Lipid Oxidation in Dispersive Systems with Monoacylglycerols

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Abstract: Model fat blends with a monoacylglycerol emulsifier with different acyl chain (C10, C12, C14, C16, C18, C18:1, C20, C22) were prepared and stored under oxygen atmosphere 8 weeks at temperature 20°C. Influence of monoacylglycerol on oxidation and oxidation stability of the model fat blends was studied. The model fat blends were prepared by mixing of fully hydrogenated structured fats that contained only palmitic and stearic acid (fully hydrogenated zero-erucic rapeseed oil and fully hydrogenated palmstearin) and half-refined soybean oil. Lipid oxidation was measured by determination of the peroxide value. Volatile oxidation products were detected by the solid phase microextraction in connection with gas chromatography-mass detector (SPME/GC-MS). The oxidative stability was measured by the Rancimat method. Lipid oxidation in model system with 1-octadecenoylglycerol (MAG18:1) was the most extended. On the other hand minimal lipid oxidation was found out in the presence of 1-tetradecanoylglycerol (MAG14) and 1-hexadecanoylglycerol (MAG16).

Keywords: lipid oxidation; fat blend; emulsifier; monoacylglycerol

INTRODUCTION

Oxidation is the most important reaction that leads to increase of oils rancidity, viscosity and volatility because the low-molecular weight off-flavor compounds are formed. The off-flavor compounds do oil less acceptable or unacceptable to consumers or for industrial use as a food ingredient. Oxidation of oil also destroys essential fatty acids and forms toxic compounds and oxidised polymers (Ashavaryu *et al.* 2000; Choe & Min 2006).

Lipid oxidation in liquid oils and O/W emulsions is described very well. However, the lipid oxidation in dispersive systems as W/O emulsions and fat crystals in liquid oil is not described enough (Frankel 2001).

It has been found out that monoacylglycerols of saturated fatty acids retarded lipid oxidation in margarine emulsion. The emulsifier in emulsion can be accumulated at three various interfaces – emulsion/air, water/oil and liquid lipid/solid lipid of the fat blend (crystals triacylglycerols). The question is: Is the lipid oxidation influenced on monoacylglycerol emulsifier in fat blends, where the emulsifier can be accumulated at two interfaces – fat blend/air and liquid lipid/solid lipid (crystal network of the structured fat) (Garti *et al.* 1998; Pokorná *et al.* 2004).

The aim of this study was to find out the influence of the monoacylglycerol with different acyl chain on the rate of lipid oxidation of liquid phase in dispersive system.

MATERIALS AND METHODS

Fat blend composition

Structured fat: 19.7% w/w fully hydrogenated zero-erucic rapeseed oil (FH ZERO) or fully hydrogenated palmstearin (FH PST) (Table 1 shows fatty acid composition of structured fat).
Liquid oil: 79.7% w/w half-refined soybean oil.
Emulsifier: 0.6% w/w monoacylglycerols (MAGs), 1-decanoylglycerol (MAG10), 1-dodecanoylglycerol (MAG12), 1-tetradecanoylglycerol (MAG14),

Table 1. Fatty acid composition of structured fat (g FA/100 g ΣFA)

Fatty acid (FA)	FH ZERO	FH PST
C16:0	5.53	54.91
C18:0	91.04	42.43
C18:1	0.12	0.09
C18:2	0.00	0.24.
Others	3.31	2.33

1-hexadecanoylglycerol (MAG16), 1-octadecanoylglycerol (MAG18), 1-octadecenoylglycerol (MAG18:1), 1-eicosanoylglycerol (MAG20), 1-docosanoylglycerol (MAG C22) were synthesised (Martin 1953), purity > 95%.

Storage conditions

250 ml of fat blends were stored under the oxygen atmosphere (oxygen volume was 450 ml, oxygen atmosphere was > 84% v/v) in glass jars (700 ml) with Twist-Off lids. The storage temperature was 20°C.

