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Influence of primary homogenization step on microfluidized emulsions formulated with thyme oil and Appyclean 6548

Luis A. Trujillo-Cayado, M. Carmen Alfaro*, Jenifer Santos, Nuria Calero, José Muñoz

Departamento de Ingeniería Química, Facultad de Química, Universidad de Sevilla, C/P. García González, 1, E41012 Sevilla, Spain

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ABSTRACT

This contribution deals with the development of emulsions formulated using thyme essential oil and a new biomass-derived surfactant. In addition, this work extends our knowledge concerning the factors that can influence stability and droplet size distributions of microfluidized emulsions, such as the geometry of the rotor–stator used and the homogenization rate in the primary homogenization. Stable thyme oil-in-water emulsions (30 wt%) containing submicron droplets were formed. Interestingly, laser diffraction results reveal that mean droplet sizes are mainly controlled by homogenization rates and polydispersity by the rotor–stator geometry used in the first step of homogenization. In addition, higher droplet sizes for pre-emulsions seem to be a key factor in order to reduce both the degree of recoalescence and the size of the droplets in the second homogenization step. Furthermore, higher droplet sizes in the pre-emulsion favour higher physical stability of the final emulsions. Finally, this research highlights the importance of controlling primary homogenization conditions for the physical stability of microfluidized emulsions that contain natural ingredients.

Introduction

There is a growing interest in the use of essential oils, like thyme oil, due to their antimicrobial activity and biocompatible properties. These properties make them widely used in fields such as food, pharmaceutical and cosmetics. In addition, these natural resources have been recognized as GRAS (Generally Recognized As Safe) by U.S. Food and Drug Administration [1], which makes them the most promising natural antimicrobials. Thyme oil, obtained from *Thymus vulgaris* L., is divided into two different classes: red and white. Red thyme oil is the product of the distillation of dried thyme leaves while white is obtained from red thyme oil re-distillation [2]. The potential application of white thyme oil as a food preservative to replace synthetic chemicals, which are potentially toxic to humans, has been demonstrated [3]. Nevertheless, the major disadvantage of utilizing essential oils is their high volatility and their tendency to oxidise. Emulsion-based systems are a very attractive way to increase their stability by reducing their volatility and conserving their biological characteristics [4]. Oil-in-water emulsions are systems consisting of oil phase dispersed in aqueous phase, usually in the form of droplets. These systems are important vehicles for the delivery of hydrophobic bioactive compounds and have found a wide range of applications in many industries including food, pharmacy, cosmetics and agrochemistry [5–7].

Emulsions need an emulsifier since they are thermodynamically unstable. In recent years, the use of green surfactants has been attracting attention. Appyclean 6548, a new surfactant derived from wheat waste (alkyl poly pentoside), fulfils all the requirements to be considered a green surfactant; namely it is derived from renewable resource and manufactured by environmentally friendly processes. In fact, this emulsifier possesses the ECOCERT certification.

In order to produce emulsions with specific physicochemical and functional properties, controlling the droplet size distribution is required. Droplet size distributions are strongly influenced by the emulsification method and conditions used. Emulsions can be developed using low-energy and high-energy approaches. However, the latter are more likely to be used in the food or cosmetic field since their scale-up is easier and the equipment is more readily available. A multitude of homogenizers, such as rotor–stators, ultrasounds, colloid mills or high-pressure valve homogenizers, can be used to prepare these systems. Emulsions can be prepared in two steps: primary and secondary homogenization. The aim of the primary homogenization is to create droplets of dispersed phase such that a coarse emulsion is formed. The goal of

* Corresponding author.
E-mail address: alfaro@us.es (M. C. Alfaro).

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the second step (secondary homogenization) is to reduce the size of pre-existing droplets, which usually involves the use of a different homogenizer. There are several studies concerning the influence of homogenization rate and the device used on physical stability, rheology and droplet size distribution for emulsion-based systems [8–13]. One homogenizer used in the second step that has received a lot of attention recently is the Microfluidizer, due to several results that suggest its use provides narrower distributions at smaller droplet sizes [14,15]. Some research has been carried out in order to extend our knowledge about the influence of the number of cycles and homogenization pressure in Microfluidizers [9,16,17]. Furthermore, the comparison between using single- or dual-channel Microfluidizers and one or two interaction chambers have been reported [18–20]. The main novelty of this research is the study of the influence of the pre-emulsion properties on the droplet size distribution and physical stability of the final emulsions. For this reason, the present work aims to provide an exhaustive study of the influence of the primary homogenization on microfluidized emulsion properties. On top of that, a further aim of this research was to obtain stable ecological emulsions of thyme oil formulated with an emulsifier obtained from wheat. The results of this study could be useful to design and develop functional oil-in-water emulsions.

