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Production of vegetable oil in milk emulsions using membrane emulsification

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Abstract

The production of emulsions using milk as the continuous phase has a number of applications of interest from the food industry's point of view. In addition, producing an emulsion with a narrow drop size distribution is interesting since their increased stability could avoid Oswald ripening and creaming.

Membrane emulsification is a novel technique which helps to obtain a narrower distribution compared to other emulsification techniques such as homogenizers or ultrasound. Moreover the use of membrane emulsification may reduce the energy cost.

The food industry is interested in reducing the use of food additives, both to save money and increase consumer acceptance. Therefore the aim of this work was to investigate the use of the intrinsic emulsifying capacity of milk proteins to act as stabilizers for oil droplets produced by membrane emulsification.

Using tubular SPG membrane (4.8 μm pore diameter) in recirculation mode, at dispersed phase fluxes of either 5 L/hm^2 or 50 L/hm^2, a stable final emulsion of 30% w/w oil was obtained. The fat globule size distribution was more bimodal at higher oil concentrations and at the higher flux.

Keywords: Membrane emulsification; Milk; Drop size; Operating parameters; Milk proteins

1. Introduction

Emulsions are commonly used in several industries such as the cosmetic, pharmaceutical, food, and paint industries. The stability of the emulsions formulated is important, since, the more stable the emulsion is, longer is their life. Emulsion stability is closely related to the drop size distribution, since wider drop size distributions may enhance the Oswald ripening effect, increasing the size of the larger drops which in turn favours drop coalesce and creaming. The

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required emulsion stability depends on the application, it can be years in the case of cosmetic applications or just days in some food applications, but in all cases should be stable during the time the components present in the emulsions keep their properties and thus fit for its intended use.

Milk is a liquid that contains water, minerals, lactose, fat and proteins. The proteins present in milk could be divided into three groups:, the whey proteins, proteins of milk fat globule membrane (MFGM), and the caseins in aggregates known as casein micelles, which represent 80% of the total milk proteins [1]. The main casein proteins are α_{S1}-casein, α_{S2}-casein, β-casein, and κ-casein, all of them are responsible of the formation of complex micelles. The α-caseins and β-caseins form the main micelle structure while the κ-caseins are present around the micelle structure and give more stability to the structure [1,2]. In native milk the whey proteins and casein are not associated with fat; the MFGM proteins have only recently been well characterized [3,4].

During homogenization of milk, as the size of fat globules is decreased and their number and total surface area increased, caseins are incorporated into the newly created fat surface and provide stability against coalescence. Homogenization is also used for the production of recombined milk from skim milk powder and butter fat, and of filled milk, with fat of non-dairy origin such as vegetable oils.

Dairy emulsification processes need to control the drop size and distribution drop size, since a change in these factors may alter rheological and organoleptic properties of the final product [5]. For larger droplet sizes, there are several techniques used to make emulsions, as for example high speed mixers or ultrasound techniques. During the last 20 years, an alternative emulsification technique has been studied, "membrane emulsification" or "microchannel emulsification" [6,7]. These techniques produce a narrower drop size distribution than conventional techniques [7], and much lower energy consumption [8].

Membrane emulsification technique had been developed in two different designs—direct emulsification and premix emulsification. (i) In direct membrane emulsification, the continuous phase flows tangentially to the membrane surface while the dispersed phase is pressed through the membrane's pores, the drops of the dispersed phase grow at the openings of pores in the membrane and when they reach a certain size, detach. (ii) Premix emulsification is based on the formation of a pre-emulsion by a traditional mechanical technique, which is then passed through the membrane in order to obtain a narrow drop size distribution.

During membrane emulsification process several forces act in order to detach the droplets found at the membrane surface (Fig. 1). These forces are described extensively elsewhere [9,10]. In order to produce drops of dispersed phase, the pressure should be enough to allow the dispersed phase to overcome the interfacial tension and pass through the membrane pores.

The minimum pressure required is the critical pressure (P_c), P_c which is calculated from equation 1.

$$P_c = \frac{4\gamma\cos\theta}{d_p} \tag{1}$$

where γ is the oil/water interface tension, θ is the contact angle between the dispersed phase and the membrane surface and d_p is the pore diameter.

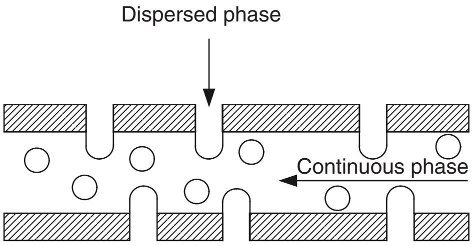


Fig. 1. Schematic diagram of membrane emulsification.

