Journal of Engineering Science Vol. XXVII, no. 1 (2020), pp. 69 - 74
Fascicle Food Engineering ISSN 2587-3474
Topic Food Technologies and Food Processes eISSN 2587-3482

DOI: 10.5281/zenodo.3713370
CZU 664.3

PECULIARITIES OF WALNUT OIL STATE IN SOME FOOD EMULSIONS

Oxana Radu*, 0000-0001-9260-6314

Technical University of Moldova, 168, Stefan cel Mare bd., Chisinau, Republic of Moldova
**oxana.radu@sa.utm.md*

Received: 12. 22. 2019
Accepted: 02. 24. 2020

Abstract. The replacing of traditional lipids with more health-promoting oils containing polyunsaturated fatty acids (PUFA) is a modern trend in food industry. The principles of emulsions formation containing walnut oil (up to 90% PUFA) were studied in order to accumulate information that would help to design new functional products. The phase diagrams of the state of three-component systems – *Walnut oil / Water / Ethanol* and *Walnut oil / Polyphenol extract / Water* were investigated. It was shown that walnut oil was more prone to form W/O emulsions than O/W ones, that can possibly be explained by the presence of natural surfactants in it. This property of walnut oil was used within the functional spread obtaining. It has been established that the elaborated product represents an emulsion, in which water micelles and air inclusions are dispersed in continuous lipid phase, consisting of solid lipids. Withal, the structure stability of spread rich in PUFA from walnut oil was ascertained being almost analogous to milk-based butter, retaining its functionality and high biological value within a month at the temperature regime up to 5°C.

Keywords: *polyunsaturated fatty acids, microstructure, phase diagrams, spread, aggregative stability.*

Introduction

There has been an increasing tendency within food industry toward relating physicochemical, organoleptic, and nutritional properties of food emulsions to the type, concentration, structure, and interactions of their constituent components [1].

A wide variety of different types of oils has been used in food emulsions, including soybean, corn, canola, olive, safflower, and sunflower oils. The trend has been to replace traditional oils with more health-promoting oils containing polyunsaturated lipids. Walnut oil is one of these beneficial oils, which further study can provide good perspectives for food industry developing [2]. Walnuts are valuable sources of polyunsaturated fatty acids (PUFA; up to 90% of the oil), predominantly linoleic (47.4%) and α-linolenic (15.8%) acids [3]. The walnut oil consumption reduces serum cholesterol levels in humans, decreasing the total triacylglycerol levels and the risk of cardiovascular diseases [4, 5]. However, these fatty acids limit the shelf life of walnuts and walnut-containing products due to their high susceptibility to oxidation. The lipid oxidation of walnut-containing products during storage affects their quality parameters by decreasing their nutritional, sensory, and chemical properties, in addition to their economic value [6, 7]. The susceptibility of lipids to oxidation is a major cause of quality deterioration in food emulsions. The reaction mechanism and factors that influence oxidation are appreciably different for emulsified lipids than for continuous lipid phase [8]. The physical state of the droplets in an emulsion can influence a number of its most important physicochemical, organoleptic, and biochemical properties, including appearance, rheology, stability, and gastrointestinal transformations. The production of margarine, butter, whipped cream, and ice cream depends on a controlled destabilization of an O/W emulsion containing partly crystalline droplets [1]. The improved principles understanding of emulsions formation to contain walnut oil will aid to design a range of new functional products.

The aggregative stability of emulsions containing walnut oil

Walnut oil obtained through cold pressing represents a complex composition that includes, besides various fatty acids, phospholipids (16.5 g/kg) [9]. These substances contain hydrophilic groups and therefore have a surface activity [10]. Thus, cold-pressed walnut oil, unlike refined oils, should have its own surface activity [11]. From this point of view, it was proposed to investigate the aggregative stability of emulsions with walnut oil.

