Reducing the Negative Effects of Lipid Oxidation

By RP Bruno and Associates

Abstract

Lipid oxidation is a major cause of quality deterioration in food emulsions, and ultimately, in the deterioration of many foods ***(1)***. The design of foods with improved quality (less spoilage, longer shelf life*)* depends upon an advanced understanding of the physicochemical mechanisms of lipid oxidation in these systems.

A recent study compared lipid oxidation in 10% fish oil-in-water emulsions prepared with a Microfluidizer processor and with a Panda two valve high pressure homogeniser *(Horn et al, National Food Institute, Technical University of Denmark**(2)**).*One finding from this study demonstrated that the Microfluidizer processor, when compared to the homogenizer, a standard in the dairy industry, significantly reduced lipid oxidation when using whey protein from milk as an emulsifier.

Background

In recent years, foods have become more prone to lipid oxidation through (1) the removal of hydrogenated fats, (2) the addition of more unsaturated fatty acids (to improve nutritional content) and (3) the desire of consumers to remove synthetic food additives, which include antioxidants. These trends have eliminated many of the tools that have been used to control oxidation in the past and, therefore, detailed knowledge of the mechanisms and factors that impact lipid oxidation in food emulsions is needed now more than ever to develop novel antioxidant technologies ***(3).***

The food industry often utilizes milk proteins because of their favorable emulsifying properties. In addition, milk proteins also can provide oxidative stability to foods. However, different milk proteins, or protein components, have been shown to differ in their anti- oxidative properties. Also, their localization in emulsions has been shown to be affected by the emulsification conditions.

The study conducted by Horn et al investigated the influence of a Microfluidizer processor vs. a homogenizer on lipid oxidation in test samples of 10% fish oil-in-water emulsions, each prepared with two different milk proteins; whey***(4)*** and casein (sodium caseinate)***(5).*** Results showed that the Microfluidizer processor produced lower levels of lipid oxidation than the homogenizer when whey protein was used as an emulsifier. In contrast, however, emulsions prepared with sodium caseinate were not influenced by either of the two processes.

Lipid Oxidation

Lipid oxidation can occur rapidly in oil-in-water emulsions due to the large surface area that they create which facilitates interactions between the lipids and water soluble pro-oxidants. There are many factors that can potentially influence the rate of lipid oxidation in oil-in-water emulsions including: (1) fatty acid composition, (2) aqueous phase pH and ionic composition, (3) type and concentration of antioxidants and pro-oxidants, (4) oxygen concentration, (5) lipid droplet characteristics such as particle size, concentration and physical state and (6) emulsion droplet interfacial properties such as thickness, charge, rheology, and permeability.

Emulsions

An emulsion is a mixture of two or more liquids (Fig. 1) that are normally immiscible (non-mixable or un-blendable). Emulsions are part of a more general class of two-phase systems of matter known as colloids. Although the terms colloid and emulsion are sometimes used interchangeably, emulsion should be used when both the dispersed and the continuous phase are liquids. In an emulsion, one liquid (the dispersed phase) is dispersed in the other (the continuous phase). Examples of oil-in-water emulsions include: milk, infant formula, salad dressing, mayonnaise, sauces, soups, beverages, cream and vinaigrettes.

