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Production of O/W emulsions using SPG membranes, ceramic α - Al_2O_3 membranes, microfluidizer and a microchannel plate – a comparative study

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Abstract

The O/W emulsions containing Tween 80 dissolved in demineralized water as the continuous phase and vegetable oil as the dispersed phase were produced using different emulsification methods. The influence of operating conditions on the emulsification results was discussed and compared.

1. Preface

The most commonly used membranes for the preparation of emulsions are Shirasu porous glass (SPG) membrane developed by Nakashima and Shimizu [1] and ceramic Al_2O_3 or Zr_2O_3 membranes [2, 3], conventionally used for microfiltration. The aim of this study is to compare the emulsification process and the properties of O/W emulsions prepared using SPG membranes and ceramic Al_2O_3 membranes under the same operating conditions and using the same phase compositions. In addition, the results obtained using microfluidizer[®] and a silicon microchannel (MC) plate were also given.

2. Experimental

Vegetable (rape seed) oil (Floreol GmbH) with a viscosity of 58 mPa s and a density of 920 kg m⁻³ was used as the dispersed phase. The continuous phase was 2% (w/w) Tween 80 (polyoxyethylene (20) sorbitan monooleate, Merck GmbH) dissolved in demineralized water. The oil was treated before usage with 60 g l⁻¹ silica gel (Silica gel 60, Merck) to remove surface-active species and components which could cause membrane fouling. This treatment involved adsorption of impurities on silica particles in a stirring vessel for 24 h, followed by centrifugation at 9000 rpm for 2 × 30 min.

The tubular SPG membranes (10 mm outer diameter × 0.7 mm wall thickness) were supplied from SPG Technology Co., Ltd (Sadowara, Japan) with a mean pore size in the range of 0.4-6.6 μm and wall porosity between 0.53 and 0.60. The effective length of the membrane tubes was 116 mm and the membrane area 31.3 cm². The Al_2O_3 membranes were supplied from Membraflow GmbH & Co. KG (Aalen, Germany) with a mean pore size of 1.4 and 0.5 μm . These membranes are composed of thin skin layer (with a thickness of 20-30 μm and porosity of 0.35), supported by a porous substructure (2 mm thickness). The silicon MC plate was consisted of microchannels with 16 μm width, 7 μm depth, and 70 μm length containing a terrace with a width of 50 μm and a length of 60 μm . The experimental set-up used in this work for MC emulsification was given elsewhere [4].

The experimental set-up used for membrane emulsification (ME) is shown in Fig.1. The continuous phase was recirculated in cross flow inside the membrane using a Netzsch model NL 20 Mohno-pump (Waldkraiburg, Germany). The Reynolds number inside the membrane tube was 1700-34000 and the

Fig. 1 (left): Schematic diagram of the cross-flow membrane emulsification system used in this study; Fig. 2 (right): Schematic diagram of the experimental system used for microfluidization.

shear stress at the membrane wall was 0.3-140 Pa. The oil phase was placed in a pressure vessel and introduced at the outer space of the module by compressed air. The weight of the oil phase permeated through the pores was measured by a digital balance on which the pressure vessel rested. The balance was interfaced to a PC computer to continuously collect time and mass data. After each experimental series, the whole ME system was cleaned in place with 1 wt % cleaning agent P3-ultrasil 53 (Henkel KGaA) at 323 K. After that, the module was dismantled and the membrane (SPG or α -Al₂O₃) was additionally cleaned by ultrasonic treatment for several hours using commercial detergent solutions.

The experimental set-up for emulsification using microfluidizer[®] (MF) is shown in Fig. 2. The microfluidizer[®] (Microfluidics Corp., Newton, USA) is a special type of high-pressure homogenizer, allowing the generation of homogenizing pressures of up to 2750 bar. Inside the microfluidizer valve the premix is divided into two streams which collide at high velocities into a single stream afterwards. In this study, a single pass or two consecutive passes of the premix through the valve were applied. The droplet size distribution for all samples was measured by a Coulter LS 230 particle size analyser using PIDS technology, which allowed the detection of droplets in the range of 0.04-2000 μ m.

