Emulsions Prepared by Two-Stage Ceramic Membrane Jet-Flow Emulsification

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To solve the paradox between the flux and droplet size in conventional membrane emulsification, a process including a two-stage ceramic membrane emulsification under jet flow was proposed. An apparatus integrating slurry reactor and membrane emulsification was used in this investigation. In the first stage, a ZrO_2 ceramic membrane, with a nominal pore size of 0.16 μm, was used. The flux of the membrane was 150 L m^{-2} h^{-1} at a pressure of 0.35 MPa and a temperature of 20°C, and the droplet size of the emulsion was 54.69 μm. To obtain monodispersed emulsions with a small droplet size, a second ceramic membrane jet-flow emulsification was used. An α-Al_2O_3 ceramic membrane with a nominal pore size of 1.5 μm was selected as the emulsification medium. The flux was attained at 454 L m^{-2} h^{-1} at a pressure of 0.2 MPa, and the monodispersed emulsion with droplet size (D_{50}) of 2.29 μm could be obtained. The effects of pressure, stirring speed, and emulsifier concentration on the second stage of the process were discussed in detail.
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Introduction

Membrane emulsification (ME) is a relatively new emulsification technique that makes it possible to obtain uniform emulsions at low energy input compared to emulsions prepared by high-pressure homogenizers and rotor/stator systems.[1,2] The ME process includes the following steps: droplets are formed at membrane pore outlets by forcing the dispersed phase to permeate through a membrane and stripped from the membrane surface into the continuous phase by action of the shearing force.[3,4] It is highly attractive because of its simplicity, potentially lower energy demands, less surfactant, and narrow droplet-size distribution.[3] However, the low membrane flux of the dispersed phase and the possibility of droplet coalescence hinder the application of this technology in practice.

The pore structure (pore size, porosity) of membranes and operational conditions (such as pressure) influence membrane flux in a membrane process. It is generally thought that a membrane separation system with larger pore size and/or higher porosity of membrane, or under a condition of higher pressure, will show higher flux. However, the higher flux could also lead to an increase in the droplet size or widen the range of the droplet size distribution in the ME process. Many studies[4-11] have observed these phenomena. First, Schröder et al.,[4] Katoh et al.,[5] and Mine et al.[6] reported that the pore size of a membrane determined the droplet size of the emulsion. The droplet size (D_d) of an emulsion can be related to the pore size (D_p) of the membrane by a linear relationship for a given operating condition: $D_d = xD_P$, where x typically ranges from 2 to 10. For the process of preparing an emulsion with small droplet size, therefore, the flux is very low. Typical fluxes for producing oil/water (O/W) emulsions range from 2 to 40 L m^{-2} h^{-1} for membranes with a nominal pore size from 0.2 to 0.8 μm.[3] Second, to prevent coalescence of droplets aggregating on neighboring pores, the theoretical maximum porosity should be very small. Abrahamse et al.[7] calculated the theoretical maximum porosity by computational fluid dynamics, which is only 1.5%. However, the actual porosity of the mem-

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brane is generally >30%. Vladisavljevic and Schubert[8] found that only no more than 2% of the pores were active at any moment in their experiment. Third, if the transmembrane pressure increases, the membrane flux increases in the ME process. In many cases, however, this result leads to emulsions with a greater mean droplet size and polydispersed droplets.[9-11]

Monodispersed emulsions were difficult to obtain, especially when ceramic membranes were used as the emulsification medium, because the ceramic membranes have a small number of coarse pores.[3,12] However, because of their characteristically high performance of mechanical strength and chemical stability, ceramic membranes have shown great potential in large-scale application of membrane emulsification.[9,12]

To solve the paradox between the flux and droplet size in the conventional membrane emulsification, a two-stage ceramic membrane jet-flow emulsification process was proposed in this work. In the first stage, the coarse emulsion was prepared by ceramic membrane emulsification under jet flow. The flux was high for the process operating at high pressure, but the droplet size of the emulsion was far larger than that of the emulsion prepared at low pressure. To obtain monodispersed emulsion with a small droplet size, the coarse emulsion (which was used as the dispersed phase) was pressured through the pores of the second membrane into the continuous phase under jet flow. The ceramic membranes with larger pore size were used in this stage, so a high flux could be obtained. The effects of pressure, stirring speed, and concentration of the emulsifier in the continuous phase on the process were investigated.