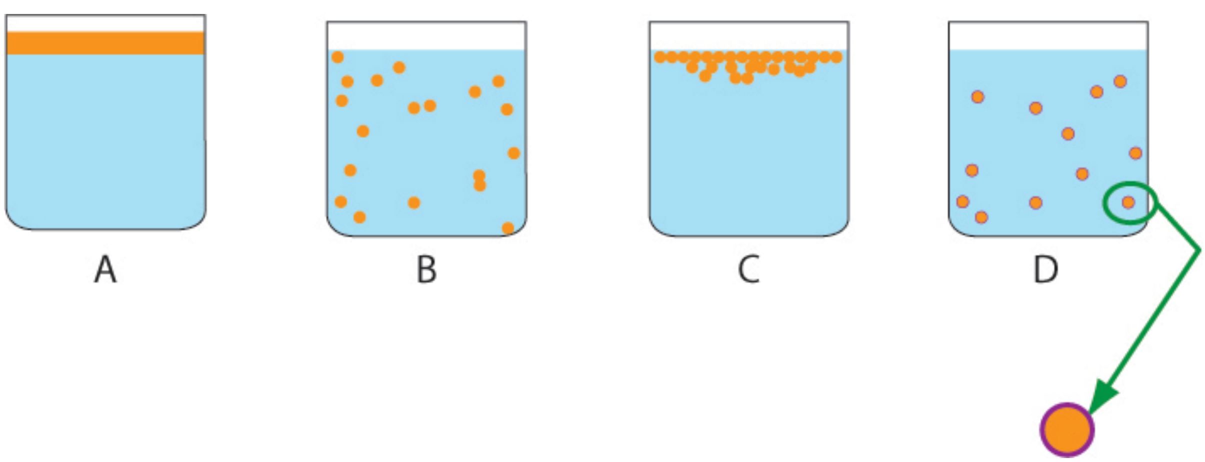

Fig. 1
A. Two immiscible liquids, not yet emulsified
B. An emulsion of Phase II dispersed in Phase I
C. The unstable emulsion progressively separates
D. An emulsifier, (shown as a purple outline around particles) is a compound that lowers the surface tension of a liquid or lowers the interfacial tension between two liquids, or that between a liquid and a solid. (*Wikimedia Commons)*

Emulsifiers (or surfactants) are commonly added to the two dispersed fluids that form the emulsion to prevent the emulsion from becoming unstable and separating as shown in Fig. 1C. The emulsifier (shown as a purple outline around particles) is a compound that stabilizes the emulsion by lowering the surface tension of a liquid or that lowers the interfacial tension between the two liquids.

The word "emulsion" comes from the Latin word for "to milk", as milk is (among other things) an emulsion of milk fat and water.

Two liquids can form different types of emulsions. For example, oil and water can form an oil-in-water emulsion in which the oil is the dispersed phase and water is the dispersion medium. They can form a water-in-oil emulsion, in which water is the dispersed phase and oil is the continuous phase. Multiple emulsions are also possible, including a "water-in-oil-in-water" emulsion and an "oil-in-water-in-oil" emulsion.

Anti-oxidants and Pro-oxidants

Anti-oxidants are vitamins and nutrients that have the ability to neutralize or oxidize unwanted pro-oxidants. They are often referred to as free radicals.

Experimental Approach

The objective of the Horn et al study was to compare lipid oxidation in 10% fish oil-in-water emulsions processed using a two-valve high-pressure homogenizer, shown in Fig. 2 below and a Microfluidizer processor (Model M110L) shown in Fig. 3 below.

Sample batches of equal droplet size distribution emulsions were prepared with: (*a)* 1% sodium caseinate as the emulsifier and (*b)* 1% whey protein isolate as the emulsifier. Iron (FeSO4) was added to all sample batches to accelerate lipid oxidation. Sodium azide also was added to prevent microbial growth. Great care was taken to hold all conditions common between the two methods of emulsification to assure that any differences between the two equipment types could be attributed to the emulsification process, rather than extraneous variable effects.

Fig. 2 Two-valve high-pressure homogenizer (Panda 2K, GEA, Niro Soavi, Parma, Italy).

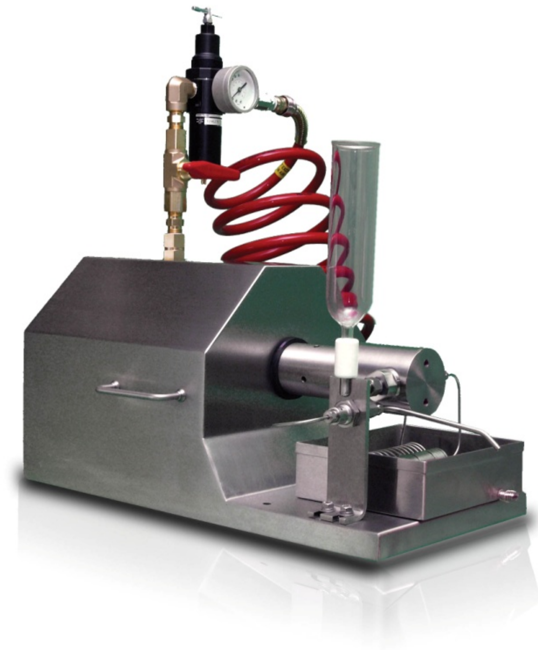

Fig. 3 Model M110L Microfluidizer processor (Microfluidics, Newton, MA, USA) equipped with a ceramic interaction chamber.

