Production Characteristics of Large Soybean Oil Droplets by Microchannel Emulsification Using Asymmetric Through Holes

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This study investigated the production characteristics of large soybean oil droplets dispersed in an aqueous solution containing an emulsifier using newly designed microchannel (MC) emulsification chips. The silicon MC emulsification chips consisted of numerous asymmetric through holes with a characteristic cross-sectional size of 20\(\mu\)m to 50\(\mu\)m, each consisting of a microslot and a circular MC. MC emulsification using such chips enabled the stable production of uniform large droplets with average diameters of 75\(\mu\)m and 179\(\mu\)m and a coefficient of variation below 2%. The detachment behavior of the large droplets generated from the asymmetric through holes was analyzed and discussed based on results obtained by real-time optical microscopy. The size of droplets smaller than 100\(\mu\)m was independent of the flow rate of the cross-flowing continuous phase \((Q_c)\) applied in this study. In contrast, the size of droplets larger than 100\(\mu\)m became sensitive to \(Q_c\) in its range over a critical value. The results for the effect of \(Q_c\) is discussed by analyzing the force balance acting on a dispersed-phase droplet that expands over the microslot. Large droplets with a very narrow size distribution were obtained at dispersed-phase fluxes \((J_d)\) of 50 \(L \cdot m^{-2} \cdot h^{-1}\) or less, whereas their average diameter was somewhat dependent on \(J_d\).

Key words: microchannel emulsification, large droplet, asymmetric through hole, droplet generation, droplet detachment

1. Introduction

Large droplets with sizes of 50\(\mu\)m to 1000\(\mu\)m dispersed in another immiscible liquid are thermodynamically unstable. They are stabilized by emulsifier molecules dissolved in a continuous phase for a finite period of time. Liquid–liquid dispersions consisting of large droplets are usually used as templates for producing microparticles and microcapsules through gelation, polymerization, and other secondary reactions or processes in the food and pharmaceutical industries. In particular, monodisperse microparticles and microcapsules, which require uniform large droplets as templates, are useful microcarriers for micron-scale biological materials, having a high potential for controlled release of the bioactive substances yielded inside the micromaterials. To date, uniform large droplets have been applied to produce seamless microcapsules containing lactobacilli [1] and gel microbeads containing living cells [2].

In practice, a single nozzle set in a flow channel is used to produce uniform large droplets with sizes exceeding 200\(\mu\)m [1,3]. In this technique, a dispersed phase that has passed through a nozzle is injected into a coflowing continuous phase (Fig. 1a), and droplets are generated individually. This droplet generation process differs from conventional emulsification techniques in which larger droplets are broken up into non-uniform smaller ones by inhomogeneous extensional, shear, and/or cavitation forces [4]. Droplet generation mechanisms in a coflowing two-phase system may be divided into dripping driven by absolute instability and jetting driven by convective instability or absolute instability [3,5]. The size of the generated large droplets can be varied in a droplet production setup [3], indicating that their size is sensitive to the flow rates of both phases. It is also challenging to parallelize nozzles in a single setup. Vladisavljević and Williams recently reported that rotating–membrane emulsification is capable of producing uniform large droplets with sizes of 100\(\mu\)m by injecting a dispersed phase through a rotating cylindrical membrane with laser–drilled pores into a continuous–phase region (Fig.
The resultant droplet size depends greatly on the rotating speed of the membrane used and is considered to be sensitive to the flow rates of both phases. It is necessary to note that the continuous phase suitable for this technique is restricted to viscous liquids with an apparent viscosity of $>100 \text{ mPa s}$, which would be useful for cosmetic applications.