3. Results and discussion

Fig. 3: Influence of emulsification method on droplet size distribution (dispersed phase content $\approx 1 \%$)

As shown in Fig. 3, the SPG membrane is suitable for the preparation of O/W emulsions with a very narrow droplet size distribution over a wide range of mean droplet sizes using a small wall shear stress of 8 Pa. The span of the droplet size distribution of 0.26-0.45 for the SPG membrane was much lower than 1.1-2.3 for the microfluidizer[®] at homogenizing pressure of 50-1100 bar. However, the microfluidizer[®] is a more appropriate device for producing O/W emulsions with the mean droplet size of less than 0.2 μ m. Furthermore, using two passes of emulsion through the homogenizing valve at 1100 bar, a mean droplet size of only 0.085 μ m can be obtained. Using the SPG membrane with the smallest possible mean pore size of 0.05 μ m, a mean droplet size of over 0.15 μ m could be expected, but the dispersed phase flux would be too small for practical applications.

The span of the droplet size distribution was higher for the emulsions produced by using the α -Al₂O₃ than SPG membrane (Fig. 3). However, the obtained span values of 0.51-0.59 for the α -Al₂O₃ membrane at the wall shear stress of 8 Pa and at the dispersed phase flux till 9 l m⁻² h⁻¹ were much smaller than that reported by other authors [3, 5]. E.g., Williams et al. [5] have obtained the span of 0.83 at the oil flux of 8 l m⁻² h⁻¹ using a ceramic α -Al₂O₃ membrane with the pore size of 0.5 μ m.

As shown in Fig. 4, the dispersed phase flux increased with increasing the mean pore size and the transmembrane pressure. The dispersed phase flux was proportional to Δp_{tm}^x , where exponent x was in the range of 2.3-2.7, due to a higher percentage of active pores at the higher transmembrane pressure. The minimal dispersed phase flux was 1.2-4.4 l m⁻² h⁻¹ and under these conditions 1-4 % of the pores were found to be active (open). The capillary pressure, p_{cap} increased with the mean pore size, which is in correspondence with the Laplace equation. It should be noted that for the same membrane (1.4 μ m- α -Al₂O₃), the dispersed phase flux increased with increasing the shear stress in the continuous phase at the membrane surface, which was found earlier by Schröder [2].

Fig. 4 (left): The influence of transmembrane pressure on the dispersed phase flux for SPG and α - Al_2O_3 membranes; Fig. 5 (right): The variation of mean droplet/pore size ratio with pressure ratio.

The ratio of mean droplet to mean pore size increased with increasing the $\Delta p_{tm}/p_{cap}$ ratio (Fig. 5). However, for $\Delta p_{tm}/p_{cap} \leq 2$, the mean droplet size was almost independent on the pressure. For the α - Al_2O_3 membrane, it was even detected a small decrease of the mean droplet size in that range. It can be explained by the fact that when $\Delta p_{tm}/p_{cap} \rightarrow 1$, only the largest pores are active and therefore, the mean droplet size is higher than at somewhat higher pressure, when droplets are also formed at the smaller pores. The droplet/pore size ratio of 3.4 for the SPG membrane at $\Delta p_{tm}/p_{cap} \leq 2$ is very similar to 3.25 reported by Nakashima et al. [6]. Here, the smaller $d_{3,2}/d_p$ ratio was found for the α - Al_2O_3 than for SPG membrane. The influence of transmembrane pressure on the mean droplet size is less pronounced at the higher wall shear stress. It means that at high pressure ratio ($\Delta p_{tm}/p_{cap} > 4$), the shear stress in the continuous phase should be high enough to enable a successful operation. For MC emulsification, the mean droplet size was 2.9 times larger than the equivalent diameter of the MCs.

