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## Microstructural design to reduce lipid oxidation in oil-inwater emulsions

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#### Abstract

The influence of emulsifier type (Tween 20 and sodium caseinate (CAS)) and oil phase volume fraction (5% and 30%) on emulsion oxidative stability was investigated. The primary and secondary lipid oxidation products of emulsions stored at 40°C were measured over 7 days. The results indicated that the oxidative stability of samples stabilised with CAS was significantly higher compared with emulsions stabilised with Tween 20. We propose that this is due to iron binding ability of CAS. Moreover, the impacts of Pickering emulsions (Silica particles) on lipid oxidation were studied and compared with Tween 20 stabilised emulsions. The results showed that silica particles could increase the oxidative stability of 20% sunflower oil-in-water emulsions by acting as a physical barrier between pro-oxidants located in continuous phase and hydroperxide at droplet interface.

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Keywords: Lipid oxidation stability; Oil-in-water emulsions; Interfacial microstructure; Emulsifiers and Particles.

#### 1. Introduction

The susceptibility of lipid to oxidation is a major concern for food manufactures as lipid oxidation has negative effects on food quality such as; taste, appearance, texture and shelf life. Lipid oxidation leads to the development of off-flavours (rancidity) and toxic compounds [1]. Transition metals (iron) are normally presents in foods and may originate from water, certain food ingredients, processing equipment and packaging materials [2].

So far, a great deal of research has been carried out on the ability of antioxidants to inhibit the rate of lipid oxidation in emulsions by chelate irons in continuous phase or scavenge free radicals. The most common chelators in food industry are Citric acid, Ethylenediaminetetraacetic acid (EDTA) and phosphoric acid [3]. The use of natural antioxidants (proteins and phenolic compounds) in food products

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has been receiving an increasing level of interest in recent decades due to the potential hazardous effects of synthetic antioxidants [2],[4].

The lipid oxidation stability can also be increased by producing thick interfacial layer around droplets. Proteins are able to make a rigid barrier around droplets. It has been reported that, casein was able to form thicker interfacial layer around droplets (10 nm) compared to whey protein (1-2 nm) [5, 6]. Besides proteins, solid particles (Pickering emulsions) are also able to make thick interfacial layer. This type of emulsions has been receiving an increasing level of attention recently, due to a wide range of industrial applications (food, pharmaceutical and cosmetics) [7, 8]. However, there is very little information available regarding the ability of Pickering emulsions to inhibit lipid oxidation.

The objective of this study was to investigate the effects of the physical properties of the emulsion such as emulsifier type and oil-phase volume fraction on lipid oxidation rate. Moreover, in order to determine the ability of Pickering emulsions to reduce lipid oxidation, different concentrations of silica particles were used to stabilise oil-in water emulsions and the lipid oxidation rate was also studied.

#### 2. Materials and Methods

#### 2.2 Methods

#### 2.2.1 Oil-in-Water Emulsion

2% CAS was added to distilled water and was stirred at 55-60°C for 2h to ensure complete dispersion. However, 2% Tween 20 was added in distilled water and mixed for 15 minutes at room temperature. The sunflower oil (5% and 30% oil) was then added to the aqueous solution and the oil-in-water emulsions were prepared using a Silverson L4RT with a fine emulsion screen of 19 mm diameter and a speed of 10,700 rpm for 7 min.

#### 2.2.2 Pickering Emulsions

Silica particles (0.5% (w/w) and 1% (w/w)) were dispersed in the aqueous phase using an ultrasonic vibracell processor for 3 min at 95% amplitude and at 25°C. The pH of the aqueous silica dispersion was adjusted to 2 with 0.1M HCL. Zetasizer (Malvern Instrument, UK) was used to determine the charge of the particles at pH 2. The results obtained from Zetasizer showed that particles had no charged at this pH. Then 20% sunflower oil was added to the aqueous silica dispersions and emulsified with a Silverson L4RT with a fine emulsion screen of 19 mm diameter for 7 min

#### 2.2.3Measurements of lipid oxidation

Emulsions (10 mL) immediately after formation were placed in a sealed glass tube and were kept in an oven at 40°C for 7 days to accelerate oxidation. The peroxide value was measured according to the method proposed by Shantha and Decker (1994) [9]. 0.3 mL of the emulsion were mixed with a 1.5 mL isooctance/isopropanol mixture (3:1, v/v) and subsequently centrifuged for 5 min at 10,000 rpm. Then 0.2 mL of the clear upper solvent layer was mixed with a 2.8 mL of methanol/1-butanol (2:1, v/v) and 30  $\mu$ L of thiocyanate/ferrous iron solution. The thiocyanate/ferrous iron solution was prepared by mixing 15  $\mu$ L of 3.94 M ammonium thiocyanate solution with 15  $\mu$ L of 0.072M ferrous iron solution. The ferrous iron solution (0.132M BaCl2 in 0.4M HCl) and 25ml of 0.144 M FeSO4 solution. After 20 minutes the absorbance of each sample was measured at a wavelength of 510 nm using Biochrom Ltd PC32 spectrophotometer.

The secondary products were measured using the anisidine value ( $\rho$ -AV) technique explained in AOCS CD 18- 90 (1998). 1 mL of sample was mixed with 25 mL isooctane followed by centrifugation at

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