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Titre / Title:
Emulsification par membrane, un procédé économe en énergie : exemple des bases laitières à foisonner

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Catégories / Categories

- New challenges. New ambitions.
- 4.2 New emulsification technics

Communication / Paper:

Cross flow membrane emulsification is a recent technique; it results in thin w/o or o/w emulsions, obtained in controlled shear conditions (1, 2). Its interest consists in the low energy density provided to the system ($10^3$ up to $10^5$ J.m$^{-3}$ versus $10^5$ up to $10^6$ for the other usual techniques); this allows the processing of raw materials sensitive to great shear rates and/or high temperatures.

The mechanism is based on the detachment in a circulating continuous phase of droplets of dispersed phase which have been forced through pores of microfiltration membranes (Fig. 1).

Droplets grow at the mouth of pores, distort and finally detach when their size becomes sufficient. This phenomenon depends on the balance between forces which tend to detach droplets (the drag force from the circulation of the continuous phase and the pushing force caused by the pressure drop between the two parts of the membrane) and forces which oppose to the detachment (interfacial forces).

Therefore, the characteristics of the emulsion, especially its size distribution, are governed by parameters related to the membrane (nature, hydrophilicity, pore size and uniformity), working conditions (transmembrane pressure, tangential velocity, dispersed phase flux, volume fraction of the dispersed phase, viscosity of the two phases) and the emulsifiers needed to stabilise the emulsion (interfacial tension reduction, velocity of diffusion to the interface).
The size distribution of sunflower oil/water emulsions depends much more on the membrane pore size and the shear rate at the membrane surface than on the oil flux (3), either with a fast emulsifier (SDS), or two proteins with very different structures (b casein and 11S soya globulin) at low (5%) and high (up to 32%) oil volume fraction.

With a fast emulsifier, the size distribution of the emulsion is mainly influenced by the membrane pore size: it reached 0.7 and 2.2 mm for pore size of 0.1 and 0.5 mm respectively. With a proteic emulsifier, the emulsions were coarser than those stabilised by SDS, and were rarely monodisperse. The emulsions stabilised by 11S globulins were thinner than those stabilised by b casein.

**Emulsions containing up to 32% of oil could be made by microfiltration. The influence of the factors is still the same, even at high oil volume fraction. The increase of the oil volume fraction leads to an increase of the droplet size and of their dispersion; mainly above 25%. The membrane emulsions were more resistant against coalescence than emulsions obtained with a rotor/stator system.**

In this study, we have compared membrane and high pressure homogenisation for emulsifier sweet dairy products which were further whipped, giving toppings (4, 5).

### 1 MATERIAL AND METHODS

#### 1/1. Formulation

The topping formulation contained 20% w/w of anhydrous milk fat (Lactalis, France), 0.35% of E472B (lactic ester of fatty acid mono and di-glyceride, having a low HLB, Degussa, France),
6.5% of skimmed dairy powder (Lactalis) and 15% of sucrose (Beghin-Say, France). The continuous phase contained additionally a stabilizer: 0.5% of 175 bloom degree gelatine issued from bovine skin (Degussa) or a mix of hydrocolloids constituted of 0.05% xanthan, 0.05% carrageenan and 0.1% guar (Rhodia Food, France), called X.

1/2 Membrane Emulsification

The cross flow microfiltration loop was equipped with commercial ceramic Pall-Exekia membranes (Bazet, France): 2 profiles P19-40 in series (area 0.48 m²). The pore sizes were 0.1 and 0.5 mm respectively and the corresponding skin layer ZrO₂ and alumin.

The dispersed and aqueous phases were heated separately to 80°C. The aqueous phase was pumped into the retentate loop, then the fatty phase was pumped into the continuous phase through the membrane with a controlled flux (6 or 14 kg h⁻¹ m⁻²) at the highest tangential velocity allowed by the equipment (3.4 m.s⁻¹) in order to maximise the wall shear stress. When the final fat volume fraction was reached, the emulsion (10 kg) were cooled under mixing then stocked at 4°C during 12 hours for maturing then dispatched for being whipped.

1/3 Emulsification by high pressure homogenization

Some emulsions were prepared by pre-emulsification, high pressure homogenisation, sterilization, cooling and finally maturing at 4°C.