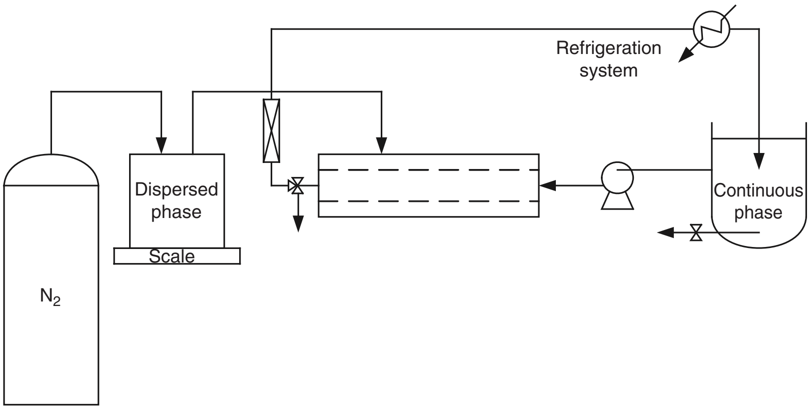


Fig. 2. Schematic diagram of the equipment used in the experiments.

In membrane emulsification, different types of membranes are used, as for example Shirasu porous glass (SPG) membranes and ceramic membranes [11]. The diameter of the drops produced is approximately between 2 and 10 times the diameter pore [7,12]. The membrane should by hydrophobic for the formation of W/O emulsions and hydrophilic for the formation of O/W [7,12].

In the present work we report, for the first time to our knowledge, the use of membrane emulsification without added surfactant, utilizing only milk's intrinsic capacity to stabilize an emulsion.

This work has a potential number of applications in dairy industries as culinary creams and producing creams with properties not normally obtained without the addition of external emulsifying agents and with a clean label.

2. Materials and methods

2.1. Materials

The fluids used for emulsification are market skimmed milk (with less than 0.1% fat, Skånemejerier, Malmö, Sweden) and two different oils—market rapeseed oil (Zeta AB, Stockholm Sweden) and soy oil (Sigma Aldrich Sweden AB, Stockholm).

A tubular membrane (SPG Technology Ltd., Japan) was used, with a nominal membrane pore size of 4.8 μm, effective membrane area 55 cm^2, tube length 250 mm and inside diameter 7 mm.

2.2. Equipment

Mechanical emulsification was performed using Ultra Turrax mixer TP 18-10 (Janke and Kunkel KG, Staufen, Germany).

The membrane emulsification equipment is depicted in Fig.2. It consisted of a tank containing the continuous phase which was pumped through the membrane tube in the module, and re-circulated. The initial volume of the continuous phase was 900 ml. The dispersed phase was added from a vessel pressured by nitrogen. The dispersed phase passed through the external part of the membrane to the inside through the porous structure of the membrane forming small drops. The emulsion was re-circulated until the desired concentration of the dispersed phase was achieved.

The loss of weight of the dispersed phase vessel indicated the quantity of oil present in the emulsion.

To avoid temperature increase in the system, a cooling mantle was used in the circuit.

The continuous phase flow rate was 200 L/h in all experiments and the pressure of the dispersed phase was 0.75 bar or 0.90 bar.

2.3. Cleaning procedure

After each experiment the equipment was cleaned by the following procedure. The membrane was rinsed with deionised water at room temperature twice, then cleaned with the detergent Ultrasil 56, 0.5 % w/w at 45ºC, and rinsed again with deionised water at 50ºC, if oil was observed in the last rinse water, the procedure was repeated until the water obtained was apparently clean.

The membrane was then removed from the module for the second cleaning step because SPG membranes are sensitive to high pH . The module was reassembled and cleaned by pumping water at 60ºC through the circuit for 30 min. Then a solution of 1.5% w/w, of detergent Ultrasil 11 (Henkel AB, Stockholm Sweden) was prepared at 50ºC and run through the circuit for 40 min, and then rinsed with deionised water at 60ºC several times until the water was clear.

The dispersed phase vessel was cleaned just when the dispersed phase changed, using warm water at 50ºC and the detergent Ultrasil 11, and rinsed several times with water at room temperature until the water was completely clear; the vessel was then carefully dried before re-filling.

2.4. Particle size measurements

The particle size of the emulsion was measured by laser diffraction sizer Coulter L5130 and observed by a microscopy with a camera SONY model DXC 1514P (both LRI Instrument AB, Lund Sweden).

