Technical paper

Characteristics of the Membrane Emulsification Method Combined with Preliminary Emulsification for Preparing Corn Oil-in-Water Emulsions

Kanichi Suzuki, Ikuko Shuto and Yoshio Hagura

Department of Food Science, Faculty of Applied Biological Science, Hiroshima University, 1-4-4, Kagamiyama, Higashi-Hiroshima 739, Japan

A novel membrane emulsification method was used to prepare corn oil/water (O/W) emulsions (25 wt% oil phase) with sharp particle diameter distribution. When pre-emulsified O/W emulsions were used as dispersing fluids instead of the oil phase (corn oil+emulsifier), the membrane emulsification was carried out easily with a high emulsifying rate up to 3.5 m³/(h·m²-membrane). Mean particle diameters of the emulsions were about twofold those of the mean pore sizes of the porous glass membranes used. The particle diameter of the emulsions decreased with increasing applied pressure or flux of the pre-emulsified emulsion through the membrane. Because of the high stability of the membrane emulsified emulsion particles, little change in particle diameter distribution occurred over several weeks. The kind of emulsifying agent influenced the particle diameter distribution and the creaming rate.

The properties of emulsions such as stability, creaming and rheological behavior are strongly affected by the particle diameter distribution even if the emulsions were prepared with the same formulation. Generally, the stability of the emulsions increases with an increase in the narrowness of particle diameter distribution even though their mean particle diameters are the same. It is also desirable to obtain emulsions of uniform particle diameter such as a monodispersed emulsion for studying the interfacial phenomena of emulsion particles that affect the physical properties of emulsions directly. However, it has been almost impossible to prepare a monodispersed emulsion of desired particle diameter or emulsions with controlled particle diameter distribution by commercial scale conventional emulsifying apparatuses, although emulsions of fine particle diameter with relatively narrow particle diameter distribution can be prepared using a high-pressure homogenization method such as microfluidization (Dickinson & Stainsby, 1988; Latreille & Paquin, 1990). Further, most of the conventional emulsifying equipment requires high mechanical energy that often leads to an unstable emulsion state during the emulsifying processes. Therefore, it has been expected to develop a simple and easy emulsifying method that prepares monodispersed emulsions of desired particle diameter for both industrial and academic purposes.

In this connection, a novel emulsifying method that prepares emulsions with quite narrow particle diameter distribution was proposed recently (Nakashima & Shimizu, 1993). The method, called the membrane emulsification method, prepares an emulsion by passing the oil or water phase directly through the micropores in a porous glass membrane by applying pressure and dispersing it into a continuous phase as fine particles. The particle diameter distribution of the emulsions is analogous to the pore size distribution of the membranes used (Nakashima & Shimizu, 1993). This means that monodispersed emulsions could be prepared if porous membranes of uniform pore size were available. It is also expected that we can prepare stable food emulsions with narrow particle diameter distribution by applying the membrane emulsification method (Katoh, 1993; Nakashima *et al.*, 1994). However, this emulsification method has some restrictions in the process conditions (Nakashima & Shimizu, 1993; Nakashima *et al.*, 1993). For preparing O/W emulsions, the membrane has to be hydrophilic and remain wetted well with the water phase during the membrane emulsification process. When the membrane losses hydrophilicity or is wetted by the oil, membrane emulsification becomes difficult, and/or the particle diameter distribution of the prepared emulsion becomes wide. Because of these restricted conditions, the permeating rate of the oil phase through the porous glass membrane or the emulsifying rate of the membrane emulsification method has to be limited to a low value to obtain the desired membrane emulsified emulsion (Nakashima & Shimizu, 1993; Katoh *et al.*, 1995). This is one disadvantage for utilizing the membrane emulsification method in food industries (Katoh, 1995). Regarding this, the authors have shown the capability of improving the membrane emulsifying rate by passing a preliminarily emulsified emulsion of rough particle diameter through the porous membrane instead of the direct passing of the oil or water phase (Suzuki *et al.*, 1994; Suzuki, 1994).