Theory

In the ME process, the transmembrane pressure is defined as

$$\Delta P = P - P_c \tag{1}$$

where P is the disperse-phase pressure and P_c is the pressure of the continuous phase. The critical pressure can be estimated according to the following equation[12]

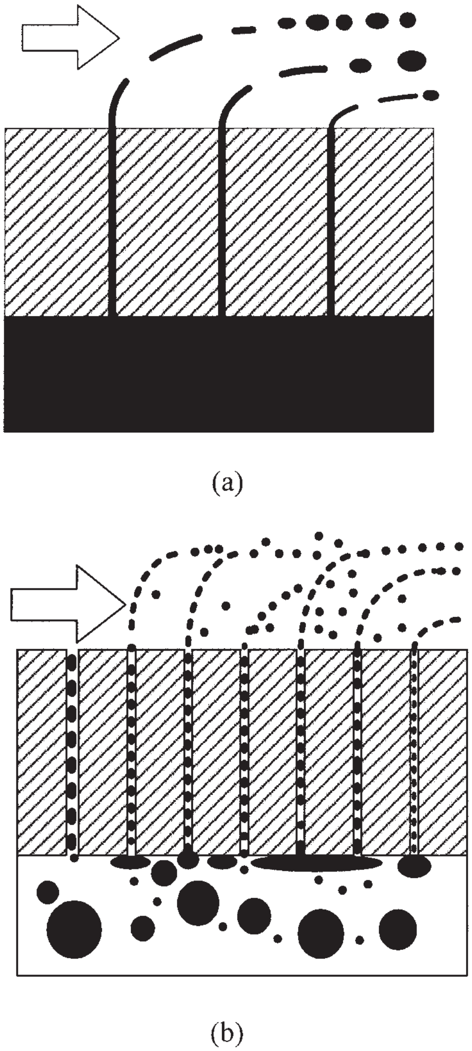
$$P_{cr} = \left| \frac{4\sigma \cos \alpha}{D_p} \right| \tag{2}$$

where σ represents the oil/water interfacial tension; α is chosen as 140°, assuming that the oil did not wet the membrane that is hydrophilic.[12]

Pressure factor β is defined as the ratio of the transmembrane pressure and the critical pressure

$$\beta = \frac{\Delta P}{P_{cr}} \tag{3}$$

To obtain a monodispersed emulsion, the value of β is generally 1.1; thus the flux is very low. By increasing the value of β, the ratio of active pores increased and the potential of coalescence of droplets aggregating at neighboring pores also increased.[8,13] If the pressure is too high, the dispersed phase may be forced out as a jet stream and produce extremely large droplets of variable sizes. There is no reliable theoretical approach to estimate the usable maximum membrane pressure, which is affected by the membrane itself and the process conditions. Williams et al.[14] suggested that the value of β should be in the range of 2 to 10, and the actual value had to be obtained by experimental approach.


(a)

(b)

Figure 1. Two-stage ceramic membrane jet-flow emulsification.

(a) The first jet-flow membrane emulsification; (b) the second jet-flow membrane emulsification.