3. Results

3.1. Mechanical and membrane emulsification

Assuming typical values of interfacial tension and contact angle of 18 mN/m and 150ºC respectively, the critical pressure is 0.13 bar for membranes with pore size of 4.8 μm.

In this membrane emulsification experiment with milk and soy oil, at dispersed phase pressure of 0.90 bar, a constant oil flux of 50 L/hm^2 was observed.

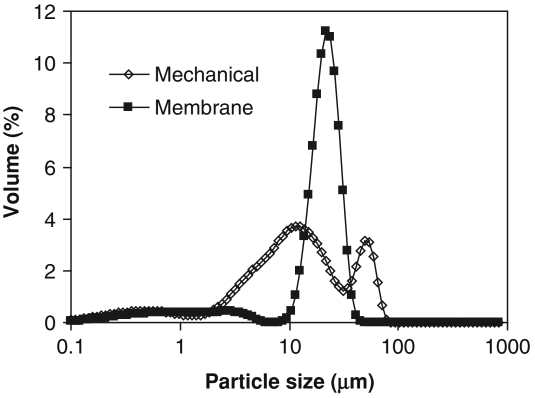


Fig. 3. Particle size obtained after emulsification with mechanical process versus membrane emulsification.

For comparison, a trial was made using mechanical equipment (Ultra Turrax) for 2 min at 5000 rpm. In Fig. 3 particle size versus volume is represented for both experiments for the concentration of 6 % w/w soy oil in both cases.

A clear difference was seen, a narrower size distribution with one peak is present when membrane emulsification was used, while using mechanical emulsification the peak was wider and two peaks were present, even so the mean value in both cases were very close 10.1 μm for mechanical emulsification and 11.8 μm for membrane emulsification.

Using membrane emulsification the ratio between nominal pore size and average drop size was slightly more than 2. We have not made an independent determination of the membrane pore size, but the result might indicate that the tangential drag force generated by the flowing continuous phase may be assisting droplet detachment under the operating conditions used in this study.

3.2. Influence of type of oil used

In order to see if different types of oil would affect the emulsification result, a comparison of

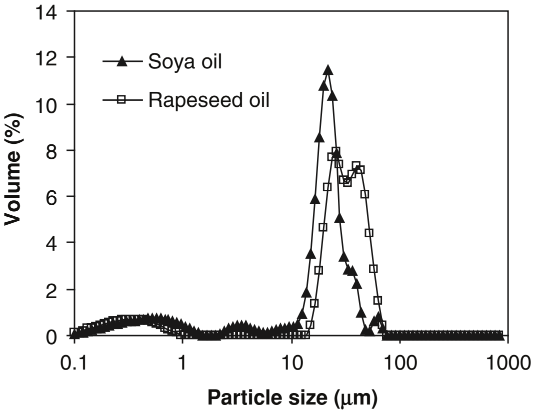


Fig. 4. Particle size obtained after membrane emulsification with 15% w/w of oil as dispersed phase. Pressure = 0.90 bar.

15% w/w of soy and rapeseed oil was made. The particle size distributions obtained is presented in Fig. 4. The volume means ($d_{4,3}$) values corresponds to 12.4 and 19.8 μm for soy and rapeseed oil respectively.

The soy oil emulsion was almost unimodal whereas the rapeseed oil emulsion was bimodal. It is likely that this difference depended on the difference in the purity of the oils. The rapeseed oil used in the present work was a commercial food oil and did not have the same level of purity as soy oil which was analytical grade from Sigma Aldrich. Small impurities presents in vegetables oils tend to reduce interfacial tension and could absorb differentially to the membrane and thus affect its wetting properties.

3.3. Effect of oil concentration

In order to study the milk proteins' capacity to stabilize oil a series of experiments were carried out.

The experiments started with skimmed milk continuous phase, and rapeseed oil was passed through the membrane. When the concentrations of 10, 15, 20, 25 and 30% w/w were reached, samples were taken. Calculations to account for

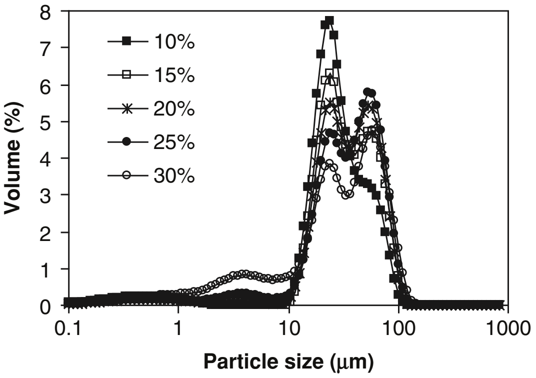


Fig. 5. Particle size, membrane emulsification at 0.75 bar dispersed phase pressure, comparing several oil concentrations.

sample volume being removed were made and taken into account during the experiments.

