

Encapsulation of Flavors in Emulsions for Beverages

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Abstract

Though stable in dilute form for very long periods of time, simple mono-emulsifier flavor emulsions based on gum acacia or modified starch are fairly limited in their ability to provide functionality beyond simple dispersion. This review highlights many of the enhancements on traditional emulsions, ranging from new materials to novel combinations of materials and processes. The development of more sophisticated dispersion technologies employing complex mixtures of biopolymers as well as low molecular weight surfactants, and novel multilayered interfacial structures, is on an intersecting course with a growing need for enhanced emulsion functionality in beverages, such as controlled release, protection, taste masking, and targeted delivery. Novel raw materials, molecular assemblies, processes and applications are discussed in this review.

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1. Introduction

Beverage emulsions are unique compared to all other food dispersion systems in that they are very dilute, containing as little as 20 mg/L dispersed oil phase in finished product, and must remain physically stable for relatively long periods of time, usually between 4 and 12 months.

Dilute emulsions are typically composed of a flavor oil blend in which a weighting agent is dissolved to increase the density, and a polymeric emulsifier/stabilizer consisting of either gum acacia or modified corn starch (Fig. 1). Two-stage high pressure homogenization (2000–5000 psi) is employed to reduce particle size to between 0.2 and 2.0 microns diameter. For the sake of discussion, these emulsions will subsequently be referred to as “macroemulsions” in order to discriminate them from “micro-emulsions” with particle diameters substantially less than 0.1 micron. Beverage macroemulsions are turbid because their particle size falls at the center of the visible light wavelength spectrum. Long term stability is the result of numerous, interactive factors: particle size homogeneity, density balance between

dispersed phase and continuous phase, chemical integrity of dispersed phase, and degree of “intertness” of the particle exterior. By this I mean minimal charge or reactive moieties on the surface. Gum acacia and modified starch polymers stabilize via steric hindrance as contrasted with charge repulsion systems.

Excellent review articles are available for additional detail: Ref. [1] discusses dispersed phase, interfacial membrane and continuous phase compositions, microstructure, production, and physicochemical properties in great detail. Properties of beverage emulsions used to create visual turbidity or “cloud” are reviewed in detail by Ref. [2]. A more general and thorough treatment of food emulsions can be found in Ref. [3], in which dilute emulsions and beverages are covered.

This chapter will focus on developments in beverage macro-emulsions; specifically emulsifiers, novel emulsion system developments, processes, and characterization approaches. Limited discussion of the application of beverage emulsion technology to deliver nutritional components is included.

2. Developments in beverage emulsion systems

Virtually all beverage flavor macroemulsions employ biopolymeric emulsifiers. Biopolymers can be roughly divided

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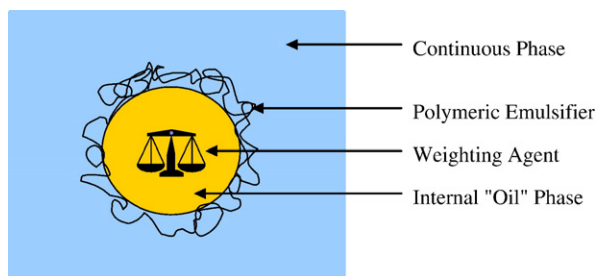


Fig. 1. A typical beverage flavor emulsion composed of a weighted flavor oil surrounded by an emulsifying polymer, providing the “hairy” layer.

into naturally occurring and chemically modified. Octenyl succinylation (OS) renders amylopectin from corn starch amphipathic, i.e., makes starch an excellent emulsifier for flavor oils and other lipophilic substances. Emulsifying function is achieved by adding hydrophobic groups throughout the starch molecule, and is coupled with either acid or enzyme hydrolysis to control molecular weight and solubility. This approach was further leveraged in Ref. [4] to modify a wide range of hydrocolloids including gum acacia seyal (a poorly-emulsifying gum acacia), other arabinogalactans, guar gum, and inulin. Low concentrations of modified polymers compared favorably to gum acacia senegal in model flavor emulsions (from 50% to 75% less). Beta-amylase modification of the 1,4- α -D-glucosidic linkages from the non-reducing ends of OS starch, or native starch prior to modification, resulted in enhanced emulsifying action [5]. Unique amylase enzymes have been patented for the purpose of improving the functionality of modified starch [6]. Two articles compare the properties of emulsions produced using different emulsifiers (whey protein, gum acacia and modified corn starch) as a function of continuous phase variables: pH, CaCl_2 concentration, and storage temperature [7,8]. Not surprisingly, whey protein was most affected by continuous phase alterations because it stabilizes emulsions primarily by charge repulsion (net positive at pH below its isoelectric point). While gum acacia emulsion stability is fairly pH-independent, a mixture of gum acacia and gum ghatti demonstrated decreasing stability with decreasing pH between 2.0 and 5.0 pH [8].