Figure 1 shows the possible mechanism of the two-stage ceramic membrane jet-flow emulsification. First, the oil used as the dispersed phase is pressured through membrane pores into the continuous phase at a higher pressure. Thin streamlines of oil are formed under jet flow and then ruptured into a number of droplets by action of shearing force (Figure 1a). It is difficult to obtain the critical pressure forming the jet flow, although we conjecture that the process is on jet-flow condition when the droplets of the emulsion and flux of membrane are much larger than those obtained when the emulsification is operated at 1.1 times the critical emulsification pressure. To obtain a monodispersed emulsion with small droplet size, the coarse emulsion used as the disperse phase is pressured, thus driving the pores of the second membrane into the continuous phase by shearing force. The second stage is more like preparation of multiple

Table 1. Properties of Membranes Used in This Work

Nominal Pore Size, D_p (μm)	Material	Average Pore Size, D_a (μm)	Maximum Pore Size, D_m (μm)
0.16	ZrO_2	0.16	1.35
1.5	α-Al_2O_3	1.5	3
5	α-Al_2O_3	5	10

emulsions by using membrane emulsification,[15,16] so we designated the process *secondary jet-flow membrane emulsification*. Because the droplets are far larger than the membrane pore size, the droplets could not directly penetrate through the membrane. When the droplets arrive at the membrane surface, they are first squashed, then become distorted, and finally form smaller oil plugs into membrane pores at an appropriate pressure. To lower flow resistance in hydrophilic channels, the oil plugs become thinner and are forced into the water flow. Then the jet flows mixing water and oil plugs rupture into smaller droplets and are dispersed in the continuous phase by shearing force (Figure 1b). Compared with the first jet-flow membrane emulsification, a partial emulsifier has adsorbed onto the surface of oil plugs and the supply of the oil is discontinuous, which facilitates the larger droplets dividing into much shorter oil plugs and then rupturing into smaller droplets.

Experimental

Membranes and materials

The ceramic membranes were prepared by our lab. Dimensions of the membrane tubes used were 12 × 80 mm (OD × length). A zirconia oxide membrane having a nominal pore size of 0.16 μm, which was coated on the outer wall of α-Al_2O_3 tubular support, was used. The two other ceramic membranes, having nominal pore sizes of 1.5 and 5 μm, were made of α-Al_2O_3. The pore size distribution of membranes used in this study was measured by the bubble point method.[17] Table 1 details the properties of membranes.

Toluene (AR grade) was used as the dispersed phase. Pure water was prepared by reverse osmosis (conductivity $\cong$ 4 μS/cm). The emulsion was stabilized with sodium dodecyl sulfate (SDS, CP grade).

Apparatus

The two integrated emulsification apparatuses were used in series (Figure 2). Each consisted of three main components: a stirred vessel with 2000-mL capacity, a tubular ceramic membrane, and a container with 300-mL capacity. The droplets form on the outer surface of the membrane and the vessels were made of glass, which was suitable for direct observation of the experiment. A slurry-stirred vessel was provided with a variable-speed magnetically driven impeller, sample inlet, sample outlet, and external heating. The speed of the stirrer could be adjusted. The oil was pressed through the pores of the membrane using gas-pressurized nitrogen. The temperature in the vessel was measured by a thermocouple.

Procedure

Yuyama et al.[18] suggested that the membrane should be immersed into sodium lauryl sulfate solution and treated by ultrasonication before use so that the surface is thoroughly wetted with the aqueous phase. In our experiments, the ceramic membranes were immersed in the continuous phase (water containing 2 wt % SDS) for 20 min.

