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Factors influencing droplet size distribution in SPG membrane emulsification

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Summary
Membrane emulsification is a new emulsification method proposed in 1988 by Nakashima and Shimizu [1]. This method enables the production of highly uniform droplets of controlled mean sizes [2]. The additional advantage over traditional processes is a low mechanical stress, because small droplets are directly formed by pressing the dispersed phase through the pores into the flowing continuous phase (Fig. 1). Due to uniform pores, the wide spectrum of available mean pore sizes (0.05-30 µm) [3], and the possibility of surface modification, the Shirasu-porous-glass (SPG) membrane is a suitable membrane for mechanical emulsification. The aim of this work was to investigate the influence of the mean pore size of the SPG membranes and the various operating parameters on the droplet size distribution.

Experimental
The oil-in-water emulsions consisting of vegetable (rape seed) oil (Floreal GmbH) as the dispersed phase, demineralized water as the continuous phase, and Tween 80 (2 wt %, Merck GmbH) as the emulsifier were produced using porous glass membranes supplied from SPG Technology Co., Ltd. The mean pore size of the membranes was 1.4, 2.5, 5.0, and 6.6 µm, determined by a Shimadzu model 9320 mercury porosimeter. The SPG membrane (125 mm length × 10 mm OD × 0.7 mm wall thickness) was installed inside a laboratory made stainless steel module providing the effective membrane area of 31.4 cm². In the most experiments, the continuous aqueous phase was recirculated inside the membrane tube at a flow rate of 305 L/h corresponding to a velocity of 1.42 m/s. The dispersed phase was placed in the pressure vessel and introduced at the module shell side. The weight of oil permeated through the membrane was measured by a digital balance on which the pressure vessel rested (Fig. 2). The balance was interfaced to a PC computer to continuously collect time and mass data. The droplet size distribution was measured by a light scattering particle size analyser using PIDS technology (Coulter LS 230), allowing the detection of the droplets in the range of 0.04-2000 µm.

Fig. 1 (left): Schematic diagram of the O/W emulsion formation using SPG membrane; Fig. 2 (right): Schematic diagram of the membrane emulsification system used in our experiments.
Results and discussion

A. Properties of the SPG membranes used in this study

The hydraulic and morphological properties of the SPG membranes used are listed in Table 1. The hydraulic membrane resistances were calculated by the permeation of pure water through the membrane and using the equation: \( R_m = \left( \eta_w \frac{\partial J_w}{\partial \Delta p_{tm}} \right)^{-1} \), where \( J_w \) is the water flux through the membrane, \( \Delta p_{tm} \) the transmembrane pressure, and \( \eta_w \) the water viscosity. The derivative \( \partial J_w / \partial \Delta p_{tm} \) was determined as the slope of \( J_w \) vs. \( \Delta p_{tm} \) plot (Fig. 3). The membrane porosities \( \varepsilon \) were measured by the pycnometric method, according to the procedure given by Palacio et al. [4]. The mean tortuosity factors \( \xi \) were calculated from the Hagen-Poiseuille law: \( \xi = \varepsilon d_p^2 R_m / (32 \delta_m) \), where \( \delta_m \) is the membrane thickness and \( d_p \) the mean pore diameter.

The \( \varepsilon \) values listed in Table 1 are within the range of 50-60 \%, reported by Kandori [5] for a typical SPG membrane and somewhat higher than 51-52 \%, found by Palacio et al. [4] using the same experimental method for the \( \gamma \)-Al\(_2\)O\(_3\) membranes with \( d_p = 0.1-0.2 \) µm.

<table>
<thead>
<tr>
<th>Pore size, ( d_p ) (µm)</th>
<th>1.4</th>
<th>2.5</th>
<th>5.0</th>
<th>6.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_m \times 10^{-9} ) (m(^{-1}))</td>
<td>28.6</td>
<td>9.01</td>
<td>3.18</td>
<td>1.52</td>
</tr>
<tr>
<td>Porosity, ( \varepsilon ) (-)</td>
<td>- 0.53</td>
<td>0.60</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td>Tortuosity, ( \xi ) (-)</td>
<td>- 1.34</td>
<td>2.12</td>
<td>1.72</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3 (left): Plot of transmembrane pressure versus transmembrane flux for the permeation of pure water through the SPG membranes with different mean pore sizes.

B. Application of the SPG membranes for emulsification

In the permeation of pure water through the membrane, the water flux exists for each \( \Delta p_{tm} \) value above zero. However, the permeation of dispersed phase through the membrane is only possible if \( \Delta p_{tm} \) is at least equal to the capillary pressure, \( p_c \). The \( p_c \) values at the beginning of the experiments and the parameters of the droplet size distribution for the emulsions obtained at \( \Delta p_{tm} = p_c \) are given in Table 2. Under these conditions, the steady-state dispersed phase flux ranges from 2.2 to 9.1 L/(m\(^2\)h) and 0.9-4.2 \% of the pores were found to be active (open). The fraction of active pores was calculated as: \( k = J_d R_m \eta_d / \Delta p_{tm} \), where \( \eta_d \) is the dispersed phase viscosity (in our study \( \eta_d = 58 \) mPa\(\cdot\)s) and \( J_d \) is the dispersed phase flux.

