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Zero *trans* fats from soybean oil and fully hydrogenated soybean oil: Physico-chemical properties and food applications

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ABSTRACT

Blends of soybean oil (SO) and fully hydrogenated soybean oil (FHSBO), with 10%, 20%, 30%, 40% and 50% FHSBO (w/w) content were interesterified under the following conditions: 0.4% sodium methoxide, 500 rpm stirring, 100 °C, 20 min. The original and interesterified blends were examined for triacylglycerol composition, melting point, solid fat content (SFC) and consistency. Interesterification caused considerable rearrangement of triacylglycerol species, reduction of trisaturated triacylglycerol content and increase in monounsaturated and diunsaturated triacylglycerols, resulting in lowering of respective melting points. The interesterified blends displayed reduced SFC at all temperatures and more linear melting profiles as compared with the original blends. Yield values showed increased plasticity in the blends after the reaction. Isosolid diagrams before and after the reaction showed no eutectic interactions. The 90:10, 80:20, 70:30 and 60:40 interesterified SO:FHSBO blends displayed characteristics suited to application, respectively, as liquid shortening, table margarine, baking/confectionery fat and all-purpose shortenings/biscuit-filling base.

1. Introduction

Most natural oils and fats offer limited application in their unaltered state, due to their particular fatty acid and triacylglycerol composition (Chiu, Gioielli, & Grimaldi, 2008; Rozendall, 1992). Accordingly, oils and fats are modified chemically by hydrogenation or interesterification; or physically, by fractionation (Erickson, 1995; Fattahi-far, Sahari, & Barzegar, 2006).

Although used for a long time, partial hydrogenation also results in substantial formation of *trans* fatty acids, compounds that act as coronary artery disease risk factors by modulating the synthesis of cholesterol and its fractions and acting on the eicosanoids. A number of studies have suggested a direct relationship between *trans* isomers and increased risk of vascular disease. In response, many health organizations have recommended reducing consumption of foods containing *trans* fatty acids (Enig, 1996; Gurr, 1990; Hunter, 2005; Lichtenstein, 1993; Mensink & Katan, 1990).

In this connection, chemical interesterification has proved the main alternative for obtaining plastic fats that have low *trans* isomer content or are even *trans* isomer free. Unlike partial hydrogenation, this process does not isomerize the fatty acids' double bonds and does not affect their degree of saturation (Haumann, 1994; Norizzah, Chong, Cheow, & Zaliha, 2004; Ribeiro, Moura, Grimaldi, & Gonçalves, 2007). In the interesterification, the fatty acids are not altered, but are redistributed in the triacylglycerol molecules. The process thus consists in simultaneously breaking the existing ester bonds and forming new bonds in the glycerol molecules (Rozendall, 1992). In this way, chemical interesterification modifies the triacylglycerol composition of the oil or fat and thus its physical properties, crystallization and melting behavior, solid fat content (SFC), texture and crystal habit, contributing to greater availability of oil fractions for food product applications (Dian, Sundram, & Idris, 2007).

A number of studies have investigated the influence of chemical interesterification on the physico-chemical properties of oils and fats or their blends, including the work of Gioielli and Baruffaldi (1988), List, Emken, Kwolek, Simpson, and Dutton (1977), List, Mounts, Orthoefer, and Neff (1995), Lida and Ali (1998), Marangoni and Rousseau (1998a, 1998b), Petrauskaite, De Greyt, Kellens, and Huyghebaert (1998), Kok, Fehr, Hammond, and White (1999), Khatoon (2000), Rodríguez, Castro, Salinas, López, and Miranda (2001), Rodrigues, Gioielli, and Anton (2003), Rodrigues and Gioielli (2003), Norizzah et al. (2004), Karabulut, Turan, and Ergin (2004), Ramli, Said, and Loon (2005), Grimaldi, Gonçalves, and Ando (2005), Khatoon and Reddy (2005), Silva and Gioielli (2006), Piska, Zárubová, Louzecký, Karami, and Filip (2006), and others. The interesterification of liquid oils with hardfats is the most versatile way for producing zero *trans* fats, yielding fat bases with excellent characteristics for preparation of margarines, shortenings and spreads (Karabulut et al., 2004; Khatoon & Reddy, 2005; List et al., 1995; Lo & Handel, 1983).

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In world vegetable oil consumption, soybean oil (SO) stands out for its nutritional qualities, permanent supply, considerable economic value and high functionality, making it a particularly interesting raw material for producing special fats (O'Brien, 2004). Fully hydrogenated soybean oil (FHSBO), a relatively low-cost product of total hydrogenation, can be used as *hardstock* for producing interesterified fat bases. Zeitoun, Neff, List, and Mounts (1993) report on a chemical interesterification of blends formulated with FHSBO and nine different vegetable oils, at a ratio of 1:1 (w/w).

In addition to its economic feasibility, the advantage of using FHSBO as *hardstock* derives from its high (approximately 85%) content of stearic acid, which is not atherogenic and therefore has no adverse effect on cardiovascular disease risk (Hunter, 2005; O'Brien, 2004; Rao & Lokesh, 2003). Although a saturated fatty acid, consumption of stearic acid does not significantly alter total serum cholesterol and LDL cholesterol levels, unlike most – lauric, myristic and palmitic – saturated fatty acids. Numerous clinical studies have shown that the effect of stearic acid on plasma lipoprotein concentrations is similar to that of oleic acid (Dirienzo, Lemke, Petersen, & Smith, 2008; Mensink, 2005; Nielsen, 2006; Sampath & Ntambi, 2005; Sanders & Berry, 2005; Tholstrup, 2005). Therefore, FHSBO is used in producing interesterified fats with a view to the stability and functionality required of fats for food applications and does not entail adverse health effects.