The objective of this paper was to investigate the characteristics of the membrane emulsification method combined with the preliminary emulsification for preparing O/W food emulsions. Effects of constituent concentration, emulsifying pressure or permeating rate of the preliminarily emulsified emulsion through the porous glass membrane and pore sizes of the membranes on the particle diameter distribution of the

emulsions prepared were studied. Creaming phenomena and stability of the emulsions were also discussed.

Materials and Methods

Preparation of membrane emulsified O/W emulsion Corn salad oil (Ajinomoto Co., Inc., Japan) was used for the oil phases and distilled water for the water phase. The porous glass membranes used were the tube type (MPG membranes, Ise Chemical Corp., Japan) with 10 mm ID, 170 mm in length, and a thickness of 0.5 mm. We used two glass membranes of different pore sizes, the mean pore sizes of which (2.70 mm and 4.20 mm measured by a mercury porosimeter) were given by the producer. For preparing O/W emulsions by the membrane emulsification method, hydrophilicity of the membrane is an essential condition (Nakashima & Shimizu, 1993; Katoh *et al.*, 1995). Thus, the washed and dried porous glass membrane was dipped in 2 N-HCl solution at 70°C for 2 h to insure the hydrophilicity of the membrane, then rinsed with distilled water before each membrane emulsifying procedure. Polyglycerol polyricinoleate (PGPR) and high HLB polyglycerol fatty acid esters (PGFE, HLB=10-15) were used as emulsifying agents for the oil phase and water phase, respectively. Both PGPR (CR-500: Hexaglycerol ester) and PGFE were the products of Sakamoto Yakuhin Kogyo Co., Ltd., Japan. The concentrations of PGFE ranged from 0.75 wt% to 3.0 wt% of the emulsions. The PGPR concentration was 0.5 wt%.

In this study, we adopted a two-step procedure, i.e., preliminary emulsification followed by membrane emulsification, to improve the emulsifying rate and to reduce the restrictions of the membrane emulsification. In the second step, i.e., the membrane emulsifying process, the preliminarily

emulsified (pre-emulsified) O/W emulsion was dispersed into the continuous phase via a porous glass membrane instead of direct dispersion of the oil phase. In the preliminary emulsifying process, we prepared a high concentration O/W emulsion (50 wt%-oil phase, 300 ml) of particles larger than the mean pore size of the glass membrane by regulating the mixing rate and time of a conventional homogenization method (HV-M, Tokushukikakogyo, Japan). The pre-emulsified O/W emulsion was then degassed at about 60 Torr (8 kPa-abs) in a vacuum chamber before using it as a dispersing liquid for the membrane emulsifying process. The diagram of the membrane emulsifying apparatus used in this study, together with the schematic illustration of the membrane emulsifying process of the pre-emulsified O/W emulsion, is shown in Fig. 1. The porous glass membrane was ultrasonicated in the continuous phase to wet it well with the water phase in advance of fitting the membrane in the module. An appropriate amount of the continuous (water) phase (200 ml in this study) was then circulated through the inner side of the tube-type membrane (0.14 m/s). The pre-emulsified large particle emulsion was permeated through the micropores of the membrane by applying pressure and was dispersed into the flowing continuous phase or the dilute emulsion phase. The permeating flux or emulsifying rate was controlled by regulating the pressure. The oil phase concentration in the final O/W emulsions was adjusted to 25 wt% in this study.

Measurement of particle size distribution The emulsion was diluted with distilled water, photographed (×400), and the particle diameter distribution was analyzed by projecting the negatives on a digitizer (Graphtec-KW4300, Japan) connected to a personal computer (NEC 9801RX, Japan). About 1,000 particles were counted.

Observation of creaming phenomena The particle diameter distribution of the O/W emulsion was narrow enough so that the boundary between the creamed dense layer and the dilute (water) layer became clear. Thus, the creaming rate was evaluated by measuring the change in height of the dilute layer of the O/W emulsion in a graduated glass cylinder (ID=22 mm, H=200 mm) at room temperature (25°C). To measure the change in particle diameter distribution with time, the creamed emulsion was stirred gently but well by hand, and then the distribution was measured by the same procedure described above.