Arabinogalactan has been isolated from green or roasted coffee by hydration followed by enzymatic hydrolysis [9]. Though not specifically isolated as an emulsifier, coffee arabinogalactan may well possess amphipathic character or be amenable to chemical modification as described above. Hemicellulose and hemicellulose hydrolyzate have been employed to produce beverage flavor emulsions [10]. Emulsifiers were created via enzymatic modification of pectic substances using esterases (E.C.3.1), glucosidases (E.C.3.2.), and lyases (E.C.4) [11], or proteolytic enzymes selected from the group consisting of proteases and peptidases [12]. Modified pectin can be applied to emulsions, microencapsulation, foam stabilization, and film formation. Soybean soluble polysaccharide (SSPS) forms stable oil-in-water emulsions [13]. Gel filtration fractionation of SSPS into high and low molecular weight fractions, coupled with heating experiments, indicate that heat-instability is linked to

degradation of protein impurities in the low molecular weight fraction. Fruit pulp has been applied to further stabilize an emulsion containing both oil-soluble tastants and oil-soluble pigments [14]. This is analogous to the role of pulp in 100% orange juice where pulp has been demonstrated to adsorb substantial quantities of citrus oil and carotenoids. Fruit solids have also been employed directly as emulsifiers/stabilizers. Fruit juice and fruit pulp (5–80%) were combined with a mixture of pectin and guar flour (but not pectin and carob bean flour), and 2–20% milk proteins [15]. The polysaccharides are hydrated first, followed by addition of milk proteins then fruit components, and the mixture is deaerated and homogenized to obtain a stable emulsion.

Whey protein stabilized O/W emulsions of citrus oil containing citral, a very unstable lemon-tasting flavor molecule, were more stable against oxidation than comparable emulsions produced using gum acacia [16]. Significantly less *p*-cymene, one of the primary oxidation products of citral in beverages at pH 3.0, was formed in whey protein emulsions compared to gum acacia emulsions. This result is thought to be due to the whey protein’s positive charge repulsion of trace iron in the continuous phase. The same authors conducted a similar study where gum acacia emulsions were compared to those made using a combination of sodium dodecyl sulfate (SDS) and chitosan [17]. The SDS–chitosan complex outperformed the gum acacia emulsion as measured by reduced *p*-cymene formation from citral over time; like whey protein, chitosan has a net positive charge at pH 3.0 and can repel iron ions in solution. Emulsions can be further stabilized by applying secondary or tertiary biopolymers. Addition of a combination of gellan gum and carrageenan to a macroemulsion improved dispersion stability against high salt concentrations and heating [18].

Electrostatic interactions between proteins and polysaccharides have been utilized to create more robust interfacial complexes than single biopolymers can achieve. Beta-lactoglobulin emulsions of corn oil were combined with either alginate, iota-carrageenan, or gum acacia and tested for stability against ionic strength, pH, and heating [19]. Stable emulsions were formed when just enough polysaccharide was employed to coat the net droplet surface area, and emulsions made using alginate or carrageenan demonstrated superior stability to ionic strength and heat over a pH range of 3.0 to 7.0. High methoxy pectin (HM pectin) was shown to improve the acid stability of 0.5% casein emulsions of 10% soybean oil [20]; increasing pectin levels >0.2% also prevented aggregation of emulsion particles.