The flow rate of the continuous phase was 200 L/h in all cases. Experiments were performed at two different pressures, 0.75 and 0.90 bar, corresponding to permeate fluxes of 5 and 50 L/hm^2 respectively. In membrane emulsification there is a theoretical minimum pressure which needs to be exceeded for flow to begin (Eq. 1). In this case it is on the order of magnitude of 0.1 bar. However, due to the pore structure of the membrane, not all pores become active at once. For this reason we cannot assume a linear relationship between pressure and

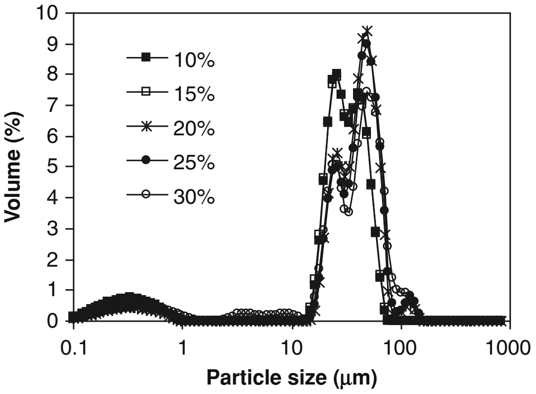
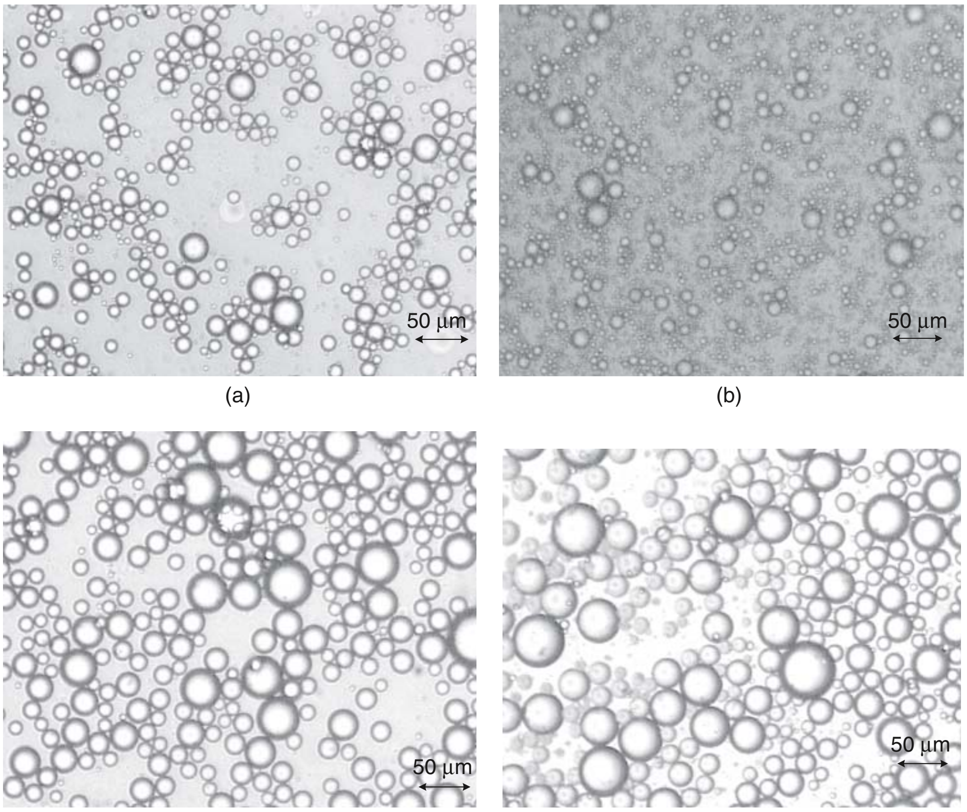


Fig. 6. Particle size, membrane emulsification at 0.90 bar dispersed phase pressure, comparing several oil concentrations.



(a) (b)

(c) (d)

Fig. 7. Microscopic images of emulsification at 0.75 bar (a and b) and 0.90 bar (c and d) with oil concentration of 10% (a, c) and 30% (b and d).

flux, over all pressures. The activation of pores and the accelerated rate of drop formation which ensues as pressure increases beyond the critical pressure may explain the tenfold increase in flux between the two pressures used.