Test results showed that the emulsions processed with whey protein on the homogenizer oxidized faster during storage than those processed on the Microfluidizer processor. Interestingly, however, it was found that oxidation rates did not differ between the two emulsions prepared with sodium caseinate, when processed on the two different equipment types.

Discussion

In reviewing these findings, Horn et al concluded that a likely explanation for the differences lay in the mechanism by which the protein components stabilized the emulsions.

For sodium caseinate emulsions, it was suggested that the metal chelating*(6)* effect of the casein proteins in the aqueous phase might be the most important factor for stabilization, rather than the actual protein components at the interface.

For the whey proteins, on the other hand, the suggestion was that the composition of the protein components at the interface seemed to influence the lipid oxidation the most. Thus it was hypothesized that for the whey proteins the differences in the geometry of the interaction chamber (Microfluidizer processor), the homogenizer and the droplet formation between the two equipment types influenced the distribution of the protein components between the interface and the aqueous phase. That difference can be seen when comparing the Microfluidizer processor to the homogenizer process as depicted in Figs 4 and 5 respectively (below).

In fact, the above conclusions drawn from the Horn et al study dovetail nicely with an earlier work done by Dalgleish et al(7). In this study, it was found that small fat globules were involved in a different way with milks processed with a homogenizer and with a Microfluidizer processor. These globules seemed to be embedded in casein micelles which supported the speculation that the more intense energy provided by the impingement of particles in the Microfluidizer processor allowed for the formation of differently structured particles between the two equipment types.

Combining the results of these two studies suggests the Microfluidizer processor could expand capabilities to explore improved emulsion/emulsifier stability in all types of emulsions. Its unique ability to integrate both shear and impingement energy to droplets provides the means to change droplet size distribution, structural composition and interface location under controlled conditions. It is a clear opportunity for food product development programs to discover and achieve what is possible in optimizing emulsion technology to minimize lipid oxidation and position food product management for competitive advantage.

Fig. 4 below is a flow diagram of the interaction chamber which is the heart of a Microfluidizer processor. A single stream of the pressurized emulsion arrives at the high pressure inlet after which time the stream splits into two streams with each entering a high shear zone. Upon exiting the high shear zone, the two high velocity streams impinge on each other within the high impact zone after which time the processed emulsion flows out the low pressure outlet.

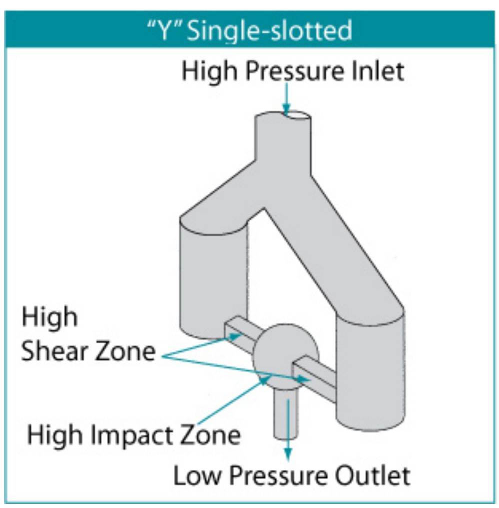

Fig. 4 Flow diagram of the Microfluidizer processor *(courtesy of Microfluidics, Newton, MA)*

Fig. 5 below is a flow diagram of a two-valve homogenizer. The homogenizer process originates with a reservoir of the premixed emulsion. The emulsion is pressurized with a positive displacement pump sending a high velocity stream of the premix through two homogenizer valves placed in series (1st stage and 2nd stage). The valves create "restrictions to flow" that result in high shear forces on the emulsion. There is no provision for creating impingement in this process as there is in a Microfluidizer processor.