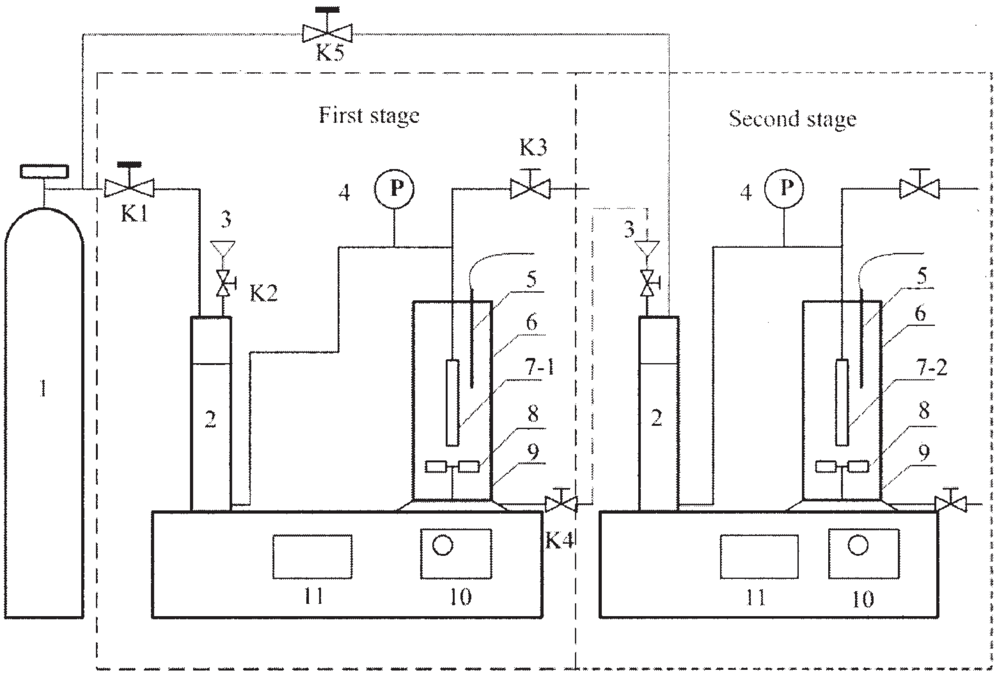


Figure 2. Integrated emulsification apparatus.

1: N_2 gas cylinder; 2: pressurized container; 3: sample inlet; 4: pressure gauge; 5: thermocouple; 6: vessel; 7-1: ceramic membrane 1; 7-2: ceramic membrane 2; 8: impeller; 9: container; 10: speed governor; 11: thermal control meter; K1–K5: valves.

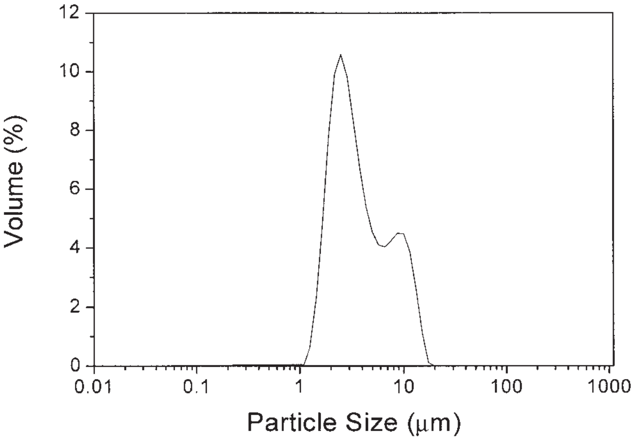


Figure 3. Droplet size distribution of the emulsion prepared by conventional membrane emulsification using a ZrO_2 membrane, with a pore size of 0.16 μm, at 60 kPa, 280 rpm, and 2 wt % SDS.

The procedures for the process are as follows: First, 1.5 L pure water, containing 2 wt % SDS, was used as the continuous phase and charged to the container of the first apparatus. The dispersed phase, 300 mL toluene, was stored in the pressurized container and then forced into the continuous phase at a given pressure, a rotation speed of 280 rpm, and temperature of 20°C. The pressure of the continuous phase could be neglected in the process using the integrated apparatus because the stirring speed is slow.[19] Thus, the transmembrane pressure is equal to the working pressure. With increasing pressure, the jet flow of oil could be observed in the process and the coarse emulsions with large droplet size were prepared. To obtain a higher flux, the experiment was operated at 350 kPa (the maximum safe working pressure of the apparatus). Then the coarse emulsion of 300 mL was used as the dispersed phase and introduced to the pressurized container of the second apparatus and finally pressed into the continuous phase under jet-flow conditions.

At the end of each experiment, the membranes were required to be cleaned to recover the membrane flux. Because toluene and emulsifier may lead to membrane fouling in the process, the membrane was washed by pressing 100 mL ethanol and 200 mL NaOH solution (1 wt % NaOH) through the membrane at 0.2 MPa pressure and room temperature, respectively. Finally, the membrane was rinsed with 900 mL pure water at 0.1 MPa pressure and 70°C. The membrane flux can be effectively recovered near its original permeate flux by this cleaning procedure.