Building on a basic knowledge of biopolymer electrostatic interactions to form robust interfacial complexes, various combinations of protein (net positive) and select polysaccharides (net negative) or low molecular weight anionic emulsifiers, like lecithin, were developed to form stable O/W emulsions under acidic conditions for beverages [21]. Interactions between oppositely charged components were evaluated by measuring zeta-potential of the emulsion droplets. This approach also constitutes the basis for a technique termed “layer-by-layer” whereby sequential multilayers of oppositely charged molecules, typically polymers, are added to build droplet shell integrity and stability against various continuous phase or environmental

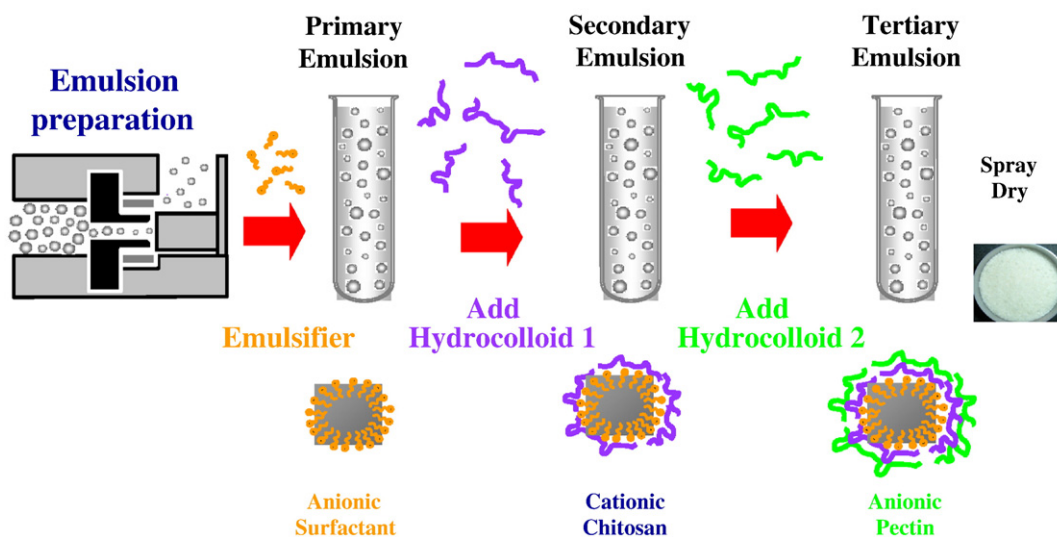


Fig. 2. Illustration of layer-by-layer application to encapsulation (emulsification) of a lipophilic oil phase — Ref. [22] with permission.

stresses (ionic strength, pH, presence of oxidation catalysts, heat, sunlight, etc.) (Fig. 2). Layer-by-layer is explained in slightly more depth in reference [22].

As mentioned in the introduction, flavor oils are often weighted to bring the density closer to the finished product continuous phase. This prevents creaming of the emulsion particles which would result in a visible “ring” at the beverage/headspace interface, and also contribute to aggregation, coalescence, and potentially gross emulsion failure and oil-slicking on the surface. There are three predominate materials in use today, driven mainly by global food regulations: glycerol esters of wood, gum, or tall oil resins (ester gum); sucrose acetate isobutyrate (SAIB); and brominated vegetable oil (BVO). Gum rosin-based ester gum has recently obtained US FDA GRAS status, and tall oil-based ester gum has obtained FEMA GRAS status, expanding the ingredient choices available to end-product manufacturers. SAIB is a very viscous liquid at room temperature making it difficult to weigh accurately during formulation. Various oil-soluble diluents have been applied to SAIB to render it more “user-friendly”, e.g., limonene, ethyl alcohol, medium chain triglyceride oil, and proprietary fatty-like substances [23].

Beverage flavor macroemulsions are created via high pressure homogenization to achieve uniform particles having sub-micron diameters. The protocol generally involves production of an emulsifier solution, followed by addition of oil phase and development of a “premix” by simple or high shear mixing. The premix, having an average particle size in the 5–20 micron range, is then homogenized in a two-stage homogenizer in either one pass or two passes depending upon the formula and desired outcome. In Ref. [24], homogenization parameters were systematically studied using gum acacia and modified starch emulsions which were evaluated by particle size analysis and stability over time. One example of an optimum set of parameters for gum acacia emulsions is 45–55 MPa in the first stage followed by approximately one third of that pressure in the second stage. The authors state that homogenization parameters

must be tailored to each emulsifier and formulation system for optimum performance in finished product. A novel variation on the typical homogenization sequence was developed [25] whereby the emulsifier solution and the flavor are separately pressurized, and forced to impinge on each other at high pressure (50–250 MPa). This micronizing treatment is claimed to yield superior emulsions that do not cream or develop floating oil over long periods of time.