Systems containing nonpolar phase – cold-pressed walnut oil, and polar phase – water and ethanol obtained by rectification have were investigated. Walnut oil was obtained from freshly picked and manually peeled nuts, aged for 24 h over anhydrous sodium sulfate to uniquely remove the aqueous phase with its attendant substances.

"Three-component" emulsions were obtained, and diagrams of the type "*property = f (composition)"* in the form of Gibbs-Roseboom Triangle were developed. The phase stability of the system was investigated by the microscopic analysis of the physical state of samples prepared according to the 10 reference points (Figure 1 and Figure 2).

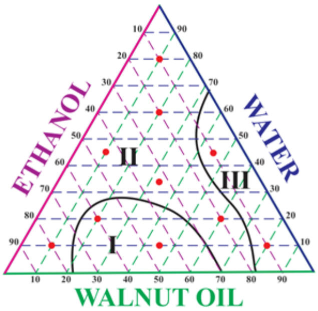


Figure 1. Different types of emulsions in *Walnut oil/ Water / Ethanol* System.

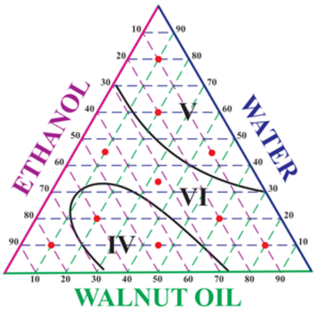


Figure 2. Phases with different aggregative stability in *Walnut oil/ Water / Ethanol* System.

According to the Figure 1, three different types of emulsions were formed: W/O emulsions (region I with 25…65% walnut oil), O/W emulsions (region II with 0…30% walnut oil) and O/W/O three-phase emulsions (region III with 40…100% walnut oil). The formation of W/O emulsions on the left side of the region was quite unexpected, because the apolar phase (in other words, dispersion medium for W/O emulsions) was less than 50%. While investigating the aggregative stability of obtained emulsions (Figure 2), it was found out that two types of samples – antipodes by water content (0…30% water in region IV and 30…100% water in region V) had a low stability, approximately 2 minutes. On the contrary, samples obtained according to the equation of straight, *Water* = *Ethanol* (region VI with 0…100% walnut oil), showed a high stability, which reached up to 5…10 minutes.

Thus, it was revealed, that walnut oil was more prone to form W/O emulsions than O/W ones. Perhaps, this fact is due to the presence of phospholipids in it, which have surfactants properties [12]. That is why it has been proposed to realize the additional study of the aggregative stability of systems, which nonpolar phase contained, besides walnut oil, a lipid extract from green tea leaves with a high content of phospholipids [13, 14]. Water was used to form the polar phase of samples. Due to the fact that obtained emulsions included two nonpolar components, the reference points for their formation were moved to the polar corner of the triangle (to water content increasing), releasing the apolar part of the diagram, located along the Water axis = 0% (Figure 3 and Figure 4).

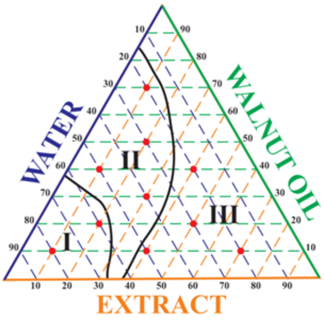


Figure 3. Different types of emulsions in *Walnut oil / Polyphenol extract / Water* system.

