

# Lipid Oxidation in Margarine Emulsions

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**Abstract:** Influence of different storage atmosphere (argon and oxygen atmosphere) and influence of monoacylglycerol's emulsifier (with the carbon chain containing 10, 12, 14, 16, 18 carbon atoms and commercial emulsifier D and a model mixture of monoacylglycerols with the carbon chains containing 10, 12, 14 carbon atoms) on lipid oxidation in margarine emulsions were observed. The rate of lipid oxidation in emulsion with oxygen atmosphere depends on oxygen diffusion through the emulsion layer, while lipid oxidation in emulsion with inert atmosphere is influenced by initial oxygen concentration in water and fat phase. Lipid oxidation in emulsion also depends on acyl combination and the acyl length in emulsifier. Emulsions with monostearoylglycerol oxidized minimally while emulsions with a mixture of monoacylglycerols oxidized maximally.

**Keywords:** emulsifier; emulsion; lipid oxidation; margarine; monoacylglycerol

## INTRODUCTION

Lipid oxidation in emulsion systems is a very complex feature which is usually influenced by many factors, for example the technological history of fat blend, the presence of oxygen in the package, the initial concentration of oxygen in the water phase and in the fat blend, the storage conditions of emulsions, the presence of prooxidants, antioxidants and the structure of interface [1, 2].

Technological fat blend history means previous oxidation of fats and oils of the blend before the emulsification. There is an effort to keep the minimal oxygen content in the fat blend which is close to zero after physical refining or deodorization.

During the storage of margarine emulsions the oxygen diffuses from the atmosphere to the fat blend and together, if the oxygen is presented in water phase, from the water phase to the fat blend.

Monoacylglycerol's emulsifier forms interface of emulsion. Type of emulsifier and its concentration also influence the rate of lipid oxidation [3, 4].

## EXPERIMENTAL

**Margarine composition.** Fat phase: fat blend: 69.6%. Emulsifier -- monoacylglycerol (MAG): the

concentration of MAGs in emulsifier was 98.4 to 99.9%. The concentration of MAGs in emulsions was 0.4%.

Synthesized MAG – Monocaprinoylglycerol (MCG) = 1-decanoylglycerol

– Monolauroylglycerol (MLG) = 1-dodecanoylglycerol

– Monomyristoylglycerol (MMG) = 1-tetradecanoylglycerol

– Monopalmitoylglycerol (MPG) = 1-hexadecanoylglycerol

– Monostearoylglycerol (MSG) = 1-octadecanoylglycerol

– A model mixture of monocaprinoylglycerol, monolauroylglycerol, monomyristoylglycerol (in the ratio of 1:8:1).

Commercial emulsifier D (the mixture of monopalmitoylglycerol, monostearoylglycerol and monooleoylglycerol), the concentration of MAGs was 94%.

Water phase: distilled water (29.9%), NaCl (0.1%), lactic acid (0.02%).

**Storage conditions.** The initial oxygen concentration was defined in emulsion. First type of emulsions: 250 ml of emulsions were stored under the oxygen atmosphere (oxygen volume was 450 ml, oxygen purity was >84% v/v) in glass jars (700 ml) with Twist-Off lids. Second type of emulsions:

250 ml of emulsions were stored under the argon atmosphere (argon volume was 10 ml, argon purity was < 99.9% v/v) in glass jars (260 ml) with Twist-Off lids. The precondition: Twist-Off lids would not allow gas exchange between outside and inside atmosphere of the glass jar. The storage temperature was 15°C.

Analytical methods used in this research.

- Peroxide value (PV) – IUPAC 2.501 (1987)
- Conjugated diens content (CD) – IUPAC 2.206 (1987)
- Anisidine value (AV) – IUPAC 2.504 (1987)
- Acid value = free fatty acid content (FA) – IUPAC 2.201 (1987)
- Oxidative stability of isolated fat blend from emulsion under the conditions of Schaal oven (the storage time at 60°C which is necessary to increase in peroxide value of fat blend to 10 milliequivalents of active oxygen per kg).

**Emulsion sample.** Figure 1(a) shows how the emulsions under the oxygen atmosphere were stored. Samples were taken from the surface (A), the core (B) and the bottom (C) for peroxide value determination and from the surface (A) and the bottom (C) for other analytical determinations. The rate of lipid oxidation in the different layers was limited due to oxygen diffusion through the emulsion.