Pre-emulsification was made with a rotor/stator (turbine) system. The coarse emulsion was passed in a two effect high pressure homogenizer (APV Gaulin, Evreux, France). In the high pressure homogenisation step, a coarse emulsion is forced under pressure through a small adjustable gap named valve. Due to high shear forces, turbulence, cavitation and recirculation, the size of the emulsion is dramatically reduced. The applied pressure was 10 MPa for the first stage and 1 MPa for the second one. The emulsion was further sterilized (130°C, 15 s) then cooled at 4°C in 30 s in a plate sterilizer coupled with a plate exchanger, and finally maturated at 4°C during 12 hours.

1/4 Whipping of emulsions

Emulsions were whipped on a continuous rotor/stator system (volume 70 ml), at a rotation speed comprised between 400 and 1,200 rpm (6). Whipping was made under pressure (3.5±0.5 bars) with a ratio of volumic flow rates of gas (nitrogen) and emulsion near 2 giving a theoretical overrun of 200%. The inlet and outlet foamer temperatures were maintained at 4-5°C and 10°C maximum respectively.

1/5. Characterisation of the emulsions
Size distribution of droplets was measured by laser diffraction instrument (Mastersizer 2000, Malvern, R.-U.) after dispersion of the emulsions in 1% SDS, giving the volume average $d_{43}$ of droplets.

Emulsion flow curves were measured between 10 and $10^3$ s$^{-1}$ at 10°C on a controlled stress rheometer equipped with coaxial cylinders.

1/6. Characterisation of foams after whipping

The overrun OR was calculated as $\text{OR} = (r_{\text{mix}} - r_{\text{foam}})/r_{\text{foam}}$ where $r_{\text{mix}}$ and $r_{\text{foam}}$ (kg.m$^{-3}$) are the emulsion and foam densities respectively.

The bubbles are almost spheric; consequently, the gas dispersion was evaluated from their Sauter diameter $d_{32}$. The foam rheology was measured with the same apparatus than for emulsions, with a plate-plate geometry. After determination of the linear viscoelasticity domain of samples, the mechanical spectra were measured for frequencies comprised between 0.1 up to 10 Hz at 2% distortion, giving the shear storage $G'$ and shear loss $G''$ modules.

Foam bubble size was measured by optic microscopy coupled with a digital camera and an on-line image analysis system. Images were taken continuously at the foamer outlet.

2 RESULTS

Membrane emulsification was not impaired neither by emulsion viscosity nor by fat volume fraction (20%). In a same manner, membrane cleaning needed no extra detergent in comparison with those currently used for cleaning membranes having treated proteins.

2/1 Characteristics of emulsions

High pressure gelatine emulsions were monomodal ($d_{43} = 1.1$ mm) but membrane emulsions were not (Fig. 2). For a 0.1 mm membrane, there were two peaks of same area, but the coarser peak was dominating for 0.5 mm pores. On the opposite, X emulsions were monomodal; this difference between gelatine and X emulsions can result from the ratio between the viscosities of the dispersed and continuous phases and consequently the droplet fractionation modes. In fact, the breakdown of emulsion droplets may vary in laminar conditions upon this ratio: the emulsion will be monomodal if it is in the centre of the droplet, and multimodal if it is peripheral (7).

On the whole, membrane emulsions were coarser than the others, owing to the lesser energy density brought to the system. The greater size was obtained for the greater pore size (0.5 mm). Increasing the fat flux made coarser emulsions ($d_{43} 3.8$ mm versus 2.5).
The substitution of gelatine by X mix provokes an increase of $\text{d}_{43}$, whatever the technology used (X high pressure emulsions have a $\text{d}_{43}$ reaching 1.9 mm).

The variations of apparent viscosity in function of the speed gradient show the influence of the technology and the stabiliser used (Fig. 3). In this way, membrane emulsions have intermediate apparent viscosities versus high pressure ones. On the other hand, whatever the technology used, X emulsions are always more viscous than gelatine ones, owing to an increase of the viscosity of the continuous phase. In this case and according to Walstra (7), the lower viscosity of membrane emulsions can be explained by their greater droplet size. This droplet size - viscosity relation can also used to compare membrane emulsions, but cannot be used to compare the viscosities of membrane and high pressure emulsions because high pressure ones are monomodal while membrane ones are bimodal when stabilised by gelatine, leading to increased viscosities.
2/2 Characteristics of foamed emulsions

The overrun (OR) of the foams obtained from high pressure gelatine emulsions reached 175% when the rotation speed of the foamer equal to 400 rpm, but decreased to 110% for 600 rpm (Table 1). On the opposite, OR of foams issued from high pressure X emulsions increased with the rotation speed of the foamer from 120% at 400 rpm up to 180% at 800 rpm and above. At the same time, bubble d_{32} decreased. The difficulties to foam gelatine emulsions are due to their low viscosity: for a same overrun, X foam G’ is ten times more than does gelatine foam one.