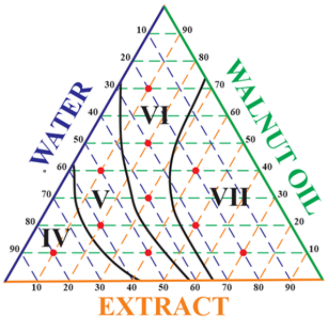


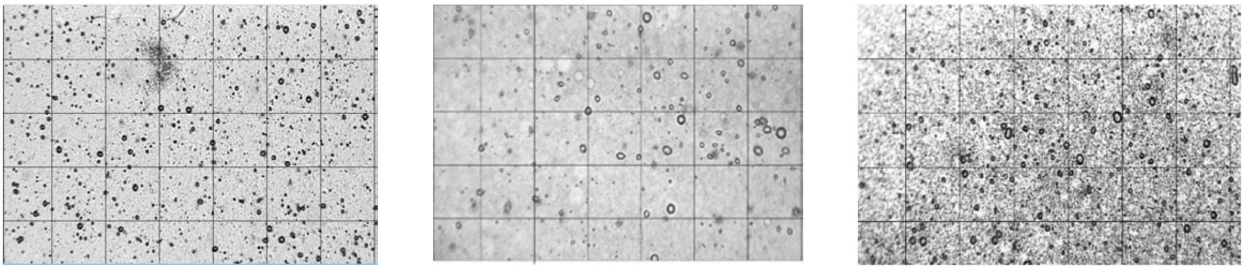
Figure 4. Phases with different aggregative stability in *Walnut oil / Polyphenol extract / Water* system.

The formation of *Walnut oil / Polyphenol extract / Water* system also revealed three regions with different phase status (Figure 3). O/W emulsions were established in samples with the highest water content (region I with 0...30% extract, 0...35% walnut oil, 60...100% water). O/W/O three-phase emulsions were formed in samples with 35...85% walnut oil, 15...65% water and in samples with 30...40% extract, 60...70% water (region II). Thus, the tendency to form three-phase emulsions was manifested more in compositions with walnut oil, than in whose with green tea extract. W/O emulsions (region III) were formed in the wide range of extract concentrations, 40...100%. In contrast, the respective range is much narrower for walnut oil, 85...100%. Thus, the diagram analysis showed that the lipid extract of green tea stabilized W/O emulsions. The aggregative state evaluation of *Walnut oil / Polyphenol extract / Water* system defined four regions, showing the stability increasing "from water to oil" (Figure 4): region IV (< 1 min), region V (2...5 min), region VI (5...7 min), and region VII (> 7 min). Therefore, the lipid extract of green tea demonstrated the pronounced effect of W/O emulsions stabilization, the most stable samples having aqueous phase content up to 30%.

The influence of walnut oil on the structure of spread type emulsions

Due to the presence of animal and vegetable components, the chemical and structural composition of spread containing walnut oil is more complicated than in milk-based butter. Spreadable products, both spreads and butter without vegetable components, represent polydisperse, multi-phase and multicomponent systems with variable composition. The polydispersity of spreads is due to the presence of solid lipid phase, aqueous phase and gaseous phase in the form of fragmented particles, whose dimensions vary: 0.01-2 µm milk fat crystals, 1...30 µm water droplets and up to 20 µm air bubbles [15].

Taking into account temperature and rate of acylglycerols cooling, different crystalline polymorphic structures are formed during the crystallization process of food emulsions [16]. Because of the large difference between the melting temperatures of dairy and vegetable fats, the lipid phase of spread containing walnut oil may be represented as either a continuous phase of solid lipid crystals, or liquid oil micelles dispersed evenly with those of aqueous between solid lipid crystals, or liquid oil incorporated and stabilized within the solid crystal network [17]. The last proposed structure, in our opinion, is the least likely from the thermodynamic point of view. In order to establish the peculiarities of walnut oil state in spread type emulsions, the microscopic analysis of spread containing sweet cream and 20% walnut oil was made [18]. It was necessary to specify in what way the presence and way of walnut oil lipids incorporation contributed to the formation of product structure and stability. With an eye to highlight spread phases, water-soluble or/and liposoluble dyes (methylene blue, sudan III) were added while samples obtaining (Figure 5).



a) b) c)

Figure 5. Spread images obtained by microscope analysis with 100x100 µm cells, where different dyes were applied:
a) sudan III, b) methylene blue, c) sudan III and methylene blue.

The microscope images of spread (Figure 5) showed that the obtained product represented an emulsion, where water micelles and air inclusions were dispersed in a continuous lipid phase, which, in its turn, was formed from solid lipid crystals (Figure 6).

