



Evaluation on oxidative stability of walnut beverage emulsions



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ABSTRACT

Walnut beverage emulsions were prepared with walnut kernels, mixed nonionic emulsifiers and xanthan gum. The effects of food antioxidants on the physical stability and lipid oxidation of walnut beverage emulsions were investigated. The results showed that tea polyphenols could not only increase the droplet size of the emulsions, but also enhance physical stability during the thermal storage at 62 ± 1 °C. However, water-dispersed oil-soluble vitamin E and enzymatically modified isoquercitrin obviously decreased the physical stability of the emulsion system during the thermal storage. BHT and natural antioxidant extract had scarcely influenced on the physical stability of walnut beverage emulsions. Tea polyphenols and BHT could significantly retard lipid oxidation in walnut beverage emulsions against thermal and UV light exposure during the storage. Vitamin E exhibited the prooxidant effect during the thermal storage and the antioxidant attribute during UV light exposure. Other food antioxidants had no significant effect on retarding lipid oxidation during thermal or light storage.

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1. Introduction

Walnut kernels contain plentiful fat and protein (Prasad, 1994). The relative ratio of unsaturated fatty acids in walnut oil (relative to total fatty acids) is apparently higher than other edible oils. The diet with polyunsaturated or monounsaturated fatty acids can lower plasma and low-density-lipoprotein (LDL) cholesterol, thus reduce the risk of heart disease (Abbey, Noakes, Belling, & Nestel, 1994). The major fatty acids found in walnut oil are oleic (18:1), linoleic (18:2) and linolenic (18:3) acids (Cunnane et al., 1993).

Although unsaturated fatty acids have many benefits, they are extremely sensitive to heat and light during the process and storage, resulting in potential alteration in nutritional composition and food quality (Choe & Min, 2006). These fatty acids are subjected to rapid and extensive oxidation by exposure to light, heat or air during the process and storage (Ng, Lau, Tan, Long, & Nyam, 2013), resulting in the generation of hydroperoxides, and subsequently, off-flavor compounds (Alamed, Chaibayit, McClements, & Decker, 2009). Thus, the lipid oxidation limits the utilization of walnut oil in processed foods.

Formulation and physical stability characterization of walnut beverage emulsions were published for the first time by Gharibzahedi, Mousavi, Khodaiyan, and Hamed (2012). The appli-

cation of walnut oil as a functional component in the production of beverage emulsions was investigated using response surface methodology (RSM). Homayoonfal, Khodaiyan, and Mousavi (2014a, 2014b, 2015) investigated the influence of ultrasonic time, walnut oil content and the emulsifier concentration on the physical stability of walnut oil in water nano-emulsion by RSM in conjunction with central composite rotatable design (CCRD). These studies revealed that a linear term of walnut oil concentration was the most significant parameter for all the responses and walnut oil in O/W emulsion could be prepared with polysaccharide, emulsifier and walnut oil. However, all the reports about walnut beverage emulsions only dealt with a buffer system, not a real food system. In the present study, we tried to use walnut kernels as the material and retained all its components in the emulsion and focus on the physicochemical stability during the process and storage.

Nowadays, walnut beverage emulsions become more and more popular in plant protein beverage market, which is similar to soybean milk. Therefore, it is necessary to study the physicochemical stability and shelf life of walnut beverage emulsions. We have evaluated the effects of pH, freeze-thaw and thermal sterilization on physicochemical stability of walnut beverage emulsions (Liu, Sun, Xue, & Gao, 2016). It consisted of three parts: an aqueous continuous phase, the droplet's oil core and the interfacial membrane. The mechanism of lipid oxidation in oil-in-water emulsion differed from bulk lipids, because the emulsions had an aqueous phase containing both antioxidants and prooxidants and the oil-water interface impacted the interaction between oil and water soluble

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components (Frankel, Huang, Kanner, & German, 1994). There are many factors that can influence the rate of lipid oxidation in oil-in-water emulsions, such as oxygen concentration, particle size, the thickness and interfacial rheology properties (Waraho, McClements, & Decker, 2011).

Lipid oxidation in oil-in-water emulsions was extensively investigated. McClements and Decker (2000) reported that the transition metals were the major prooxidants in oil-in-water emulsions. The stabilizer and emulsifier could also have an impact on lipid oxidation of emulsions by changing the charge of the emulsion droplets and the thickness of interfacial film (Hu, McClements, & Decker, 2003). Many studies revealed that the incorporation of antioxidants into foods is one of the most effective approaches in retarding lipid oxidation. Phenolics are from natural plant sources and commonly applied as antioxidants to inhibit lipid oxidation in emulsion systems. The phenolic antioxidants could increase the reactivity of prooxidant metals and the partition into the emulsion droplets where they might scavenge free radicals (Mei, McClements, & Decker, 1999).

Nowadays, more and more natural antioxidants have been applied to emulsions system, such as vitamin C, vitamin E, tea polyphenols and natural plant extracts. Grape seed extract was found to be effective in scavenging free radicals and inhibiting lipid oxidation in algae oil-in-water emulsions with certain concentration, and the major antioxidants in the seeds were proanthocyanidins (Hu, McClements, & Decker, 2004). Meanwhile, the natural antioxidants have the characteristics of high efficient and low toxicity, which are better than the synthetic ones, such as BHT, TBHQ and BHA. The antioxidative attribute of anthocyanin-rich purple corn husk extract (PCHE) in mayonnaise was compared with that of BHT and EDTA. During storage, the antioxidative effect of PCHE on the mayonnaise was more significant than that with synthetic antioxidants such as BHT and EDTA (Li, Kim, Li, Lee, & Rhee, 2014).