Figure 1(b) shows how the emulsions under the argon atmosphere were stored. Samples were taken from the core of emulsion. Lipid oxidation in this system depends only on the initial oxygen concentration in the water and the fat blend.

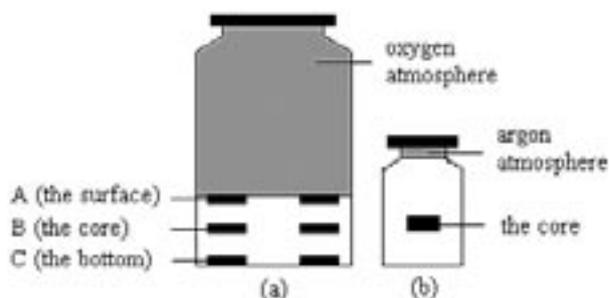


Figure 1. Samples of emulsion stored under oxygen (a) and argon atmosphere (b)

and then through the emulsion layer. The oxygen dissolves in fat phase and reacts with fatty acids to hydroperoxides (Figure 2). Samples stored under the oxygen atmosphere were oxidized faster on the surface (A) than on the bottom (C). The rate of lipid oxidation depends on the rate of oxygen diffusion through the layer of the emulsion in the propagation phase of the reaction (between 10 and 15 weeks). Samples stored under the argon atmosphere oxidized only slightly. The range of oxidation changes depends on initial concentration of oxygen in both phases of emulsion.

The same results were obtained in the determination of conjugated diens content.

The anisidine value (Figure 3) and the free fatty acid content did not change during the whole storage period at 15°C. It means that the secondary oxidative products did not form from hydroperoxides under storage temperature (15°C).

## RESULTS AND DISCUSSION

### The oxygen diffusion through emulsion layer and comparison of different storage atmosphere

During storage period the oxygen diffuses from the oxygen atmosphere to the emulsion surface

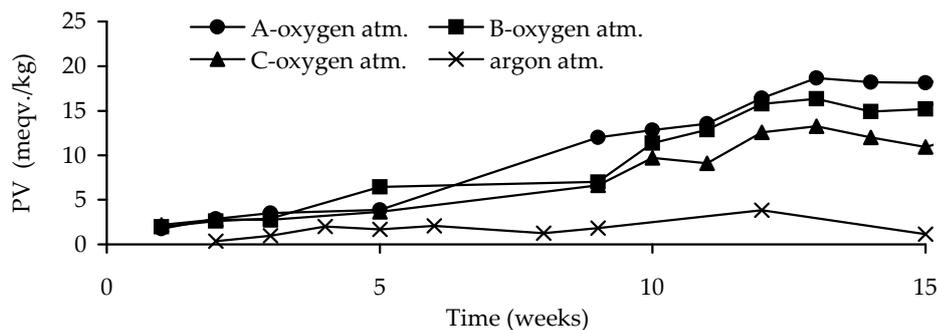


Figure 2. The dependence of peroxide value (emulsifier D) on the time at 15°C

### Determination of oxidative stability of isolated fat blend

The determination of oxidative stability of isolated fat blend represents another approach to testing the changes in lipid oxidation in emulsion during storage period at 15°C (Figure 4).