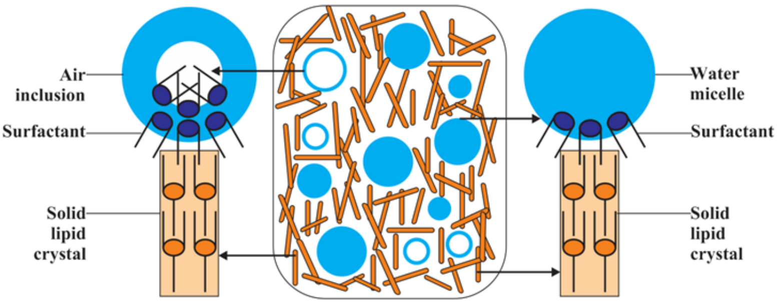


Figure 6. The schematic representation of spread microstructure:
polar (●) and non-polar (—) parts.

The structural stability of spreads containing walnut oil

Factors that affect the oxidative stability of food emulsions are the chemical structure of lipids, interfacial characteristics, droplets characteristics (concentration, dimensions) and the interaction with aqueous phase components (salt, sugars, proteins) [19, 20]. The instability phenomenon and the initial state conversion of spread can be established by evaluating the changes of the size and number of particles that form the system. That's why the aggregative stability of the microstructure of spread containing sweet cream and 20% walnut oil [18] was investigated (Figure 7). The obtained samples, with 10 - 40 g weight in each, were packaged in aluminum foil and stored at two temperature regimes: t = (3 ± 2)°C and t = – (6 ± 3)°C. The lipid phase creaming, accompanied with coalescence and aqueous phase elimination, manifested over 30 days of keeping the spread at t = (3 ± 2)°C and over 37 days at t = – (6±3)°C. The changes of spread sensory properties, established by product consistency softening, were detected along with the appearance of the first signs of water micelles coalescence.

