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Effect of enzymatic interesterification on physiochemical and thermal properties of fat used in cookies

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ABSTRACT

Lard (L), rapeseed oil (RSO) and fish oil (ROPUFA) (7:2:1 wt ratio) were enzymatically interesterified at 50 °C for 4 h in the presence of Lipozyme RM IM as a catalyst. Interesterified fat was used to bake cookies. Fatty acids composition and their distribution between triacylglycerols, acid value, polar fraction content, induction time were determined in noninteresterified and interesterified fat, and in fat extracted from cookies. The kinetic parameters of the oxidation process (activation energy, pre-exponential factor, and reaction rate constants) were calculated. Melting profiles were also monitored by DSC in order to evaluate physical properties of noninteresterified and interesterified fats. Interesterification reduced the induction time, and activation energy of oxidation process, and increased acid value and polar fraction content. Fat extracted from cookies oxidized slower than the interesterified fat used in cookies formulations. The melting range of interesterified fat is extremely wide, which generally is suitable for bakery applications.

1. Introduction

Fats are probably the most important ingredients used in cookie formulation (Dinç, Javidipour, Özbas, & Tekin, 2014). The technological application of fat in cookie products depends on its physical and chemical properties which together with nutritional properties are limited by the composition of fatty acids and stereochemistry of triacylglycerols (TAGs) in fats (Farfán, Villalón, Ortíz, Nieto, & Bouchon, 2013). Most of edible fats in the unmodified form may have limitations for their use in bakery products, because of the structure of triacyglycerols not being in the proper combinations to provide desired characteristics In order to improve technological attributes of fats and oils, many methods of fat modification have been used, such as: fractionation, blending, inter/*trans*-esterification, hydrogenation or a combination of these processes (Farfán et al., 2013; Sharma & Lokesh, 2012). The preferred way to achieve the fat with desired physical properties is hydrogenation. The partial hydrogenation can lead to the production of *trans* fatty acids (TFA), which are known to have detrimental health effects (Farfán et al., 2013; Zhong, Allen, & Martini, 2014). TFAs are associated with increased risk of cardiovascular disease, breast cancer, disorders of nervous system and vision in infants, colon cancer, diabetes, obesity, allergy (Dinç et al., 2014). The presence of *trans*-fatty acids have been also determined in the plasma of pregnant women, lactating women, newborn infants, and children (Craig-Schmidt, 2001). Some studies reported that dietary *trans*-fatty acids could inhibit biosynthesis of long-chain polyunsaturated fatty acids with 20 and 22 carbon atoms (Craig-Schmidt, 2001; Koletzko, 1994, 1995). The adverse effect of hydrogenation, makes the use of interesterification an attractive alternative (Dinç et al., 2014). Interesterification modifies the physical properties of oils and fats by rearranging the distribution of fatty acids in the glycerol

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backbone in a random manner without changing their chemical composition. This process does not change the degree of unsaturation of the fatty acids as they transfer from one position to another and, additionally, trans isomers are not created (Bryś et al., 2013; Bryś, Wirkowska, Górska, Ostrowska-Ligęza, & Bryś, 2014; Dinç et al., 2014; Dogan, Javidipour, & Akan, 2007). Interesterification with the used of specific enzymes gives the possibility to incorporate a desired fatty acid into a specific position of the glycerol backbone. Regiospecificity of this reaction gives possibility to obtain specific lipids with a defined chemical composition and structure. When compared to simple fat blending, enzymatic interesterification gives rise to new products with original triacylglycerols structure and consequently modified physical properties, such as melting and crystallization behaviors (Aguedo et al., 2009; Martin, Reglero, & Senorans, 2010). The change in TAG molecular species in the fats prepared by interesterification reaction alters the thermal properties. The effects of interesterification on melting/dropping point, crystallization, solid fat content, thermal properties and oxidative stability of interesterified oils/blends have been discussed by Costales-Rodriguez, Gibon, Verbe, and De Greyt (2009), Danthine, De Clercq, Dewettinck, and Gibon (2014), Li et al. (2010), Marangoni and Rousseau (1998), Sharma and Lokesh (2012), da Silva et al. (2010).

In the present study, interesterified mixture of lard, rapeseed oil and concentrate of fish oil at weight ratio 7:2:1 was used as fat to bake cookies. Lard is a good source for baking cookies, it is characterized by a high oxidative stability. In this fat, palmitic acid is predominantly esterified in internal position of TAGs. Concentrate of fish oil is a source of long chain polyunsaturated fatty acids and rapeseed oil – fatty acids from the n-6 and n-3. In initial mixture, interesterified fat and fat extracted from cookies the following parameters have been determined: fatty acid composition and their positional distribution to assess the chemical properties; induction time and kinetic parameters of the oxidation process in order to determine thermal properties. Melting profiles were also monitored by DSC in order to evaluate physical properties.