3. Specialized emulsion situations

A mesomorphic structure, which could assume many physical forms depending upon the composition (cubic, lamellar, hexagonal) was developed as a quasi-emulsion to disperse food ingredients in aqueous phase [26]. Options for surface-active substances include monoglycerides containing up to 90% oleic acid or 90% of a combination of oleic and linolenic acids, as well as mixtures of saturated or unsaturated di- or polyglycerol monoesters.

A transparent emulsion was developed by combining low molecular weight surfactants including a sucrose fatty acid ester having an HLB of 16–19 and composed of monopalmitate and lysolecithin, a polyglycerol fatty acid ester and/or monoglycerol fatty acid esters [27].

Refractive index can be adjusted to manipulate the visual appearance of an emulsion, i.e. if the refractive index of the dispersed phase matches the continuous phase, the particles are virtually invisible. This physical phenomenon was employed to create a novel creamer, whereby the creamer itself is visually transparent, but becomes milky-looking upon pouring into a beverage having a different refractive index than the creamer dispersion [28].

Alcohol above about 5% is generally destructive to beverage flavor emulsions, and is thus a challenge for flavored alcoholic beverages that require an hydrophobic flavor dispersion. A stable, acidified beverage containing a flavor emulsion and alcohol was achieved by employing a polyglycerol fatty acid

ester composed of at least 70% palmitic acid in conjunction with an ionic emulsifier [29].

Spice flavor retention in beverages as was achieved by employing polyglycerol fatty acid esters of the following composition: degree of polymerization 3–10; 2–18 carbon saturated fatty acids; and a refractive index of between 1.450 and 1.465 [30].

4. Non-flavor beverage emulsion applications

To address rising consumer interest in “healthy” foods and beverages, dispersion technologies are being developed or adapted to permit inclusion of hydrophobic nutritional ingredients in ready-to-drink beverages. Resistance to low pH and oxidation, taste masking, and targeted delivery in the body are additional functional features of nutrient emulsions, beyond simple dispersion. It is beyond the scope of this chapter to cover all known nutrient emulsions, but a few examples are instructive.

Plant sterols have been demonstrated to lower plasma cholesterol in humans. Sterols were dispersed in an optically transparent beverage by first mixing them with one of a group of low molecular weight surfactants (sucrose fatty acid esters, sorbitan fatty acid esters, or polyglycerol fatty acid esters), heating the mixture from 60–120 °C to melt the sterol, followed by addition of the melt under shearing conditions to a beverage or beverage containing a water soluble emulsifier [31]. Bioavailability of sterols was increased using this method, presumably due to the small particle size achieved (<0.1 micron). A complex of organic acid monoglyceride with milk protein provided emulsifying capacity sufficient to disperse an oily phase containing coenzyme Q10 (ubiquinone) [32]. The emulsion demonstrated resistance to coenzyme Q10 separation or creaming for at least two weeks. A dispersion system designed to disperse high levels (30–95%) of a healthy diglyceride, composed of high levels of linolenic acid (15–90%) was developed [33]. This system is composed of a structured diglyceride, which has surface activity, and a mixture of tocopherol, phospholipids and fat-free milk solids. It is noteworthy that this dispersion system remains stable after thermal treatment during sterile packaging. One last example concerns another popular nutrient, omega-3 fatty acids, derived from fish or vegetable sources; this material possesses the added challenge of being highly susceptible to oxidation with consequent generation of off-*aroma* and taste. Many dispersion systems have been developed and commercialized for fish oil: complex coacervates, traditional emulsions, layer-by-layer emulsions, and microemulsions. An example is a microemulsion composed of fish oil and decaglycerol monostearate and/or decaglycerol monooleate which is then dispersed in a dairy beverage [34]. Protection against oxidation is not necessarily inherent in the microemulsion as-is, but likely results from interaction of the nano-dispersed oil droplets with dairy proteins which are known to be excellent chelators of iron.

5. Emulsion characterization approaches

For practical commercial purposes, beverage emulsion stability is mainly characterized by long-term maintenance of suspension

properties, i.e., absence of creaming, sedimentation, loss of oil (slicking), or droplet aggregation leading to visible flocculation over the product shelf life. Though mass particle molecular movement kinetics (creaming or sedimentation) can be measured by semi-automated optical techniques, these are primarily subjective measures. Particle size distribution frequency (volume fraction) is one of the best objective measures that relate to physical performance. Additional commercially relevant parameters of beverage emulsions are flavor release and appearance.