Results and Discussion

The membrane emulsification for preparing O/W emulsions becomes difficult, and/or the particle diameter distribution of the prepared emulsion becomes wide when the membrane losses hydrophilicity or is wetted by the oil (Nakashima & Shimizu, 1993; Katoh *et al.*, 1995). Because of these restricted conditions, the emulsifying rate of the membrane emulsification method could not be high. Further, the corn oil phase we prepared did not disperse smoothly into the water phase through the MPG membrane, because the membrane was wetted with the oil immediately after the membrane emulsifying process started. However, the results of this study showed that O/W emulsions with narrow particle diameter distribution were obtained easily with high emulsifying rate when the preliminary emulsified O/W emulsions
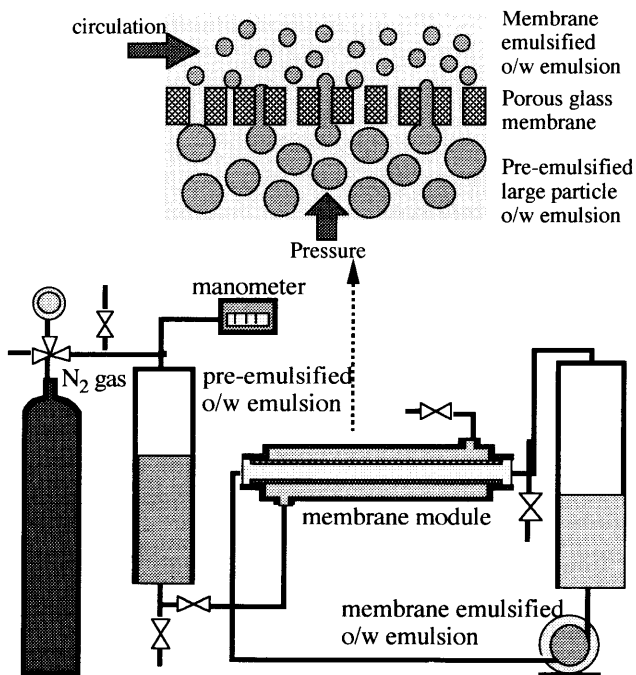

Fig. 1. Schematic explanation of the membrane emulsifying apparatus and emulsifying process in which the preliminary emulsified large particle O/W emulsion permeates and is dispersed via a porous glass membrane.
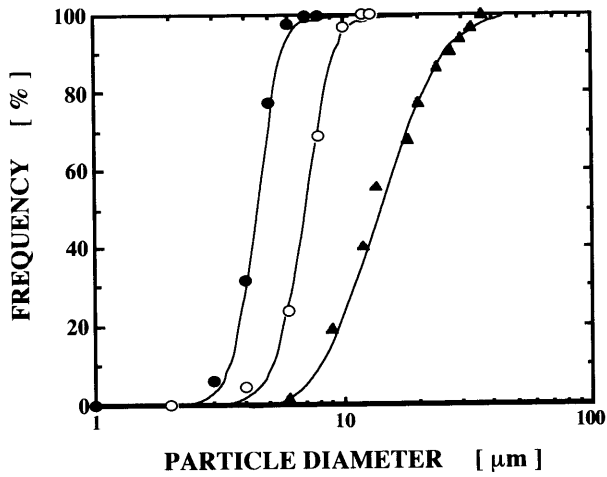
Fig. 2. Particle diameter distributions of the membrane emulsified O/W emulsions compared with that of the preliminary emulsified O/W emulsion (PGPR=0.5 wt%; PGFE (Decaglycerol monolaurate; HLB=15)=1.5 wt%). ●, Membrane emulsified O/W emulsion (Dm=2.70 μm); ○, Membrane emulsified O/W emulsion (Dm=4.20 μm); ▲, Preliminary emulsified emulsion; where, Dm is the mean pore size of the porous glass.
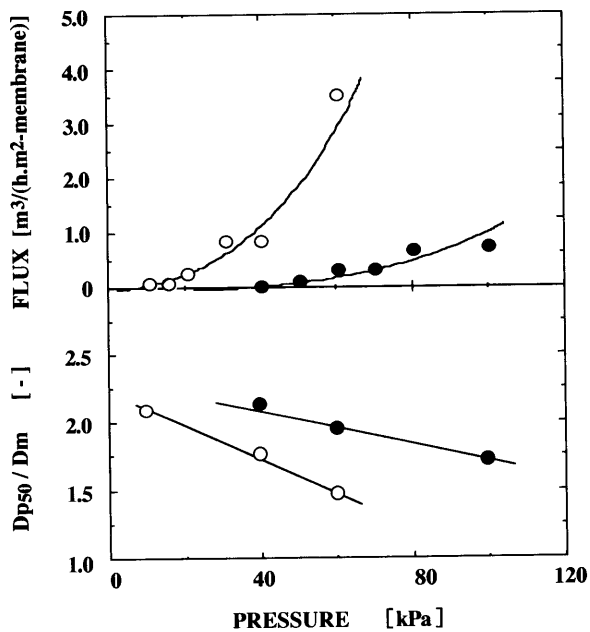