Tea polyphenols (TP) and vitamin E (V_E) are extensively utilized in bulk oils and emulsions system as natural antioxidants. However, these antioxidants have never been applied in real walnut beverage emulsions system. Natural antioxidant extract (NAE) and enzymatically modified isoquercitrin (EMIQ) would be applied as novel natural antioxidants in walnut beverage emulsions. The objective of this study focused on the effects of different food antioxidants on the physical and oxidative stability of walnut beverage emulsions.

2. Materials and methods

2.1. Materials

Walnut kernels were purchased from Dinghui Food Co., Ltd. (Hebei, China) and stored at $-19\text{ }^\circ\text{C}$ until used. Xanthan gum was obtained from Xinxhe Biochemical Co., Ltd. (Hebei, China). Glycerol monostearate (GMS, HLB: 3.8) was obtained from Danisco Co., Ltd. (Beijing, China). Decaglycerol monolaurate (DML, HLB: 15.5) was obtained from Evonik Food Development Co., Ltd. (Shanghai, China). Sodium azide, BHT and FAME MIX (C_8 – C_{22}) were purchased from Sigma Aldrich (USA). Methanol and 1-butanol were purchased from Beijing Chemical Work. Ammonium thiocyanate and BaCl_2 were purchased from Tianjin Chemical Work. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was obtained from Guanghua Sci-Tech Co., Ltd. (Guangdong, China). 1,1,3,3-Tetraethoxypropane was purchased from Xiya Reagent (China). Water-soluble tea polyphenols (purity >99%) were obtained from Hongyi Biotechnology Co., Ltd. (Henan, China). Water-dispersed vitamin E (purity >50%) and vitamin E (purity >50%) were obtained from DSM (Switzerland) and Lantian Biotechnology Co., Ltd. (Xian, China), respectively. The natural antioxidant extract (NAE, SL25933) and enzymatically modified isoquercitrin

(EMIQ; purity >30%) were gifted by Ogawa Co., Ltd. (Japan) and San-Ei Gen F.F.I. Co, Ltd. (Japan), respectively.

2.2. Walnut kernel slurry

The peeled walnut kernels were mixed with deionized water at the weight ratio of 1:4.5 and processed into the slurry. The crude slurry was treated through a colloid mill and filtered through three layers of gauze to remove the solid residues and obtain the coarse slurry.

2.3. Preparation of walnut beverage emulsions

Previously we have optimized the species levels of emulsifiers (GMS, DML, and sucrose ester) employed in the emulsion and polysaccharides (xanthan gum, soybean polysaccharides and arabic gum). In order to obtain the stable emulsion, the formulation of walnut beverage emulsions was designed as follows: coarse slurry (18%), sucrose (6.5%, wt), xanthan gum (0.09%, wt), GMS (0.18%, wt), DML (0.07%, wt), sodium azide (0.02%, wt) and deionized water (75.14%). The coarse walnut beverage emulsions were prepared by mixing the slurry with the aforementioned additives. The water-soluble antioxidants were directly incorporated into coarse walnut beverage emulsions. On the other hand, the oil soluble antioxidants were solubilized in ethanol firstly (1:10, w/w), then, the solutions were added to coarse walnut beverage emulsions. To achieve a fine emulsion with small mean particle size and narrow particle-size distribution, pre-homogenization was performed by using an Ultra-Turrax (T25, IKA, Staufen, Germany) at a speed of 10,000 rpm for 3 min, and then passed through a two-stage valve homogenizer (Niro-Soavi Panda, Parma, Italy) for three cycles at 65 MPa and $65\text{ }^\circ\text{C}$. The final emulsion was immediately cooled down to $25\text{ }^\circ\text{C}$ and then transferred into screw-capped brown bottles.

2.4. Light stability of walnut beverage emulsions

The emulsions in the presence of different antioxidants were transferred into glass bottles and put into a controlled light cabinet (Q-SUN Xe-1-B, 0.35 W/m^2 , $45\text{ }^\circ\text{C}$) (Q-LAB, USA). The temperature was regulated on black panel (Ploeger, Scalarone, & Chiantore, 2009). The contents of peroxide and malondialdehyde (MDA) were regularly determined at an interval of 2 h.

2.5. Thermal stability of walnut beverage emulsions

Emulsion samples (55 mL) were transferred into brown bottles with metal cap and tighten by the automatic capper. The oxidation reaction was accelerated in a force-draft air oven DHG-9140A (Shengxin Instruments; Shanghai, China) set at $62 \pm 1\text{ }^\circ\text{C}$ (Ramadan, 2013) and the changes of droplet size, peroxide concentration, MDA and the composition of fatty acids in emulsions were regularly determined at an interval of 2 or 3 days.

2.6. Analytical methods

2.6.1. Mean particle size

The mean particle sizes of samples were determined with a Zetasizer Nano-ZS90 (Malvern Instruments, Worcestershire, UK) at a fixed detector angle of 90° . To avoid multiple scattering effects, the emulsions were diluted with deionized water at a ratio of 1:800 (v/v). Droplet size was described as cumulative mean diameter (size, nm). All measurements were performed in triplicate.

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