correct application of the method (Amati et al., 2008). The EVOO samples were therefore subjected to the same isothermal rancidification process that occurred at 180 °C as well as PO samples, but only after being previously pretreated with active carbon in order to remove practically all of the polyphenolic compounds and other antioxidants contained in the EVOO (Campanella, Favero, Pastorino, & Tomassetti, 1999). Indeed all the measurements carried out in the present research regarding the EVOO samples were performed after treating the oil with active carbon, while all the measurements in PO were performed in the oil as such, because of the absence of polyphenols in this kind of oil.

2.3. Apparatus

The oxidative thermal degradation of PO and EVOO samples examined in this study took place in a silicon oil-based thermostatic bath (at 180 °C ± 0.1) in an air stream of 140 mL min^{-1} generated by a Unistar mod. AIR 1000–1 pump.

The transducer employed for the evaluation of free radicals in the oil sample using the SOD biosensor and to monitor oil sample toxicity was an Orion model 97-08-99 electrode able to measure O_2 concentration and connected to an Orion pH-meter SA720 and an Amel model 868 recorder.

All the SOD-sensor tests were carried out at 23 °C, while the toxicity tests were performed at 25 °C in a thermostatted glass cell equipped with a forced water circulation jacket coupled to a model VC 20B Julabo (Germany) thermostat. The solvents used in the tests were kept under slight but constant magnetic stirring using a microstirrer from Velp Scientifica (Italy).

The TG–DTG measurements were carried out at different heating rates (from 5 to 12.5 °C min^{-1}) using TG 50 Mettler TG equipment with a TC10-TA processor.

All thermogravimetric runs were performed on a 7–12 mg of sample, from room temperature up to about 550 °C under a 100 cm^3 min^{-1} air stream.

2.4. Methods

2.4.1. Artificial rancidification process

The artificial oxidation of an oil sample was obtained by placing the sample in a pyrex glass tube (containing 25 mL of sample under a constant stream of air of 140 mL min^{-1} according to the A.O.M. method (AOCS, 1964), while the tube was immersed in a silicon oil thermostatic bath at 180 °C, instead of at 98 °C, as required by the latter method (AOCS, 1964).

The apparatus used (see Fig. 1) had previously been illustrated in detail (Amati et al., 2008; Campanella et al., 1999). During the artificial rancidification process under isothermal conditions at the selected temperature fixed amounts of the sample contained in the glass test tube were collected at regular time intervals and immediately analyzed.

2.4.2. Superoxide dismutase (SOD) biosensor for radical determination

The concentration of free radicals was determined using an enzymatic SOD biosensor respectively applied both to the crude oil analysis of sample and to all the oil samples tested during thermal degradation.

For this analysis a superoxide dismutase biosensor operating in dimethylsulphoxide described in detail in a previous paper (Campanella et al., 2001a) was used. This biosensor was prepared by sandwiching a kappa-carrageenan gel disk (0.5 cm diameter) on which the SOD enzyme was adsorbed (Campanella et al., 2001a) between an external PTFE membrane and an internal 0.1 cm thick membrane of cellulose acetate, both fixed to the Clark electrode by a PTFE O-ring. It is important to stress that the membrane separating the organic solvent from the gel disk was made of PTFE in order to prevent the organic solvent from spreading over the kappa-carrageenan disk in which the enzyme was immobilized and denaturing the latter. The experiments were performed in a thermostatted cell at 23 °C under continuous magnetic stirring (200 rpm). As already extensively reported in literature (Campanella, Sammartino, Tomassetti, & Zannella, 2001b; Campanella et al., 2004; Kiritsakis & Markakis, 1987), heating of oil samples determines chemical changes leading to the formation of different compounds (Biffoli, 1984, chaps. 9–10); among the latter, the radical species are those

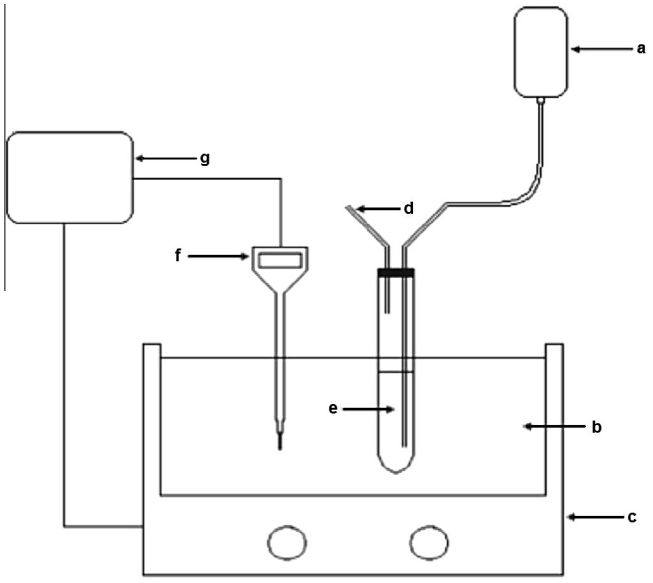

Fig. 1. Scheme of the apparatus used to study the isothermal degradation of EVOO at 180 °C under an oxidized atmosphere. (a) Air pump; (b) silicon oil bath (SOB) heated at 180 °C; (c) heating unit for the temperature of SOB; (d) breather pipe; (e) EVOO sample in *pyrex* tube with teflon cap; (f) Vertex-thermometer; (g) feeder.