Good results were found for both dispersed phase pressures. The particle size distribution is presented in Figs. 5–6 for both pressures. The distribution was bimodal and in the course of the experiment, the proportion of the larger droplets increased. An illustrative example of the microscopy images of the fat droplets is given in Fig. 7.

To test whether the coarsening during the course of the experiment was caused by the recirculation, an emulsion with 30% w/w of

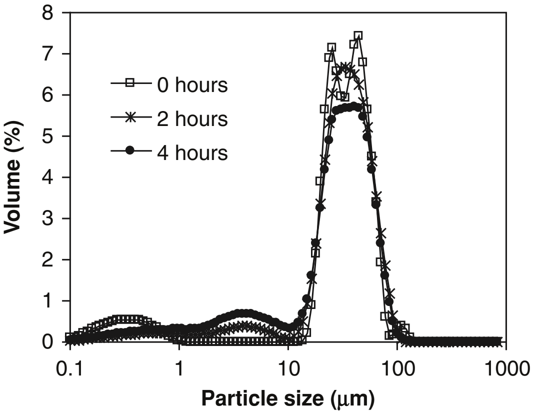


Fig. 8. Particle of the emulsion with 30% w/w of oil produced at 0.90 bar dispersed phase pressure after 0, 2 and 4 h recirculation.

rapeseed oil was made at 0.90 bar, and once the concentration of 30% w/w was achieved, the emulsion was pumped for an additional 4 h through the circuit and, samples were removed every two hours for drop size analysis. The results are presented in Fig. 8.

The two typical peaks from rapeseed oil emulsions tended to disappear with time and a peak of intermediate size was formed, thus the coarsening of the emulsion must be caused by some other factor, possibly again changes in the properties of the membrane with time. This may be an important factor to consider when comparing performance of membrane emulsification operating conditions.

3.4. Emulsions stability

All emulsions made were stored at 8°C for four days and particle size was measured in order to detect stability, since an increase of particle size will give an indication of coalescence and instability.

In Figs. 9–10 the results of particle size for the emulsions containing 30% w/w of rapeseed oil obtained after four days at 0.75 bar and 0.90 bar respectively are presented.

For all oil concentrations, no changes in droplet size were observed during 3 days; on day 4 the changes could be attributed to microbial deterioration as the samples spoiled shortly after.

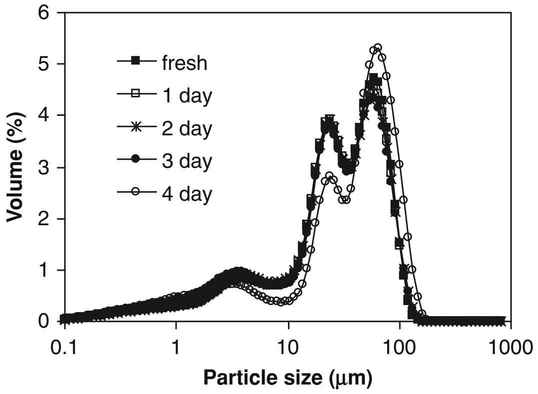


Fig. 9. Stability of emulsion with 30% w/w, emulsified at 0.75 bar dispersed phase pressure, over four days of storage at 8ºC.

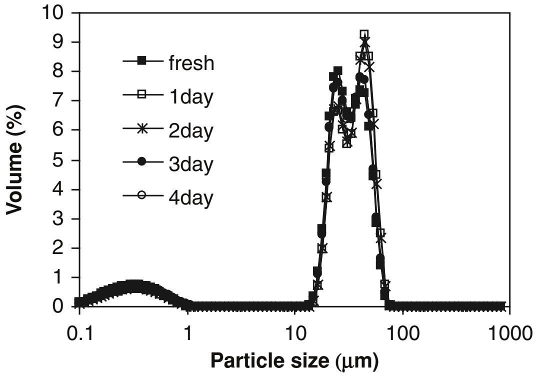


Fig. 10. Stability of emulsion with 30% w/w, emulsified at 0.90 bar dispersed phase pressure, over four days of storage at 8ºC.

4. Conclusions

Membrane emulsification is a suitable technique for the emulsification of oil and milk, the existing milk proteins could stabilise the emulsion without the use of any external agents as surfactants, achieving a concentration of 30% w/w of oil.

The drops size obtained were around 2 to 6 times the size of the membrane pore. The type of oil affected droplet size, the use of oil free of impurities offered narrower size distribution, nevertheless using a commercial oil, stable emulsions were also obtained.

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