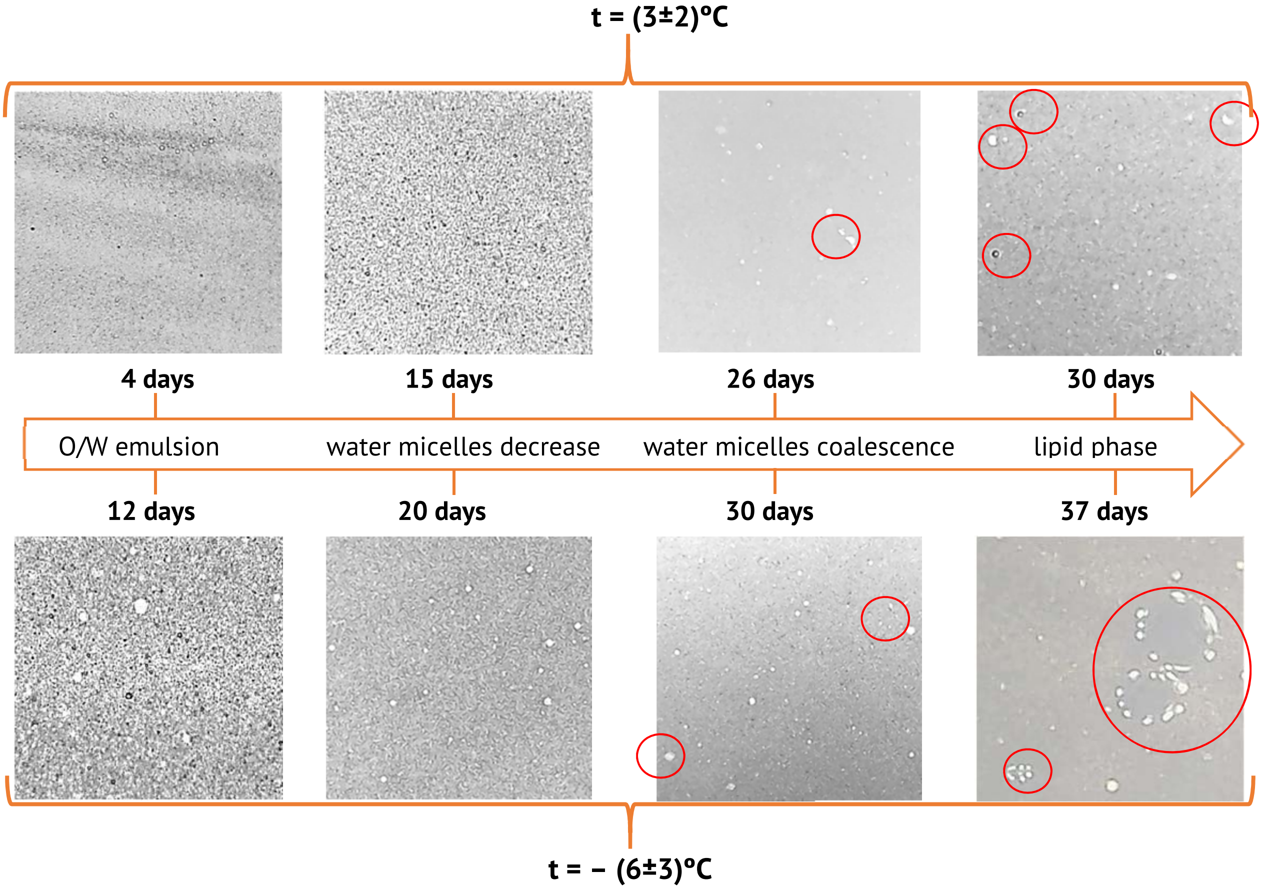


Figure 7. The aggregative stability of the microstructure of spread containing walnut oil.

Conclusions

The physical state of droplets in emulsions containing walnut oil depends on its composition (PUFA and phospholipids content) and influence on most important product physicochemical, organoleptic, and biochemical properties, including appearance, rheology, stability, and gastrointestinal transformations. Thus, it was demonstrated, that walnut oil is more prone to form W/O emulsions than O/W ones. We explain this fact by the presence of phospholipids in its composition, which have surfactants properties. It was confirmed through the analysis of emulsions with an increased phospholipids concertation – *Walnut oil / Green tea extract / Water* system, that showed the pronounced effect of W/O emulsions stabilization, the most stable samples having aqueous phase content up to 30%.

The microstructure of spread containing sweet cream and 20% walnut oil represents an emulsion, where water micelles and air inclusions are dispersed in a continuous lipid phase, which, in its turn, is made of solid lipid crystals. This contributes to the fact that spread containing walnut oil possesses the rate of structural degradation analogous to milk-based butter and retains its functionality and high biological value within a month at the temperature regime up to 5°C.

Acknowledgments. Gratitude and great appreciation are expressed to the National Scholarship Programme of the World Federation of Scientists for the support in a scientific activity.