In the case of ME at $\Delta p_{tm}/p_{cap} \leq 2$, the mean droplet size was almost independent on the dispersed phase content up to 20 % (v/v), as shown in Fig. 6. A small decrease of $d_{3,2}$ with time of 1.1-1.3 % was observed in the range of $\varphi = 1.2$ -5. Presumably, at the beginning of the emulsification process the smaller pores are inactive, which leads to a slightly higher mean pore size at the initial stage of the process. In the subsequent stage, these pores become more and more activated. The microfluidizer[®] (MF) is able to produce smaller droplets than membranes, but the mean droplet size is more influenced by the dispersed phase content. It is especially pronounced at the higher homogenizing pressures ($p_h \geq 700$ bar) and can be explained by partial droplet coalescence immediately after disruption.

As shown in Fig. 7, the mean droplet size decreased with increasing the wall shear stress, σ_w , both for the α - Al_2O_3 and SPG membrane. The influence of wall shear stress is especially large at $\sigma_w < 10$ Pa and much stronger at the higher $\Delta p_{tm}/p_{cap}$ ratio.

Fig. 6 (left): The influence of dispersed phase concentration on the mean droplet size for different emulsification devices; Fig. 7 (right): The variation of mean droplet size with the wall shear stress.

As shown in Fig. 9, at the same $\Delta p_{tm}/p_{cap}$ ratio the percentage of active pores is higher for $\alpha\text{-Al}_2\text{O}_3$ than for SPG membrane, due to much smaller thickness of active layer in the former case (20-40 vs. 700 μm). In order to avoid contact between two rigid neighboring droplets at the pore openings, the fraction of active pores must be kept below $k_{max} = (\pi/4\varepsilon)(d_{drop}/d_p)^{-2}$, where ε is the membrane porosity. The mean porosity of the SPG membranes used in this work was 0.58 and the mean droplet/pore size ratio was typically in the range of 3-4, as shown in Figs 5 and 7. Therefore, to avoid any contact between droplets at the surface of the SPG membrane, the proportion of active pores must be kept below 8-15 %, depending on the exact droplet/pore size ratio. The maximum percentage of active pores for unhindered droplet growth is higher for the $\alpha\text{-Al}_2\text{O}_3$ membrane (37-39 % at $\Delta p_{tm}/p_{cap} = 1$ -3 for the conditions as in Fig. 9), due to the smaller porosity of active layer and smaller d_{drop}/d_p ratio. For both membrane type, coalescence due to steric hindrance occurred at $\Delta p_{tm}/p_{cap} = 5$ -6. It is in agreement with a strong increase of the droplet size dispersion coefficient at $\Delta p_{tm}/p_{cap} = 5$ -6 (Fig. 8).

Fig. 8 (left): The influence of pressure ratio on the span of the droplet size distribution for SPG and $\alpha\text{-Al}_2\text{O}_3$ membrane; Fig. 9 (right): Maximum and actual percentage of active pores vs. pressure ratio.

4. Conclusion

The microporous membranes (SPG and ceramic $\alpha\text{-Al}_2\text{O}_3$) were successfully used to produce O/W emulsions with the span of the droplet size distribution, i.e. the dispersion coefficient of 0.26-0.59 at the transmembrane/capillary pressure ratio of less than 5-6. For the same pore size and under the same experimental conditions, the droplet size distribution was narrower in the emulsions produced by using the $\alpha\text{-Al}_2\text{O}_3$ than SPG membrane. The maximum percentage of active pores for unhindered droplet growth was higher for the $\alpha\text{-Al}_2\text{O}_3$ membrane, due to a smaller porosity of active layer. By using a silicon MC plate, the emulsion with a span value of 0.45 was produced, which was comparable with the SPG membrane. For preparing O/W emulsions with the mean droplet size of less than 0.2 μm , the microfluidizer[®] is more appropriate device than microporous membranes. However, the span of the droplet size distribution for the emulsions produced by microfluidization was in the range of 0.9-2.7. The additional disadvantages of the microfluidizer[®] is that the mean droplet size is more influenced by the dispersed phase content and that the required mechanical stress is much higher.

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