An excellent overview of the most important properties of emulsions of interest to the food industry was recently published [35]. It discusses the merits and limitations of analytical techniques and experimental protocols.

One of the most important aspects of flavor emulsions is how they mitigate flavor constituent release properties upon consumption. A flavor release model was developed using headspace measurement and model compounds differing in their volatility and hydrophobicity in a Miglyol 812 oil plus polysorbate 80 system [36]. Good correlation was obtained between predicted dynamic flavor release, and a mouth model apparatus. In another study using O/W macroemulsions [37], emulsion parameters were evaluated for their influence on dynamic flavor release. Flavor release was independent of emulsion particle size, and surprisingly unaffected by emulsifier type or concentration. The physicochemical properties of flavor molecules were studied in relation to their release behavior as studied by static headspace analysis at thermodynamic equilibrium [38]. Flavor partitioning was principally governed by each molecule’s hydrophobicity, and the proportion of lipid phase in the matrix tested. Similar results were observed by Ref. [39], where release of ethyl hexanoate, cymene, and octanol were studied in an O/W emulsion system; again it was observed that partitioning was governed by the hydrophobicity of each molecule and the lipophilic content of the matrix. Like the previous study, volatile partitioning was not affected by emulsifier type (gum acacia or modified starch), nor emulsion particle size. An algorithm was developed to predict release; the significant terms included Log P, Log solubility, the dipole vector and the oil fraction. It is clear from these studies that technology beyond simple dispersion is required if additional functionality, e.g., controlled release, is desired in the end product.

The rheological properties of emulsions may affect consumer acceptance and “liking” scores for finished beverages based on viscosity, or indirectly from viscous effects on flavor perception. According to one study [40], gum acacia emulsions display Newtonian behavior, the Einstein equation providing best fit. It was concluded that in this type of emulsion, dispersed particles act as rigid spheres that are not significantly affected by Brownian motion due to bulk phase viscosity, and are subject to very limited range colloidal interactions. This is not surprising given that the mechanism of stabilization by gum acacia is thought to be driven by steric hindrance. A different system was developed which behaves similar to gum acacia emulsions, i.e., no viscosity change upon addition to an acidic beverage [41]. The O/W emulsion is composed of water, fat, whey protein and an emulsifier consisting of a polyglycerol esterified with oleic acid and a sucrose fatty acid ester having an HLB of 4–15. Based on these studies, one could conclude that

the dispersed phase composition or concentration of macro-emulsions have little impact on rheology and thus little impact on consumer sensory response. However, in contrast, the rheological properties of an O/W emulsion made using modified starch and coconut oil varied with both oil level and continuous phase manipulation [42]. Increasing oil phase increased opacity as well as overall emulsion viscosity; Newtonian behavior was observed at all oil phase levels. Increasing starch decreased the flow behavior index. Lastly, the microstructure of emulsions was evaluated using non-destructive Kossel diffraction technique based on the principle of backlight scattering, leading to a robust predictive model for ring formation in finished beverages [43].

6. Conclusion

Though stable in dilute form for very long periods of time, simple mono-emulsifier flavor emulsions based on gum acacia or modified starch are fairly limited in their ability to provide functionality beyond simple dispersion. Clearly, a growing need for enhanced emulsion functionality in beverages, such as controlled release, protection, taste masking, and targeted delivery, is on an intersecting vector with the development of more sophisticated dispersion technologies employing complex mixtures of biopolymers as well as low molecular weight surfactants, and novel multilayered interfacial structures. Understanding and directed manipulation of interfacial physicochemical fundamentals will ultimately dictate the success or failure of future “functional” emulsions.