Analysis

The interfacial tension of oil and water was measured by the Du Nouy Ring method (Sigma 70 tensiometer, KSV Instruments, Helsinki, Finland). The particle sizes of emulsions were determined using an optical microscope and a light-scattering particle sizer (Mastersizer 2000, Malvern Instruments, Malvern, UK). The range of the droplet size distribution is defined as follows

$$\alpha = \frac{D_{90} - D_{10}}{D_{50}} \tag{4}$$

where D_{90} is the diameter under which 90% of the droplets in the cumulative distribution fall, D_{10} is the diameter corresponding to 10% of droplets, and D_{50} is the diameter corresponding to 50% of the droplets.[12]

Results and Discussion

Coarse emulsion in the first stage

In our experiments, we first compared the first jet-flow membrane emulsification with conventional membrane emulsification. A ZrO_2 membrane, having a nominal size of 0.16 μm, was used in both cases. The oil/water interfacial tension was 2.87 mN/m when 2 wt % SDS was dissolved in the water phase, and the critical emulsification pressure (P_{cr}) was 54.96 kPa, which was calculated by Eq. 2. Figure 3 shows the droplet size distribution of the emulsion prepared by the conventional membrane emulsification (typical operating conditions: pressure = $1.1 \times P_{cr}$ (60 kPa); stirring speed = 280 rpm; temperature = 20°C; emulsifier concentration = 2 wt %). As shown in Figure 3, the volume average size of the emulsion was 3.53 μm. The range of droplet size (α) was 2.5, calculated from Eq. 4. However, we observed that the flux was very low, 4.8 L m^{-2} h^{-1}. This phenomenon can be explained by the smaller numbers of active pores taking part in the formation of droplets under the lower pressure.[7] The emulsion was still not monodispersed because of the presence of the coarse pores. Figure 4 shows the droplet size distribution of emulsions prepared at a pressure of 350 kPa. The droplet size was 54.69 μm and the flux in the first stage was 150 L m^{-2} h^{-1}, values that are much greater than those obtained when the emulsification is operated at $1.1 \times P_{cr}$. Membrane flux were stable in both cases; neither a decrease nor an increase in flux was observed in our experiment. Because a membrane itself is of pore size distribution, the value of β is dependent on the pore size of the membrane. The corresponding value of β for the nominal pore size (0.16 μm in this experiment) was 6.4, whereas a larger pore size corresponds to a larger value of β. In particular, the value of β for the maximum pore size (1.35 μm) was 53.8. Therefore, the

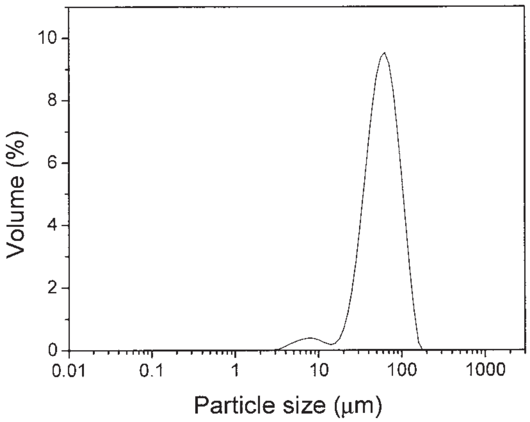
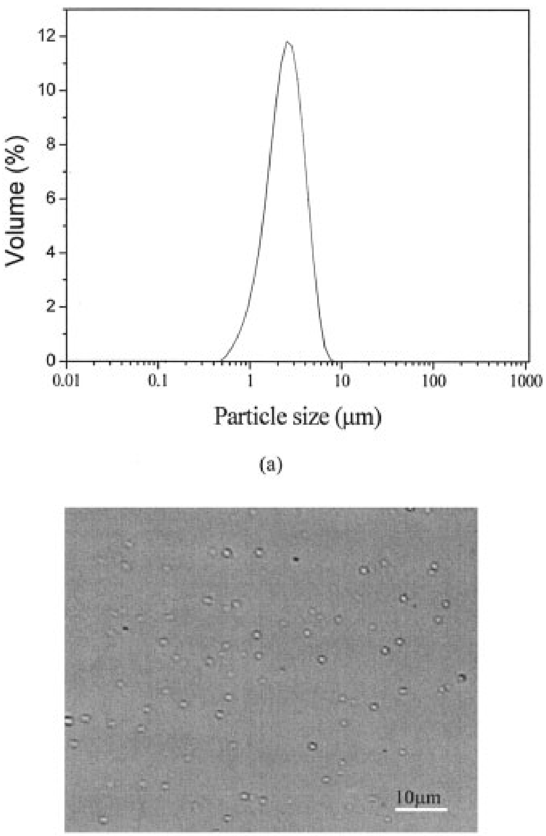