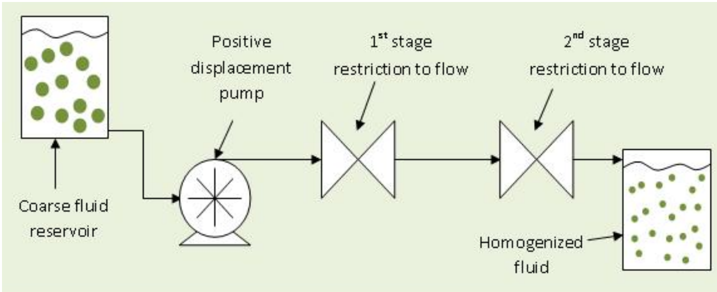

Fig. 5 Flow diagram of the two valve homogenizer *(courtesy of Niro Soavi, Parma, Italy)*

Looking Forward

In 2008, Food Production Daily newsletter www.foodproductiondaily.com) estimated the food industry to be $500 billion on a global basis. Market needs continue to change as food distribution has become global and the global population is anticipated to grow significantly from 7 billion to 9 billion by 2050.

In light of this, it is not surprising to find that food spoilage is of major concern to the food industry worldwide. The future food supply, the nutritional health of the public and the institutions supporting the highest quality of products for consumers will benefit from ongoing and future studies of lipid oxidation in food emulsions*(8) (9) (10)*. These referenced sources suggest that the main concern for food manufacturers worldwide is the preservation and shelf life longevity of their products so as to reduce spoilage and to ensure that the freshest, safest, most nutrient filled and healthiest products are readily available to consumers.

Given the important ongoing research by Horn et al and other researchers, some of whom are noted above, it is clear that a Microfluidizer processor with its combination of high shear and impingement forces is unique in forming stable food emulsions leading to potential opportunities unavailable with only the high shear forces produced by high a pressure two valve homogenizer.

Although the scope of his paper does not address what the potential positive fiscal impact may be on the food industry as a result of reducing or eliminating lipid oxidation, it is obvious it would be of great significance.

References

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2) "*The choice of Homogenization Equipment Affects Lipid Oxidation in Emulsions" A.F Horn, N.S. Nielsen, L.S. Jensen, A. Horsewell, C. Jacobsen (2012), Food Chemistry 134 (2012), pp 803-810*

3) *"Mechanisms of Lipid Oxidation in Food Dispersions" T. Waraho, D.J. Clements, E.A.Decker, Dept of Food Science, 236 Chenoweth Lab, Univ of Massachusetts USA. Trends in Food Science & Technology (2011) pp. 3-13*

4) *Whey proteins – It is estimated that 20% of the total proteins of bovine milk are whey proteins. Whey proteins are effective in scavenging free radicals and, therefore, work best when free radicals create lipid oxidation*

5) *Casein proteins –* o*ften listed as sodium caseinate, calcium caseinate or milk protein) work best countering lipid oxidation induced by transition metals. Transition metals, most commonly iron, exist naturally in the aqueous phase.*

6) *Metal Chelation - Metal chelation is the formation of soluble, complex chemicals composed of certain metal ions (e.g. Fe2+) and chelating agents (e.g. EDTA) which effectively inhibit or inactivate the metal ion from reactions with other elements and ions that could lead to unwanted oxidation or precipitation. Jacobsen suggests the caseinate proteins act as better chelating agents than the whey proteins and as a consequence better tie up metal ions (especially Fe2+ ions) which tend to catalyze reactions generating free radicals leading to oxidation.*

7) *"Beyond Homogenization: The Formation of Very Small Emulsion Droplets During the Processing of Milk by a Microfluidizer" D.Dalgleish, S.M.Tosh, S. West, Dept of Food Science, Univ. of Guelph, Guelph, Ontario CA. Netherlands Milk & Dairy Journal 50 (1996), pp 135 - 149*

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