Analytical methods used in this research

- Peroxide value (PV) – ČSN ISO 3960:1994.
- Solid phase microextraction in connection with gas chromatography-mass detector (SPME/GC-MS) – detection of volatile oxidation products (adsorption at 20°C), GC conditions: column HP5 (max. temperature 325°C, 0.25 mm × 30 m, thickness of stationary phase 0.25 μm, carrier gas He 0.9 ml/min), SPME fibre: Divinylbenzen/Carboxen/Polydimethylsiloxan (DVB/CAR/PDMS) 50/30 μm, length of fibre 1 cm, pH 2–11, max. temperature 270°C.
- Oxidation stability was estimated on the Rancimat instrument (conditions: air flow 20 l/h, temperature 120°C) and evaluated as time of induction period (h).
- Methods used for data processing – rectangle method (calculation of areas under the curves) and Student's *t* test at significance level α = 0.05 (Eckschlager *et al.* 1980).

Fat blends samples

Fat blend was separated to three layers: the surface, the core and the bottom. Samples were taken from the surface, the core and the bottom for the peroxide value determination. Samples for Rancimat method were taken from the core. Lids of the glass jars were equipped with septum to take directly sample of volatiles above the fat blend for SPME/GC-MS.

RESULTS AND DISCUSSION

Primary products of lipid oxidation

Oxygen diffuses from the oxygen atmosphere to the fat blend, dissolves in the fat blend and reacts with fatty acids to hydroperoxides. The amount of hydroperoxides decreases from the surface to the bottom. Figures 1 and 2 show the areas under the curves, which correspond with total content of hydroperoxides in 1 kg sample for 8 weeks. Fat blend (with FH ZERO as well as FH PST) with MAG18:1 had the highest content of hydroperoxides and was statistically significant different from the others fat blends. The lowest content was detected in fat blends with FH ZERO with MAG10, MAG14, MAG16 and MAG22 (Figure 1) and in fat blends with FH PST with MAG14 and MAG16 (Figure 2).

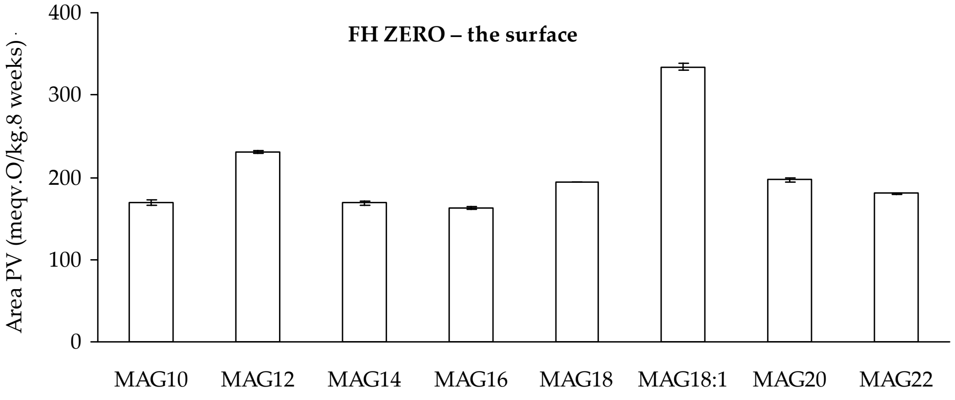

Figure 1. Areas under the curves of the peroxide value of fat blends with FH ZERO