Emulsions manufactured with 0.5 mm membrane did not foam, contrary to all the emulsions obtained with 0.1 mm membrane: their OR was close to the stœchiometric value (200%) whatever the rotation speed of the foamer. G’ of foamed membrane emulsions stabilized by gelatine was comprised between 500 and 1000 Pa., which means a firm topping. G’ was increased by more than 3, even at low rotation speed for emulsions stabilized by hydrocolloids. Moreover, the average bubble size decreased and was independent of the rotation speed, with a narrow size distribution (Fig. 4).

Table 1 Influence of the foamer rotation speed (Rs) on the characteristics of the foamed emulsions. Abbreviations (Cf. Figure 2); OR overrun; G' storage module (Pa); d_{32}: Sauter diameter of bubbles (mm).

<table>
<thead>
<tr>
<th>Rs (rpm)</th>
<th>G-0.1-6</th>
<th>X-0.1-6</th>
<th>G-HP</th>
<th>X-HP</th>
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<tr>
<td></td>
<td>OR - G'</td>
<td></td>
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<tr>
<td>RPM</td>
<td>$d_{32}$</td>
<td>OR</td>
<td>G$'$</td>
<td>175 - 240 -</td>
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<td>------</td>
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<tr>
<td>400</td>
<td>200 - 1000 - 112</td>
<td>180 - 3300 - 31</td>
<td>130</td>
<td>120 - 300 - 67</td>
</tr>
<tr>
<td>600</td>
<td>200 - 960 - 113</td>
<td>180 - 3400 - 30</td>
<td>110 - 60 - 116</td>
<td>47</td>
</tr>
<tr>
<td>800</td>
<td>200 - 800 - 110</td>
<td>180 - 3000 - 33</td>
<td>180 - 2100 - 46</td>
<td></td>
</tr>
<tr>
<td>1,000</td>
<td>200 - 500 - 93</td>
<td>nd</td>
<td>180 - 1600 - 44</td>
<td></td>
</tr>
<tr>
<td>1,200</td>
<td>200 - 850 - 77</td>
<td>180 - 2800 - 33</td>
<td>180 - 2200 - 45</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4. Structure of foamed membrane emulsions whipped at 800 rpm. Abbreviations Cf. Figure 2.
These results show that whipping of emulsions depends greatly on emulsion viscosity and size. In this way, 0.5 mm membrane emulsions were not sufficiently viscous and thin to allow a good whipping. Similarly, high pressure emulsions stabilized by gelatine show a low viscosity, which limits the foamer performances. In this case, owing to the shear thinning behaviour of emulsions, an increase of the rotation speed, even though it increases the energy brought to the system, decreases this viscosity, and consequently decreases the bubble breakdown force and favours their coalescence.

On the opposite, the high pressure emulsions stabilized by hydrocolloids were the most viscous and need a high rotation speed to be correctly whipped.

The emulsions obtained with 0.1 mm membrane were sufficiently thin and viscous to be whipped in an optimal manner.

These good results show that a very thin emulsion is not needed for being correctly whipped. Indeed, more thinner the emulsion droplets means that more fat-water interface is created, that decreases the proportion of proteins remaining in the continuous phase of the emulsion. These proteins will be needed after to stabilize the new air-water interfaces created by whipping. Moreover, a relative broad size distribution seems to favour whipping, as demonstrated in the case of membrane emulsions.

3 CONCLUSION

The results show that whipping dairy emulsions is very sensitive to rheological and size characteristic of the emulsions. In these conditions, membrane emulsification represents a serious alternative versus currently used processes for obtaining foamed emulsions like topping. These emulsions are coarser and have a larger size distribution than high pressure emulsions. In spite of this, emulsions manufactured with 0.1 mm membrane gave the best whipping results due to their size and rheological characteristics.

Although they are not as thin as those obtained with high pressure homogenizers, this means that the interfacial area of fat droplets is lower, so leaves free proteins in the continuous phase, owing to a good stabilization of the air/water interfaces further created by whipping. The whipped emulsions coming from membrane emulsions stabilized by polysaccharides where very firm and stable, due to their rheological characteristics and the size of the bubbles.

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