References

- [1] McClements DJ. Food emulsions in practice. In: McClements DJ, editor. *Food emulsions: principles, practices, and techniques*. Boca Raton: CRC Press; 2005. p. 515–43.
- [2] Shachman M. Emulsions — the cloudy drinks. In: Shachman M, editor. *The soft drinks companion*. Boca Raton: CRC Press; 2005. p. 42–53.
- [3] Friberg SE, Larsson K, Sjoblom J, editors. *Food Emulsions*. 4th ed. Boca Raton: CRC Press; 2004.
- [4] Ward FM. Special Publication — Royal Society of Chemistry, vol. 278; 2002. p. 318–22. *Gums and Stabilizers for the Food Industry* 11.
- [5] Chung Wai C, EP332027B1.
- [6] Pedersen S, Vang Hendriksen H. WO2001016348A1.
- [7] Chanamai R, McClements DJ. Comparison of gum arabic, modified starch, and whey protein isolate as emulsifiers: influence of pH, CaCl₂ and temperature. *J Food Sci* 2002;67:120–5.
- [8] Duzewska E, Smiechowski K, Kowalska M. *J Food Technol* 2005;3(4):542–5.
- [9] Curti DG, Gretsich C, Labbe DP, Redgwell RJ, Schoonma NJH, Ubbink JB. WO2005116083A1.
- [10] McPherson R, Olson R, Eads A. JP2001252013A.
- [11] Strarup A, Hansen KM, Pedersen AV, Hansen MM, Madsen SL, Jensen NM, et al. WO2002082923A1.
- [12] Strarup A, Hansen KM, Pedersen AV, Hansen MM, Madsen SL, Jensen NM, et al. WO2002082922A1.
- [13] Nakamura A, Maeda H, Corredig M. *J Agric Food Chem* 2007;55:502–9.
- [14] Saigo A, Ito M. JP2001346557A.
- [15] Kolb E, Nage Pl, Simson I, Dechent HM. EP765609B1.
- [16] Djordjevic D, Cercaci L, Alamed J, McClements DJ. *Food Chem* 2007;106(2):698–705.
- [17] Djordjevic D, Cercaci L, Alamed J, McClements DJ, Decker EA. *J Agric Food Chem* 2007;55(9):3585–91.
- [18] Nagayasu K. JP2004357654A.
- [19] Thepkunya H, Rungnaphar P, McClements DJ. *J Agric Food Chem* 2006;54(15):5540–7.
- [20] Bonnet C, Corredig M, Alexander M. *J Agric Food Chem* 2005;53(22):8600–6.
- [21] McClements DJ, Decker EA. WO2007038624A2.
- [22] McClements DJ. Structural design principles for improved food performance: nano-laminated biopolymer structures in foods, ACS (in press).
- [23] Merkt G, Jager M, Von Rymon Lipinski G-W. JP2002112748A.
- [24] Dluzewska E, Leszczynski K. *Pol J Food Nutr Sci* 2005;14:293–8.
- [25] Sagami K. JP2004210957A.
- [26] Leser M, Vauthey S. US6569478B1.
- [27] Nakajima M, Ishida H, Yoshimura K, Nakajima K, Takatsuji M, Hibi Y. JP2002281927A.
- [28] Einerson MA, Pascual TB. WO2003059077A1.
- [29] Ishitobi M. JP2005143424A.
- [30] Yamada Y, Tone T. JP2006050986A.
- [31] Yoon W, Kim K-S, Kim B-C, Han J-H, Hong H-P. WO2002028204A1.
- [32] Ikehara T, Ogino K. WO2004080208A1.
- [33] Yamamoto S, Kataoka K, Omura H. JP2004357538A.
- [34] Tamura Y, Kimura Y, Yamazaki T, Ogura R. JP2004248593A.
- [35] McClements DJ. *CRC Crit Rev Food Sci Nutr* 2007;47(7):611–49.
- [36] Rabe S, Krings U, Berger RG. *Food Chem* 2004;84(1):117–25.
- [37] Rabe S, Krings U, Berger RG. *J Sci Food Agric* 2003;83:1124–33.
- [38] Philippe E, Seuvre A-M, Colas B, Langendorff V, Shippa C, Voilley A. *J Agri Food Chem* 2003;51:1393–8.
- [39] Carey ME, Asquith T, Linforth RST, Taylor AJ. *J Agric Food Chem* 2002;50:1985–90.
- [40] Buffo R, Reineccius GA. *J Food Eng* 2002;51:267–72.
- [41] Kiyohara Y, Sato R. WO2006035543A1.
- [42] Taherian AR, Fustier P, Ramaswamy HS. *J Food Eng* 2006;77(N3):687–96.
- [43] Kong Y, Nikolov A, Wasan D, Ogawa A. *J Dispers Sci Technol* 2006;27:579–85.