Materials and methods

Materials

30 wt% oil-in-water emulsions with a surfactant (Appyclean 6548) concentration of 3 wt% were prepared using thyme essential oil as dispersed phase. Thyme oil (*T. vulgaris*) was purchased from Sigma–Aldrich. The emulsifier (Appyclean 6548) used was an alkyl poly pentoside provided by Wheatoleo. This non-ionic surfactant is solid and immiscible in water at room temperature. Deionised water obtained from a water purification system was used for the preparation of all samples. Sodium azide (0.1 wt%) was added to the formulation in order to inhibit the growth of microorganisms. All of the chemicals were used as received.

Preparation of oil-in-water emulsions

The surfactant was dispersed into the oil phase. 5.55 g of Appyclean 6548 was added to 55.5 g of thyme essential oil for emulsion batches of 185 g. Then, the surfactant was melted and dissolved in the essential oil at 70 °C in a laboratory oven according to the supplier's instructions. The continuous phase was prepared by dissolving 0.185 g of sodium azide in the corresponding amount of water.

Two different rotor–stator devices (Ultraturrax T50 with a S50NG45F dispersion unit and Silverson L5M equipped with an emulsor mesh screen) were used for the primary homogenization. Pre-emulsions were produced by adding the oil phase at 20 °C to the continuous phase (deionised water and sodium azide), also at 20 °C, using a syringe pump at a constant flow rate of 21.67 mL/min during 180 s, and then were homogenized for an additional 30 s. The homogenization speed was fixed at 2000, 4000 or 6000 rpm using Ultraturrax T50 or Silverson L5M, so three batches of six different pre-emulsions were developed. The initial and final temperatures of the emulsion and the amperage were measured during the primary emulsification process in order to determine the power density.

The secondary homogenization was performed using a Microfluidizer M110P (interaction chambers F12Y) at 2500 psi (172 bar) for one pass. These conditions were chosen in order to highlight the importance and influence of the primary homogenization for the development of oil-in-water emulsions by microfluidization. The outlet sample tube of the Microfluidizer was cooled with water at 20 °C. The pH values for the continuous phases and the final emulsions were 5.94 and 6.42, respectively

Droplet size distributions of emulsions

The droplet size distribution and mean droplet sizes were determined using a Malvern Mastersizer X. Volumetric mean diameter ($D_{4,3}$) was used to compare the droplet sizes of different emulsions:

$$D_{4,3} = \frac{\sum_{i=1}^{N} n_i d_i^4}{\sum_{i=1}^{N} n_i d_i^3} \quad (1)$$

where d_i is the droplet diameter, N is the total number of droplets and n_i is the number of droplets having a diameter d_i. Moreover, span was used to study the distribution width of droplet sizes:

$$span = \frac{D(v,0.9) - D(v,0.1)}{D(v,0.5)} \quad (2)$$

where D(v,0.9), D(v,0.5), D(v,0.1) are diameters at 90%, 50% and 10%, respectively, of cumulative volume. The absorption and refraction indexes used for the continuous medium (water) were 0.1 and 1, respectively, whereas the refraction index for the dispersed phase (thyme oil) was 1.50. Droplet size distributions were obtained using a polydisperse analysis. The influence of ageing time on droplet size distributions was studied during 20 days after preparation to analyze and quantify coalescence/Ostwald ripening effects.

Analysis of emulsion physical stability

The physical stability of emulsions whose pre-emulsions were obtained with different emulsification methods was studied and quantified by means of multiple light scattering measurements (Turbiscan Lab Expert) at 25 °C. The results are presented in the form of curves which show intensities of backscattering in reference mode (delta-backscattering, $\Delta BS\% = BS_t\% - BS_0\%$) as a function of time and height. The Turbiscan Stability Index (TSI) has been used for the comparison and estimation of the emulsion stability. The value of this parameter was calculated with the special computer program using the equation:

$$TSI = \sum_i \frac{\sum_h |scan_i - scan_{i-1}|}{H} \quad (3)$$

where $scan_i$ is the average backscattering for each time (i) of measurement, $scan_{i-1}$ is the average backscattering for the (i − 1) time of measurement and H is the number of scans carried out on the sample.

Flow curves

Flow curves for pre-emulsions and emulsions were obtained by means a controlled-stress rheometer, CS Haake-MARS (Thermo), and a sandblasted Z20 coaxial cylinder (Ri = 1 cm, Re/Ri = 1.085) at 24 h of ageing time and they were performed at 25 °C. A step-wise protocol in the 0.1–20 Pa shear stress range was applied. All samples showed Newtonian behaviour which was fitted to Newton's law.

All measurements were done in duplicate and the values shown are the average of the two replicates.

Results and discussion

Fig. 1 illustrates the power density (P_v) as a function of the residence time for five replicates of the pre-emulsion processed at