Fig. 3. Influence of pressure on the permeating flux of the preliminary emulsified O/W emulsions via a porous glass membrane and the ratio of the mean particle diameter of the membrane emulsified O/W emulsion to the mean pore size of the membranes, Dp_{50}/Dm (PGPR=0.5 wt%; PGFE (Decaglycerol monolaurate)=1.5 wt%). ●, Dm=2.70 μm; ○, Dm=4.20 μm. Dm, Mean pore size; Dp_{50}, Mean particle diameter.

Table 1. Influence of permeating flux of pre-emulsified emulsion through the membrane on particle diameter distribution and mean particle diameter.

Dm [μm]	J [m³/(h·m²-membrane)]	Dp_{50}[μm]	δ[−]
2. 70	0. 029	5. 72	0. 65
2. 70	0. 313	5. 21	0. 40
2. 70	0. 711	4. 70	0. 41
4. 20	0. 073	8. 72	0. 66
4. 20	0. 837	7. 44	0. 63
4. 20	3. 55	6. 07	0. 62

Dm, Mean pore size of glass porous membrane; J, Permeating flux of pre-emulsified emulsion through the membrane; Dp_{50}, Median diameter. $\delta=$ $(Dp_{90}-Dp_{10})/Dp_{50}$, where the number of subscripts indicates the cumulative percentage of diameter frequency.

with particle diameter larger than the mean pore size of the membrane were used as dispersing liquids. The particle diameter distributions of emulsions before and after the membrane emulsification are compared in Fig. 2.

The effect of emulsifying pressure on the permeating flux of the preliminary emulsified O/W emulsions through the porous glass membrane and the ratio of the mean particle diameter of the membrane emulsified O/W emulsion (Dp_{50}) to the mean pore size of the membranes (Dm) are shown in Fig. 3, where Dp_{50} is the particle diameter at 50% cumulative particle frequency. The highest value of the mean particle diameter was about 2.2 times the mean pore size of the membrane in this study, and the mean particle diameter (Dp_{50}), decreased with the increase in emulsifying pressure or permeating flux of the pre-emulsified emulsion as shown in Fig. 3. Furthermore, there was no upper limitation of the emulsifying pressure or the emulsifying rate. We obtained an emulsifying rate higher than 3.5 m³/(h·m²-membrane) in this study. The results were opposite the results of the previous studies (Nakashima & Shimizu, 1993; Katoh et al., 1995) in which the oil phase was dispersed directly through the membrane. They found that Dp_{av}=3.25 Dm or Dp_{av}=5.0 Dm irrespective of the emulsifying conditions, where Dp_{av} is the mean particle diameter. They also obtained polydispersed emulsions when the oil phase flux through the membrane or dispersing pressure was over an upper limitation. Therefore, the two-step membrane emulsifying method adopted in this study was useful for preparing food emulsions with narrow particle diameter distribution not only for reducing the possibility of wetting the membrane with the oil phase but also for increasing the emulsifying rate.

The particle diameter distribution or monodispersibility (δ) of the O/W emulsions prepared was fairly good (δ=0.40-0.66) as shown in Table 1, where $\delta=(Dp_{90}-Dp_{10})/Dp_{50}$, Dp is the particle diameter, and the subscripts indicate the cumulative percentages of the particle frequency (Nakashima & Shimizu, 1993). The monodispersibility was also improved by increasing the permeating flux, though the δ values were slightly higher than the result for a kerosene/water emulsion system ($\delta \leq 0.3$) (Nakashima & Shimizu, 1993). The results might depend on the difference in experimental systems in this study from those in previous studies, because the properties of oils and emulsifying agents, emulsifying conditions and method of measuring particle diameter distribution generally influence the properties of the emulsions and the experimental results. The HLB value and concentration of the emulsifying agent also influenced the particle diameter distribution. However, the quantitative tendency was not measured, because the dispersing phase flux was not the same for different emulsifier concentration systems even when we regulated the pressure at a constant value.