Figure 4. Droplet size distribution of the coarse emulsion prepared with the first jet-flow ceramic membrane emulsification using a ZrO_2 membrane, with a pore size of 0.16 μm, at 200 kPa, 280 rpm, and 2 wt % SDS.



(a)

(b)

Figure 5. Emulsion prepared by two-stage jet-flow membrane emulsification using α-Al_2O_3 ceramic membrane, with a pore size of 1.5 μm, at 200 kPa, 280 rpm, and 20°C.

(a) Droplet size distribution of the emulsion determined by a light-scattering particle sizer (Malvern Mastersizer 2000); (b) optical microscope photograph of the emulsion.

jet flow could form at least through partial pores of the membrane in this case.

Monodispersed emulsion in the second stage

Using the secondary jet-flow membrane emulsification, monodispersed emulsion with small droplet size could be obtained. Figure 5a shows the droplet size of the emulsion prepared by using an α-Al_2O_3 ceramic membrane, having a nominal pore size of 1.5 μm, at 200 kPa pressure, 280 rpm stirring speed, and 20°C temperature. The volume-average droplet size of the emulsion was 2.29 μm and α was 1.2. The droplet size was uniform and about 1.5 μm, which was observed from the optical microscope photograph (Figure 5b). The flux reached 454 L m^{-2} h^{-1}, which is attributed to the larger pore size and higher pressure. The value of the corresponding β was 34.1 and white streamlines could be observed at this stage, and the oil concentration of the final emulsion was 2.8 v/v %. The results from two methods are compared in Table 2.

Critical jet emulsion pressure (P_{cj}) and choice of membrane

Ceramic microfiltration and ultrafiltration membranes having a small pore size were previously used in the oil/water separation process.[20-22] Only water could be forced through the membrane pores at low pressure, when the droplet size of the emulsion is larger than the pore size of the membrane. To prepare the monodispersed emulsion using the secondary jet-flow membrane emulsification, the appropriate pressure and the pore size of a membrane are two important factors. Three different ceramic membranes, having nominal pore sizes of 0.16 μm (ZrO_2), 1.5 μm (α-Al_2O_3), and 5 μm (α-Al_2O_3), were compared in our experiments. Because container 9 (in Figure 2) was transparent, we could observe the phenomena during the process. The streamlines of jet flow were colorless when the separation of oil and water occurred at low pressure. With increasing pressure, the color of the streamline became white and the droplets of the emulsion were forced through the membrane pores. The critical point corresponding to the pressure is defined as the critical jet emulsion pressure (P_{cj}). When the ZrO_2 membrane with 0.16 μm pore size was used, no emulsification occurred, even after the pressure was increased to 250 kPa. The P_{cj} values of the two α-Al_2O_3 membranes are 140 and 70 kPa, respectively; the pressures are far higher than the critical pressures calculated from Eq. 2.