In the late 1990s, the authors’ group proposed a promising technique for producing uniform droplets called microchannel (MC) emulsification [7]. Droplet production for MC emulsification is performed by injecting a dispersed phase through an MC array consisting of parallel microgrooves and a slit-like terrace into a well filled with a continuous phase (Fig. 1c). MC emulsification has a unique droplet generation process based on spontaneous transformation of the dispersed phase that passes through the MCs in the absence of a cross-flowing continuous phase [8]. This spontaneous droplet generation is robust, since the resultant droplet size is basically not sensitive to the flow rate of either phase [9,10]. Kobayashi et al. recently developed MC emulsification chips with microfabricated through holes, aimed at higher droplet productivity [11,12]. These novel MC emulsification chips have demonstrated the production of uniform droplets of vegetable oil at a maximum flux of $60 \text{ L m}^{-2} \text{ h}^{-1}$ [13]. Kobayashi et al. also reported that an MC emulsification chip with asymmetric through holes is better able to stably produce uniform droplets, especially of low viscosity [12]. Existing MC emulsification chips can produce uniform (large) droplets with sizes of 2 to $100 \mu \text{m}$ [14,15]; however, these high-performance chips with asymmetric through holes were designed for producing uniform droplets smaller than $50 \mu \text{m}$. It is expected that uniform large droplets would be stably and efficiently produced using MC emulsification chips with asymmetric through holes whose dimensions have been appropriately enlarged. Moreover, these MC emulsification chips, which can produce uniform large droplets, have useful applications in various industries including food industry.

This study seeks to investigate the production characteristics of large oil droplets using newly designed MC emulsification chips with microfabricated asymmetric through holes. A model oil–in–water system consisting of refined soybean oil and an aqueous solution containing an emulsifier was chosen for this study. The effects of the size of the asymmetric through holes and the flow rates of the two phases were investigated to demonstrate the production of uniform large droplets controllable in size and quantity. The droplet-generation and droplet-detachment characteristics were also analyzed and discussed.

2. Materials and methods

2.1 MC emulsification chips

The $24 \times 24$-mm MC emulsification chip (WMS3) used in this study is depicted in Fig. 2a. Asymmetric through
holes, each consisting of a microslot and a circular MC, were compactly arranged within a 10×10-mm central area of the chip (Figs. 2a and 2b). Three types of MC arrays with the dimensions presented in Table 1 were designed for this study. The WMS3 chips were made of single-crystal silicon, and the MC arrays were fabricated by deep reactive ion etching (DRIE) [12]. As demonstrated in Fig. 2c, the fabricated asymmetric MCs were of uniform size. Before the first usage, the surface of the WMS3 chip was oxidized in a plasma reactor (PR41, Yamato Scientific, Tokyo, Japan), forming a hydrophilic silicon dioxide layer on the chip.

2.2 Materials and fluid properties

The dispersed phase used was refined soybean oil (Wako Pure Chemical Ind., Osaka, Japan). The continuous phase used was a Milli-Q water solution containing 1.0 wt% of polyoxyethylene (20) sorbitan monolaurate (Tween20, Wako Pure Chemical Ind.). The dynamic viscosity was 50.4 mPa s for the dispersed phase and 1.0 mPa s for the continuous phase [16]. The equilibrium interfacial tension between the two phases was 5.3 mN m⁻¹ [16].

2.3 Experiment setup and procedure

The MC emulsification experiments were conducted using the laboratory-scale setup depicted in Fig. 3a. The emulsification setup consists of a custom-made module equipped with a WMS3 chip, syringe pumps (Model 11, Harvard Apparatus, Massachusetts, USA) equipped with glass syringes, and an optical microscopy system [11]. Prior to module assembly, a chip soaked in the continuous phase was degassed with ultrasonication at 100 MHz (VS-100III, As One Co., Osaka, Japan). During module assembly, the chip was mounted in a holder filled with continuous phase, and two channels for flowing fluids were formed inside the module. The assembled module was mounted on a custom-made frame equipped with a high-precision XY stage and a metallographic microscope (MS-511 Seiwa Kogaku Seisakusho Ltd., Tokyo, Japan). A syringe pump was filled with each fluid, and the fluid was introduced into the module via a flexible plastic tube with an inner diameter of 2.0 mm (Fig. 3a). The continuous phase in the channel beneath the chip was replaced by pressurized dispersed phase. Afterward, the dispersed phase was injected through asymmetric MCs into a continuous-phase area over the chip to generate droplets (Fig. 3b). Droplet generation from the outlets of the microslots was monitored in real time. The flow rate of the dispersed phase ($Q_d$) was controlled in a range between 1.0 mL h⁻¹ and 12.0 mL h⁻¹. The flow rate of the continuous phase ($Q_c$) was controlled in a range between 0 mL h⁻¹ and 1000 mL h⁻¹. MC emulsification was carried out at 25±1°C.
2.4 Analysis