Even though chemical interesterification is extremely functional from the technological point of view, replacing partially hydrogenated fats in food products, particularly in shortenings and confectionery products, does pose challenges, because suitable SFC curves, plasticity, crystallization properties and texture are difficult to obtain in the absence of *trans* fatty acids. Accordingly, the study of, and application guidelines for, interesterified fats must comprehend jointly their fundamental physico-chemical properties, as regards triacylglycerol composition, SFC, consistency and melting point (O'Brien, 2004; Reyes-Hernandez, Dibildox-Alvarado, Charo-Alonso, & Toro-Vazquez, 2007).

The purpose of this study was to evaluate the chemical interesterification of binary blends of SO:FHSBO, with 10%, 20%, 30%, 40% and 50% FHSBO content, with a view to studying fat bases for application in food products. Results for triacylglycerol composition, melting point, SFC, isosolid diagram and consistency were analyzed, before and after randomization.

2. Materials and methods

2.1. Raw materials

The materials used were refined soybean oil (SO), purchased in a local store, and fully hydrogenated soybean oil (FHSBO), kindly provided by a regional supplier. The catalyst was 99%-pure sodium methoxide powder (Sigma–Aldrich).

2.2. Blends

The blends were prepared in the proportions 90:10, 80:20, 70:30, 60:40 and 50:50 SO:FHSBO (w/w), melted at 100 °C and homogenized for 10 min at that temperature to melt the crystals completely, prior to each interesterification reaction.

2.3. Chemical interesterification

For the reactions, a 500 mL, jacketed, borosilicate glass reactor with bottom drain port and conical ground glass joints was coupled to a thermostated circulator bath (LAUDA RE 212, −30 to +200 °C, +0.02 °C), stirring system (universal motor with electronic speed control up to 4000 rpm – Marconi, BR) with axial flow stirrer, vacuum pump (Vacuubrand model 30 diaphragm pump) and probe-type digital thermometer (−50 to +300 °C, ±1 °C – Incoterm). The samples (200 g) were dried for 20 min at 100 °C in the reactor itself, under vacuum with stirring at 500 rpm. Catalyst content was 0.4% and the reaction was conducted under vacuum at 100 °C, with stirring at 500 rpm, for 20 min, according to the optimization by Grimaldi et al. (2005). The reaction was terminated by adding distilled water and 5% citric acid solution. The interesterified samples were washed carefully with distilled water (80 °C) to remove any soaps that had formed and were then dried under vacuum at 110 °C for 30 min.

2.4. Fatty acid composition

Analysis of fatty acid composition was performed in a capillary gas chromatograph (CGC Agilent 6850 Series GC System) after esterification using the method of Hartman and Lago (1973). The fatty acid methyl esters were separated according to AOCS procedure 2-66 (AOCS, 2004) in a DB – 23 Agilent capillary column (50% cyanopropyl-methylpolysiloxane), dimensions 60 m, ∅ int: 0.25 mm, 0.25 μm film. Oven temperature was 110 °C–5 min, 110–215 °C (5 °C/min), 215 °C–24 min; detector temperature: 280 °C; injector temperature 250 °C; carrier gas:helium; split ratio 1:50; injection volume: 1.0 μL. Qualitative composition was determined by comparing peak retention times with the respective standards for fatty acids.

2.5. Iodine value

It was calculated from the fatty acid composition by AOCS Method Cd 1c-85 (AOCS, 2004).

2.6. Triacylglycerol composition

Triacylglycerol composition was analyzed in a CGC Agilent 6850 Series GC System capillary gas chromatograph. A DB-17HT Agilent Catalog: 122-1811 capillary column (50%-Phenyl-methylpolysiloxane, 15 m in length × 0.25 mm bore and containing 0.15 μm film). The conditions were: split injection, ratio 1:100; column temperature: 250 °C, programmed up to 350 °C at 5 °C/min; carrier gas: helium, at 1.0 mL/min flow rate; injector temperature: 360 °C; detector temperature: 375 °C; injection volume: 1.0 μL; sample concentration: 100 mg/5 mL of tetrahydrofurane. Triacylglycerol groups were identified by comparing retention times, following the procedures of Antoniosi Filho, Mendes, and Lanças (1995).

2.7. SFC

This was determined using Nuclear Magnetic Resonance (NMR) spectrometry (Bruker pc120 Minispec) and TCON 2000 high precision dry baths (0–70 °C) (Duratech, USA). AOCS Procedure Cd 16b-93: direct method, taking readings from samples in series at temperatures of 10, 20, 25; 30, 35, 40, 45, 50, 55 and 60 °C, with tempering for non-stabilized fats (AOCS, 2004). In addition, it was necessary to modify the standard tempering prescribed by AOCS Method Cd 16b-93 in order to ensure stabilization of the crystallization of the interesterified blends: the samples were kept at 0 °C for 2 h and at each reading temperature for 1 h.

2.8. Construction of isosolid diagrams

The isosolid line diagrams (i.e. showing compositions in which the SFC values of a blend are equivalent at a given temperature) were constructed from the data supplied experimentally by NMR using the modified tempering method (Braipson-Danthine & Deroanne, 2006).