The three membranes used were compared at a pressure 1.4 times that of the P_{cj}, a stirring speed of 280 rpm, and a temperature of 20°C. Although the emulsion could be pressured at the initial stage of the experiment by using the ceramic membrane with the pore size of 0.16 μm, separation of oil and water soon occurred and the coarse emulsion was concentrated. Figure 6 shows the droplet size of the emulsion prepared by using an α-Al_2O_3 ceramic membrane with a pore size of 5 μm. The droplet size of the emulsion was 3.1 μm and the α was 10.9. Although flux of the membrane having a pore size of 5 μm is higher, the emulsion is not monodispersed. Therefore, we selected the ceramic membrane with a pore size of 1.5 μm as the emulsification medium in the second stage.

Effect of operation conditions on the second stage

The transmembrane pressure and the stirring speed are two important operation parameters in the investigation. Lower pressure means lower flux and separation of oil and water. In our experiments, when the pressure is >0.19 MPa, the coarse emulsion could be completely forced into the continuous phase. Figure 7 shows the effects of the transmembrane pressure on the flux. With increasing pressure, the flux increased.

Table 2. Comparison between Jet-Flow Membrane Emulsification and Conventional Membrane Emulsification

ME Method	D_p (μm)	ΔP (kPa)	β	D_d (μm)	α	J (L m^{-2} h^{-1})
Conventional	0.16	60	1.1	3.53	2.5	4.8
Jet-flow						
First stage	0.16	350	6.4	54.69	1.2	150
Second stage	1.5	200	34.1	2.29	1.2	454

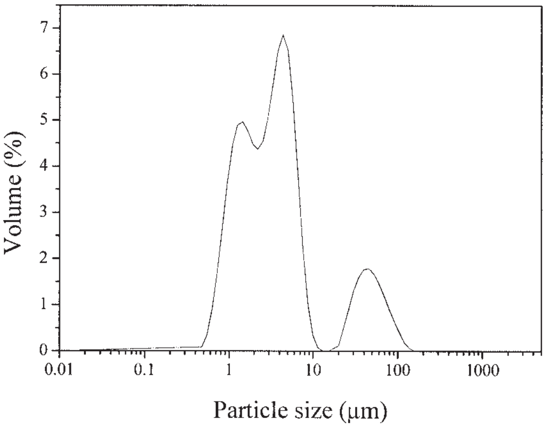


Figure 6. **Droplet size distribution of the emulsion prepared by two-stage jet-flow membrane emulsification using α-Al_2O_3 ceramic membrane, with a pore size of 5 μm, at 100 kPa and 280 rpm.**

The monodispersed emulsion could be formed when the pressure was no more than 0.23 MPa. The range of droplet size distribution and the droplet size of the emulsion prepared at the range of 0.19–0.23 MPa were similar, about 2.6 μm and 1.3. The α-value of the emulsion prepared at a pressure of 0.25 MPa was 14.84, which was polydispersed. Thus it concluded that the suitable pressure range for preparation of monodispersed emulsion is from 0.19 to 0.23 MPa.

Figure 8 shows the effects of the stirring speed on the droplet size (D_{50}) and the range of the droplet size distribution. When the stirring speed is 0 rpm, the process is identical to the dead-end microfiltration process. The droplet size of the emulsion was 3.77 μm and the α was 63.8. With increased stirring speed, the droplet size became small and the range of the droplet size distribution became narrow. When the stirring speed increased to 168 rpm, monodispersed emulsions could be formed. The droplet size was about 2 μm and the α was about 1.2. Because the shearing force is low on the membrane surface, the flux is not significantly influenced by the stirring speed in our experiments.