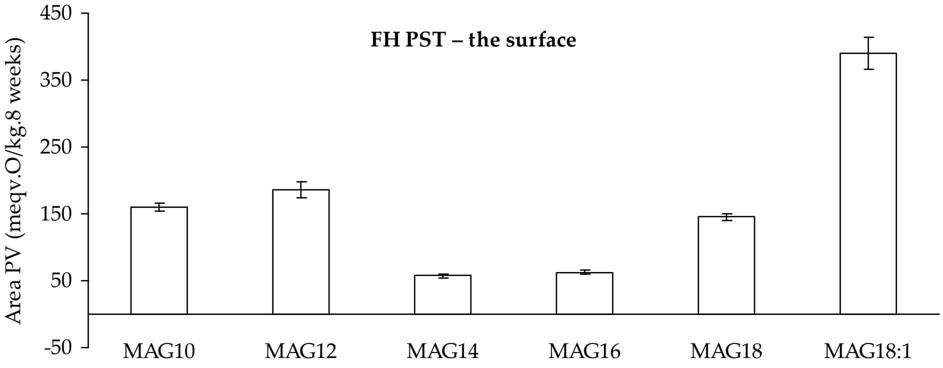

Figure 2. Areas under the curve of the peroxide value of fat blends with FH PST

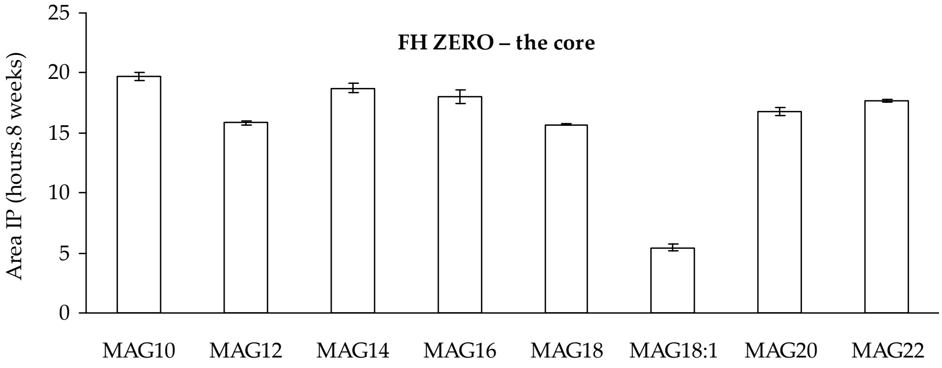

Figure 3. Areas under the curve of the oxidative stability of fat blends with FH ZERO

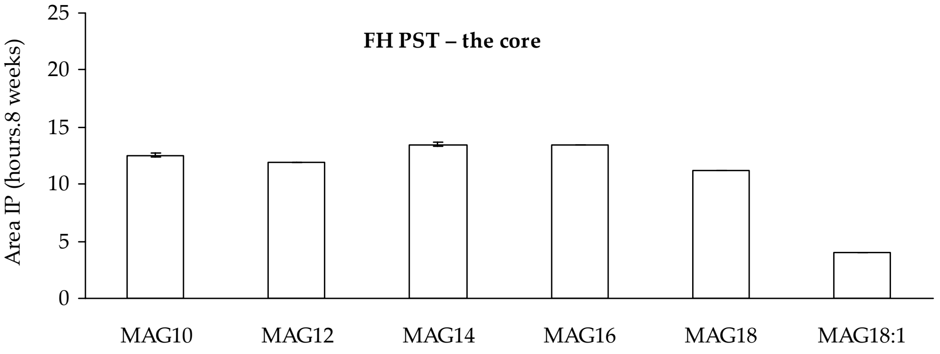

Figure 4. Areas under the curve of the oxidative stability of fat blends with FH PST

Differences between fat blends with these emulsifiers were not statistically significant.

Secondary products of lipid oxidation

Volatile oxidation products (hexanal, 2,4-heptadienal and nonanal) were detected by the method SPME/GC-MS. The maximal amount of all volatile products was detected in the second week of storage. Lower concentration was determined in fat blends with MAG12 and MAG18. Higher concentration was found out in fat blend with MAG18:1.

Oxidative stability by the Rancimat method

Oxidative stability is represented by the time (induction period – IP or induction time) in which an oil sample resists to oxidation at specific temperature. The sample was heated at 120°C and conductivity of volatile products of oxidation in the solution was measured. The oxidative stability decreases during the storage. The minimal oxidation stability had the fat blend with MAG18:1 and the maximal oxidation stability was extended in the fat blend with MAG16 (Figures 3 and 4). Statistically significant difference of areas under the curves was found out in the fat blend with

MAG18:1, which was significantly different from the fat blends with the others MAGs.

Lipid oxidation in model system with MAG18:1 was the most extended. On the other hand minimal lipid oxidation was found out in the presence of MAG14 and MAG16 at the both structured fats. Adsorption of monoacylglycerols on the crystal network with the tightest arrangement of emulsifier molecules can be expected. The presence of a *cis*-double bond in oleic acid of monoacylglycerol caused less tight adsorption of the emulsifier on the interface. Hence oxygen diffusion through the interface depends on the type of acyl chain of the monoacylglycerol emulsifier.

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