Because of the narrow particle diameter distribution of the emulsions, we could easily observe creaming phenomena. The boundary between the dilute (water phase) layer and the concentrated layer caused by creaming was distinct. The creaming rate of emulsions was influenced by the emulsifying pressure or the dispersing phase flux as well as the kind of emulsifying agent as shown in Fig. 4. The creaming rate of the emulsion prepared at higher emulsifying pressure was lower
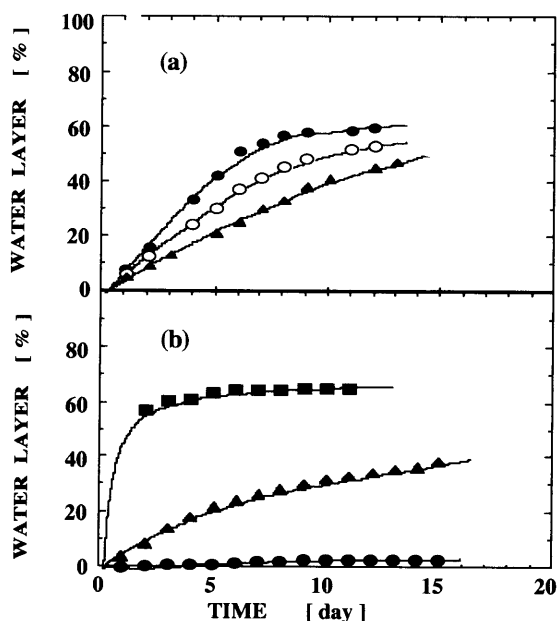
Fig. 4. Influence of emulsifying pressure (a) and kind of emulsifier (b) on the creaming rate of the membrane emulsified O/W emulsions (Dm=2.70 mm; oil phase concentration=25 wt%; PGPR=0.5 wt%; PGFE=1.5 wt%). (a) Kind of PGFE: Decaglycerol monolaurate (HLB=15). ●, 40 kPa; ○, 60 kPa; ▲, 100 kPa. (b) Kind of PGFE. ■, Decaglycerol monostearate (HLB=13); ▲, Hexaglycerol monostearate (HLB=11); ●, Decaglycerol tristearate (HLB= 10).

Fig. 5. Change in particle diameter distribution of the membrane emulsified O/W emulsion during storage in a glass cylinder at room temperature (Dm= 2.70 mm; PGPR=0.5 wt%; PGFE (Decaglycerol monolaurate)=1.5 wt%). ○, Freshly prepared emulsion; ●, 21-day-old emulsion.

than those prepared at lower pressures as shown in Fig. 4(a). This was due to the effect of the dispersing phase flux through the membrane on the mean particle diameter. The kind of emulsifying agent also influenced the creaming rate considerably (Fig. 4(b)). This was due to the effect of emulsifying agents on the viscosity of the continuous phase rather than the mean particle diameter. Decaglycerol monostearate solution (2.0 wt%) showed the lowest viscosity (1.30×10⁻³ Pa·s at 25°C; glass capillary viscometer). However, the other two emulsifying agent solutions showed time-dependent flow properties and higher viscosities. Especially, the viscosity of decaglycerol tristearate solution (2.0 wt%) increased from 3.30×10⁻³ Pa·s to more than 70×10⁻³ Pa·s within three days at 25°C.

Even though the membrane emulsified emulsions formed a concentrated dispersed phase (cream) layer, the emulsion particles were very stable, and no appreciable coalescence was observed during stationary storage over several weeks at room temperature. By stirring the creamed emulsions, we obtained emulsions of which the particle diameter distributions were almost the same as those of freshly prepared emulsions as shown in Fig. 5. Though the mechanisms of the emulsifying conditions affecting the emulsion properties were not analyzed in this study, the membrane emulsification method combined with preliminary emulsification prepared stable food O/W emulsions with a high emulsifying rate.