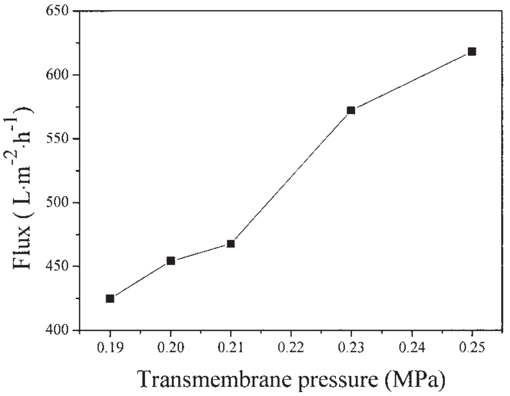


Figure 7. **Effects of transmembrane pressure on the flux of α-Al_2O_3 ceramic membrane, with a pore size of 1.5 μm, at a stirring speed of 280 rpm and temperature of 20°C.**

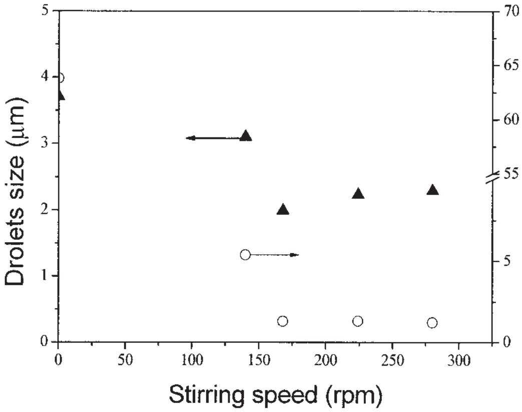


Figure 8. **Effects of stirring speed on droplet size and range of droplet size distribution (α) of the emulsion prepared by using a membrane, with a pore size of 1.5 μm, at a pressure of 0.20 MPa and temperature of 20°C.**

▲ Droplet size (D_{50}); ○ α.

Effects of emulsifier concentration on the emulsions

Figure 9 shows the effect of emulsifier concentration in the continuous phase on the droplet size. The droplet sizes were similar when the emulsifier concentration was in the range of 0–2 wt %, although the α was very wide when the concentration was <0.5 wt %, suggesting that some degrees of coalescence occur under low emulsifier concentration.

Conclusions

Monodispersed O/W emulsion can be prepared by two-stage membrane emulsification under jet-flow condition. The mono-

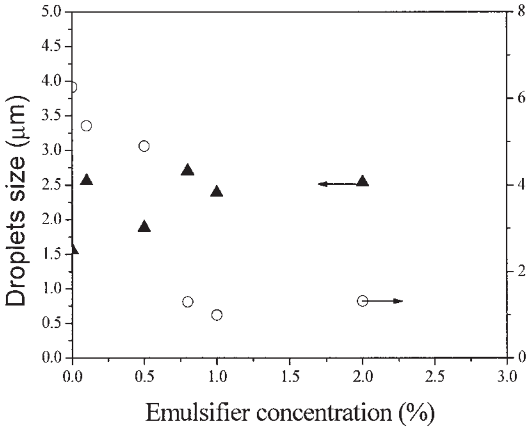


Figure 9. **Effects of emulsifier concentration on droplet size and range of droplet size distribution (α) of the emulsion prepared by using a ceramic membrane, with a pore size of 1.5 μm, at a pressure of 0.20 MPa, stirring speed of 280 rpm, and temperature of 20°C.**

▲ Droplet size (D_{50}); ○ α.

dispersed emulsion, with a volume average droplet size of 2.29 μm and range of droplet size distribution of 1.205, was obtained. The flux of the ZrO_2 membrane with pore size of 0.16 μm in the first stage was 150 L m^{-2} h^{-1}, at a pressure of 0.35 MPa and a temperature of 20°C, and the flux of the α-Al_2O_3 membrane with pore size of 1.5 μm in the second stage was 454 L m^{-2} h^{-1}, at a pressure of 0.2 MPa and a temperature of 20°C.

The second jet-flow membrane emulsification occurred only when the transmembrane pressure was higher than the critical jet emulsion pressure (P_{cj}). The flux of the membrane increased with increasing pressure, although the suitable range of pressure was 0.19–0.23 MPa. When the stirring speed was >168 rpm, the monodispersed emulsion with smaller droplet size could be prepared.

The method proposed in this study has advantages such as high flux and uniform droplet size, which in practice makes production of monodispersed emulsion possible.

Acknowledgments

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