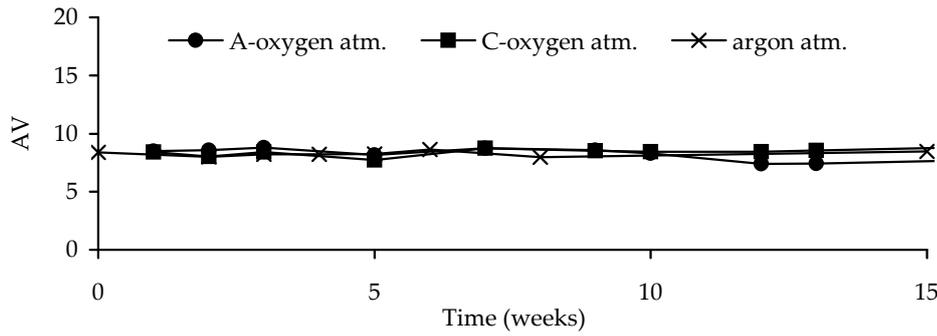


Figure 3. The dependence of anisidine value (emulsifier D) on the time at 15°C

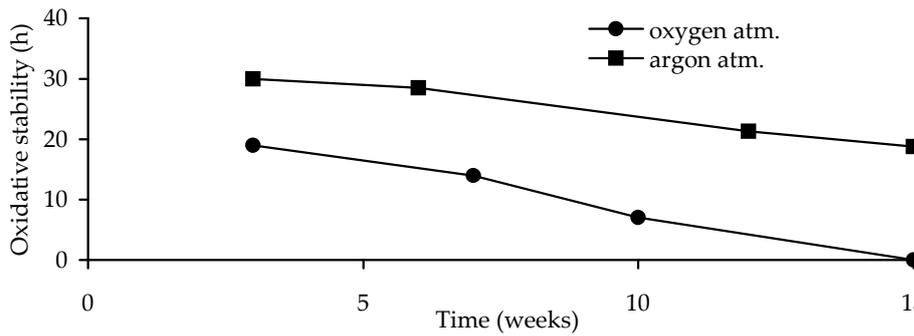


Figure 4. Oxidative stability of isolated fat blend of emulsion (MMG) under conditions of Schaal oven during storage period at 15°C

Oxidative stability of isolated fat blend of emulsion stored under oxygen atmosphere decreased to the zero during 15 weeks while oxidative stability of fat blend of emulsion stored under argon atmosphere decreased from 100% to 60%. We can suppose that it depends on the initial oxygen content in emulsion and the technological history of fat blend.

**Influence of emulsion interface on lipid oxidation (Figure 5)**

Emulsions containing emulsifier D or a model mixture of monoacylglycerols were oxidized to the

greatest extent. The interface was heterogeneous and the oxygen diffusion was increased through this interface because three different acyl chains were presented on the interface in both cases.

The emulsion with monostearoylglycerol had the lowest oxidation level of all emulsions. The interface of this emulsion was very compact. The carbon chain consisting of 18 carbon atoms was the longest carbon chain of all monoacylglycerol's emulsifiers. The oxygen diffusion decreased through this interface and the lipid oxidation was minimal. The interactions are possible between monostearoylglycerol and fat blend crystals too.

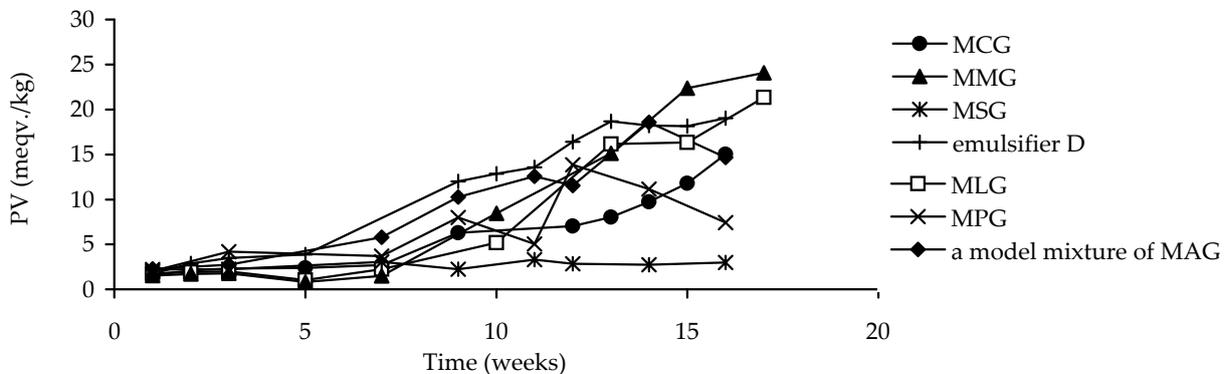


Figure 5. The dependence of peroxide value (on the surface) of emulsion with oxygen atmosphere on time at 15°C. Influence of the emulsifier type

## CONCLUSIONS

The rate of lipid oxidation in the emulsions stored under oxygen atmosphere depends on the oxygen diffusion through the emulsion layer. The range of oxidation changes in the emulsions stored under inert atmosphere depends on initial oxygen concentration in both phases of emulsion.

Lipid oxidation in emulsion depends on acyl combination and the acyl length in emulsifier. Emulsion containing only monostearoylglycerol oxidized minimally while emulsion where the interface was created by a mixture of monoacylglycerols (such as emulsifier D or a model mixture of monocaprinoylglycerol, monolauroylgly-

cerol and monomyristoylglycerol) oxidized to the maximum.

The content of secondary oxidative products did not change during whole storage period at 15°C.

## References

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