For the experimental conditions as in Table 2, the emulsions with a very narrow droplet size distribution can be prepared (Fig. 4). The width of the droplet size distribution of 0.26-0.44 obtained under these conditions is much lower than that reported for ceramic membranes [6, 7]. As an example, Joscelyne and Trägårdh [7] have obtained the width of the droplet size distribution of 0.89-1.64 in the production of O/W emulsions using ceramic membranes with a mean pore size of 0.1-0.5 µm. However, the dispersed phase flux in their experiments was 15-270 kg/(m\(^2\)h).
If the transmembrane pressure is only slightly above the capillary pressure, the mean droplet size is directly proportional to the mean pore size (Fig. 5) and the slope of this line is equal to 3.50. The ratio $d_{3,2}/d_p$ of 3.50 is very similar to 3.25 reported by Nakashima et al. [8].

Table 2. The capillary pressures, $p_c$, as well as the mean droplet sizes, $d_{3,2}$ and the widths of the droplet size distribution (the span values) obtained at $\Delta p_{tm} \approx p_c$.

<table>
<thead>
<tr>
<th>Pore size, $d_p$ ($\mu$m)</th>
<th>1.4</th>
<th>2.5</th>
<th>5.0</th>
<th>6.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_c$ (kPa)</td>
<td>53</td>
<td>26</td>
<td>11</td>
<td>5</td>
</tr>
<tr>
<td>$d_{3,2}$ ($\mu$m)</td>
<td>4.6</td>
<td>8.5</td>
<td>14.7</td>
<td>23.9</td>
</tr>
<tr>
<td>Span (-)</td>
<td>0.30</td>
<td>0.44</td>
<td>0.37</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Fig. 4 (left): Droplet size distribution at $\Delta p_{tm} \approx p_c$ for the membranes with different pore sizes.

On the conditions that the pores are arranged regularly in a cubic array over the membrane surface, the distance between the centres of the adjacent active pores is given by the equation: $z = (d_p/2)(\pi/k\varepsilon)^{0.5}$. For $\varepsilon = 0.57$ (the mean value from Table 1) and $k = 0.009-0.042$, the ratio $z/d_p$ ranges between 12.4 and 5.7. If $d_{3,2}/d_p < z/d_p$, the droplets do not touch each other at the pore openings. For the conditions as in Fig. 5, it is satisfied and no coalescence was observed.

At the operating pressures slightly above the capillary pressure, the mean droplet size is almost independent of the dispersed phase content up to 20 vol% (Fig. 6). This trend was also found by Katoh et al. [9] in the preparation of food emulsions using SPG membranes. The small decrease of the mean droplet size in the experiment with the 6.6-µm membrane can be explained by the disruption of droplets during recirculation. At the smaller cross-flow velocity of the continuous phase inside the membrane tube, the disruption is less pronounced, but the mean droplet size is higher. The size distribution is wider at the smaller cross-flow velocity of the continuous phase (e.g. the span value is 0.32 at 0.93 m/s and 0.29 at 1.42 m/s).

As shown in Fig. 7, the mean droplet size increases with increasing the transmembrane pressure, which was also observed by other authors [6, 7]. The increase in $d_{3,2}$ on increasing the transmembrane pressure is because of an increase in dispersed phase flux leading to a decrease in droplet formation time. Larger droplets are formed at shorter droplet formation times because an emulsifier is not able to stabilize the new interfaces fast enough.
Fig. 5 (left): The relationship between the mean pore size, \( d_p \) and the mean droplet diameter, \( d_{3,2} \). Fig. 6 (right): The influence of dispersed phase content, \( \varphi \) on the mean droplet diameter.

The both figures are obtained at the operating pressures slightly above the capillary pressure.

Fig. 7 (left): The influence of transmembrane pressure on the mean droplet size; Fig. 8 (right): The change of mean droplet size with time (oil content: \( \Delta \) 1.25 vol\%, \(< 2.5\%, \square 5\%, + 8\%) .

Fig. 9: Photographs of obtained emulsion droplets taken by optical microscope

As shown in Fig. 8, the emulsion droplets were very stable during storage for 2-3 months at room temperature, especially for the higher mean droplet sizes (e.g., the \( d_{32} \) value increases only 0.27% after 3 months of storage for the droplets produced with the 5 µm-membrane).

Acknowledgement. This work was supported by the Alexander von Humboldt Foundation.

Literature
3. SPG Technology Co., Ltd., SPG (Membrane), Information sheet.