2. Material and methods

2.1. Enzymatic interesterification

Flask containing the mixture of lard, rapeseed oil and concentrate of fish oil at weight ratio 7:2:1 was positioned in a thermostated mineral-oil bath shaker. After thermal equilibration of the sample at temperature 50 °C, the enzymatic catalyst (8% w/w) was added. Immobilized Lipozyme RM IM, was used in this investigation as a catalyst of interesterification. Lipozyme RM IM is a food grade granulated silica preparation of a microbial 1,3-specific lipase from *Rhizomucor miehei*. The interesterification was performed with continuous shaking. After a predetermined time (4 h) of interesterification, filtering off the catalyst stopped the reaction. Reaction conditions were determined on the basis of previous research (Bryś et al., 2013, 2014; Wirkowska, Bryś, Górska, Ostrowska-Ligęza, & Tarnowska, 2012; Wirkowska-Wojdyła, Bryś, Górska, & Ostrowska-Ligęza, 2015). Interesterified fats were purified by neutralization of free fatty acids with KOH 0.5 M hydroethanolic solution (30% ethanol). Triacylglycerols were separated by decantation of the oily phase formed after adding the hydroalcoholic solution of KOH (Jiménez et al., 2010). Lard, rapeseed oil were provided by an industrial plant. Concentrate of fish oil ROPUFA 30n-3 FOOD Oil (min. 30% omega-3) was purchased in DSM Nutritional Products company. Immobilized Lipozyme RM IM, was procured from Sigma Aldrich.

2.2. Preparation of the cookies

The following formulation for the preparation of cookies was used: wheat flour (300 g), purified interesterified fat (200 g), fructose (60 g), egg yolk (60 g), salt (0.5 g). All dry ingredients were mixed. Fat was added and all ingredients were chopped with a knife. Then the egg yolk was added, and all was thoroughly mixed until mixture was just combined. Dough was wrapped in foil and placed in a refrigerator for 24 h. Chilled dough was sheeted to a thickness of 4 mm (using a guide positioned on the pastry board). Finally, the dough was cut into a pieces of 50 mm × 50 mm. The cookies were baked in an oven at 180 °C for 10 min. After baking, cookies were cooled for 1 h at room temperature, packaged in a plastic bags and stored at room temperature.

2.3. Fat extraction from cookies

Fat was extracted from cookies according to the procedure described by Boselli, Velazco, Caboni, and Lercker (2001). Approximately 10 g of the sample was homogenised with 100 mL of a chloroform/methanol solution (1/1 v/v) in a glass bottle with a screw-cap. The bottle was kept at 60 °C for 20 min before adding an additional 100 mL of chloroform. After 3 min of homogenisation, the content of the mixture was filtered through the filter paper. The filtrate was mixed thoroughly with 70 mL of 1 M KCl solution and left overnight at 4 °C in order to phase separation. The organic phase was collected and the solvent was removed with a rotary evaporator at 40 °C. The fat sample was stored at −18 °C until it was analyzed.

2.4. Determination of acid value (AV)

Acid values were determined by titration of fat samples dissolved in the mixture of ethanol:diethyl ether (1:1, v/v) with 0.1 M ethanolic potassium hydroxide solution. Determination was done according to the Polish Standard (PN-EN ISO 660, 2010).

2.5. Determination of polar fraction content

Fats (2.5 g) were separated into TAG and polar fraction (PF) by column chromatography on silica gel (SG 60, 70–230 mesh, Merck, Germany). The TAGs were eluted with 150 mL of mixture of petroleum ether:diethyl ether (87:13, v/v) and then the polar fraction was eluted with 150 mL of diethyl ether. The percentages of the PF were determined by weight after evaporation of eluting solvent. The content of polar and TAG compounds was analyzed by the standard method ISO 8420, 2002.

2.6. Determination of fatty acid composition

The determination of fatty acid composition was carried out by gas chromatographic (GC) analysis of fatty acid methyl esters. An YL6100 GC equipped with a flame ionization detector and a BPX-70 capillary column of 0.20 mm (internal diameter) × 60 m length and 0.25 μm film thickness was used. The oven temperature was programmed as follows: 60 °C for 5 min, then it was increased by 10 °C per minute to 180 °C; from 180 °C to 230 °C by 3 °C per minute and then kept at 230 °C for another 15 min. The temperature of the split injector was 225 °C, with a split ratio of 1:100; the detector temperature was 250 °C. Nitrogen flowing at the rate of 1 mL per minute was used as the carrier gas. Measurements were done in triplicate. The identification of fatty acids was carried out using the lipid standard purchased from Sigma Aldrich.