References

1. Mcclements DJ. *Food emulsions. Principles, practices, and techniques.* In: CRC Press, 2016. ISBN-13: 978-1-4987-2669-6.
2. Nikovska K. Oxidative stability and rheological properties of oil-in-water emulsions with walnut oil. J: *Advance Journal of Food Science and Technology* 2(3), 2010. – pp. 172-177. ISSN: 2042-4876.
3. Slatnar A., et al. Identification and quantification of phenolic compounds in kernels, oil and bagasse pellets of common walnut (Juglans regia L.). In: *Food Research International*, 67, 2015. – pp. 255-263. DOI:10.1016/j.foodres.2014.11.016.
4. Patel G. Essential fats in walnuts are good for the heart and diabetes. In: *J. Am. Diet. Assoc.*, 105(7), 2005. – pp.1096-1097. DOI:10.1016/j.jada.2005.05.193.
5. Estruch R., et al. Primary prevention of cardiovascular disease with a Mediterranean diet. In: *The New England Journal of Medicine*, 368, 2013. – pp. 1279-1290. DOI:10.1056/NEJMoa1200303.
6. Grosso A.L., Asensio C.M., Nepote V., Grosso N.R. Antioxidant activity displayed by phenolic compounds obtained from walnut oil cake used for walnut oil preservation. In: *J. Am. Oil Chem. Soc.* (95), 2018. – pp.1409-1419. DOI:10.1002/aocs.12145.
7. Crowe T., White P.J. Oxidation, flavor and texture of walnuts reduced in fat content by supercritical carbon dioxide. In: *J.American Oil Chemists' Society*, Vol.80 (6), 2003.– pp.569-574. DOI:10.1007/s11746-003-0739-4.
8. Mcclements DJ., Decker, E.A. Lipid oxidation in oil-in-water emulsions: impact of molecular environment on chemical reactions in heterogeneous food systems. In: *Journal of Food Science* 65 (8), 2000. – pp.1270-1282. DOI:10.1111/j.1365-2621.2000.tb10596.x.
9. Fregapane G., Ojeda-Amador R.M., Salvador M.D. Virgin walnut (*Juglans regia L.*) oil. In: Fruit Oils: Chemistry and Functionality, 2019. – pp. 133-147. DOI:10.1007/978-3-030-12473-1_5.
10. Birdi K.S. *Handbook of Surface and Colloid Chemistry*. Taylor & Francis Group, 2016. ISBN-13: 978-1-4665-9668-9.
11. Baerle A., Popovici C., Radu O., Tatarov P. *Effect of Synthetic Antioxidants on the Oxidative Stability of Cold Pressed Walnut Oil.* Journal of Food and Packaging Science, Technique and Technologies, 2016, №9. – pp. 19-24.
12. Radu O., Baerle A., Tatarov P., Popovici C. *Aggregative stability of model emulsions containing walnut oil* (*Juglans regia L.*). Conference of Modern Technologies in the Food Industry, October 18-20, Chisinau, 2018. pp.230-231. ISBN 978-9975-87-428-1.
13. Bidlack W.R., Rodriquez R.L. *Nutritional Genomics: The Impact of Dietary Regulation of Gene Function on Human Disease.* In: CRC Press, 2012. ISBN-13: 978-1-4398-4453-3.
14. Afzal M., Safer A. M., Menon M. Green tea polyphenols and their potential role in health and disease. In: *Inflammopharmacology*, Vol. 23 (4), 2015. – pp. 151. DOI:10.1007/s10787-015-0236-1.
15. Vyshemirskij F.A. Fizicheskaya struktura i konsistenciya slivochnogo masla. [Physical structure and consistency of butter]. M: *ANO "Molochnaya promyshlennost",* 2013. – pp. 53-56. – in Russian.
16. Tatarov P. *Chimia produselor alimentare.* [*Food chemistry*] Chisinau: MS Logo, 2017. – in Romanian.
17. Arellano M., Norton I.T. Smith P. Specialty oils and fats in margarines and low-fat spreads. In: *Woodhead Publishing Series in Food Science, Technology and Nutrition*, 2015. – pp. 241-270. DOI:10.1016/B978-1-78242-376-8.00010-7.
18. Technical University of Moldova, MD. *Procedeu de obţinere a amestecului de grăsimi tartinabile pe bază de smântână dulce.* [Process of the preparation of a spreadable fats mixture based on sweet cream]. Patent no. 1281. Inventors: Radu O., Popescu L., Tatarov P., Baerle A. Publ.: BOPI, 2018-09-30.
19. Kiokias S., Dimakou C., Oreoppoulou V. Effect of heat treatment and droplet size on the oxidative stability of whey protein emulsions. In: *Food Chemistry* 105, 2007. – pp. 94-100. DOI:10.1016/j.foodchem.2007.03.053.
20. Griffiths A.D, Tawfik D.S. Miniaturising the laboratory in emulsion droplets. In: T*rends Biotechnol.* 30(10), 2006. – pp.1-8. DOI: 10.1016/j.tibtech.2006.06.009.