Conclusions

Corn oil-in-water emulsions (25 wt% oil phase) with sharp particle diameter distribution were prepared by the membrane emulsification method. When preliminary emulsified larger particle O/W e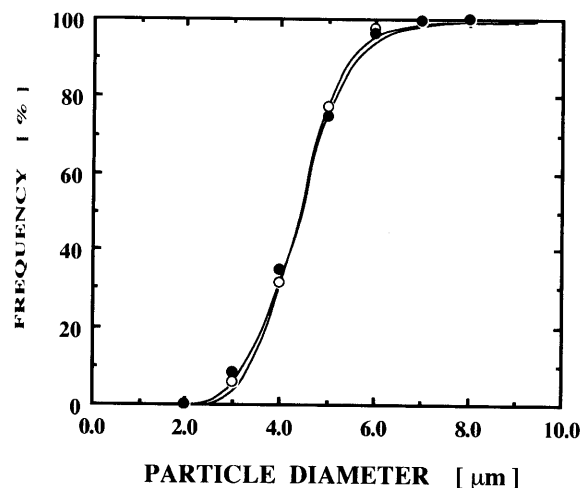mulsions were used as dispersing fluids instead of the oil phase (corn oil+emulsifier) alone, the membrane emulsification was carried out easily with a high emulsifying rate up to 3.5 m³/(h·m²-membrane). Mean particle diameters of the emulsions were about twofold those the mean pore sizes of the porous glass membranes used. Increasing the flux of the pre-emulsified O/W emulsion through the membrane or the applied pressure decreased the mean particle diameter and the narrowness of the particle diameter distribution. The membrane emulsified O/W emulsions were convenient for observing the creaming phenomena. The kind of emulsifying agents influenced the particle diameter distribution and the creaming rate. The emulsion particles were very stable, and no appreciable coalescence was observed during standing for several weeks, even though they formed a concentrated cream layer.

References

Dickinson, E. and Stainsby, G. (1988). "Advances in Food Emulsions and Foams." Elsevier Applied Science. London and New York.

Katoh, R. (1993). Application of membrane emulsification method for preparing food emulsion. Shokuhin to Kaihatu, 28(4), 9–13 (in Japanese).

Katoh, R., Asano, Y., Furuta, A. and Tomita, M. (1995). Conditions for preparation of O/W emulsions using a membrane emulsification system. Nippon Shokuhin Kogyo Gakkaishi, 42, 548–555 (in Japanese).

Katoh, R. (1995). Makunyukaho no Shokuhin heno Oyo, In "Advances in Food Science and Technology, 1995" ed. by Editorial Board, Korin, Tokyo, pp. 101–127 (in Japanese).

Latreille, B. and Paquin, P. (1990). Evaluation of emulsion stability by centrifugation with conductivity measurements. J. Food Sci., 55, 1666–1668, 1672.

Nakashima, T. and Shimizu, M. (1993). Preparation of monodispersed O/W emulsion by porous glass membrane. KagakuKogaku Ronbunshu, 19, 984–990 (in Japanese).

Nakashima, T., Shimizu, M. and Kukizaki, M. (1993). Effect of surfactant on production of monodispersed O/W emulsion in

membrane emulsification. *KagakuKogaku Ronbunshu*, **19**, 991–997 (in Japanese).

Nakashima, T., Nakamura, K., Kochi, M., Iwasaki, Y. and Morita, M. (1994). Development of membrane emulsification method and its application to food industries. *Nippon Shokuhin Kogyo Gakkaishi*, **41**, 70–76 (in Japanese).

Suzuki, K., Shuto, I. and Hagura, Y. (1994). Application of membrane emulsification method for preparing food emulsions and emulsion characteristics. In "Developments in Food Engineering. Part 1" ed. by Yano, T., Matsuno, R. and Nakamura, K., Blackie Academic & Professional, London, pp. 167–169.

Suzuki, K. (1994). Characteristics of the membrane emulsification method for preparing food emulsions. *Foods Food Ingredients J. Jpn*, **162**, 29–36 (in Japanese).