The number average diameter of the produced droplets was determined by measuring 100 droplets using image analysis software (WinRoof version 5.6, Mitani Co., Ltd., Fukui, Japan). Their coefficient of variation, which we used as an index expressing the droplet size distribution, was calculated by the following equation:

\[
CV = \left(\frac{\sigma}{d_{av,dr}}\right) \times 100
\]  

where CV is the coefficient of variation of the droplets, \(\sigma\) is the standard deviation of the droplets, and \(d_{av,dr}\) is the number-average droplet diameter. When the effect of \(Q_c\) was investigated, the droplet diameter \((d_{av})\) was determined by averaging the diameters of ten droplets generated from a microslot positioned at the center of the most upstream row in an MC array.

3. Results and discussion

3.1 Droplet generation via MC arrays

Droplet production using WMS3 chips was investigated with a \(Q_d\) of 1.0 mL h\(^{-1}\) and a \(Q_c\) of 0 mL h\(^{-1}\) or 50 mL h\(^{-1}\). Figure 4 presents typical micrographs of droplet generation from the microslots using the chips. Uniform oil droplets were periodically generated via MC arrays. Droplets were also generated in the absence of a crossflowing continuous phase, which strongly suggests that the dispersed phase that passed through the microslots transformed spontaneously into droplets in the continuous-phase area. This droplet generation process is a fundamental and unique feature of MC emulsification, as previously reported by Sugiura et al. [8]. Optical microscopy also demonstrated that droplets were generated from almost all of the microslots. The size of the resultant droplets increased as the shorter width of microslots increased (Figs. 2c and 4), since their depth \((h_{slot})\) was the same for all the WMS3 chips (Table 1). \(d_{av,dr}\) for the resultant O/W emulsions was 75.1 \(\mu m\) for WMS3-1, 118.7 \(\mu m\) for WMS3-2, and 178.5 \(\mu m\) for WMS3-3. The droplet/slot size ratio \((d_{av,dr}/w_{s,slot})\) fell between 3.6 and 4.0, which would be reasonable for MC emulsification using vegetable oil-in-water systems [17]. Although \(w_{s,slot}\) is a dominant factor in determining the size of the droplets generated by MC emulsification, it is necessary to consider that \(h_{slot}/w_{s,slot}\) also affects the droplet size to some extent [18]. As presented in Fig. 5, the produced droplets with CV values of 1.4% to 1.9% had very narrow size distributions with a monomodal peak. The preceding results demonstrate that the MC emulsification chips developed in this study can generate uniform large droplets with a maximum size of about 180 \(\mu m\) dispersed in a continuous phase.

The generated droplets remained attached to the chip surface (Fig. 4) until the next advancing dispersed phase in the microslot pushed them away. Figure 6 presents a sequence of schematic drawings of the droplet generation process via a microslot and a circular MC and the subsequent detachment of a generated droplet. The dispersed phase expanding from the slot outlet was...
attached to the chip surface (stage ii). Following that, droplet generation is completed by the instantaneous pinch-off of the neck inside the microslot (stages ii and iii). The generated droplet remained attached to the chip surface (stage iii), which can be explained as follows. The MC emulsification chips used here have a negative surface potential due to the presence of silanol groups on a silicon dioxide layer, whereas the oil droplets stabilized by a nonionic Tween20 have a negligible charge. The weak repulsive force between the droplet surface and the chip surface leads to droplet attachment. It is necessary to note that oil droplets stabilized by an anionic emulsifier (sodium dodecyl sulfate) detached smoothly from the slot outlets due to the strong repulsive force [12]. Although the next advancing disk of the dispersed phase touched the generated droplet (stage iv), no coalescence occurred during the experiments. Optical microscopy demonstrated that the time scale between stages iii and

Fig. 4 Typical droplet generation results using WMS3 chips. (a) WMS3-1. (b) WMS3-2. (c) WMS3-4. The continuous phase was forced to flow from top to bottom as designated by arrows.

Fig. 5 Size distributions of the oil droplets produced using WMS3 chips. (a) WMS3-1. (b) WMS3-2. (c) WMS3-4. $d_{dr}$ is the droplet diameter.
iv was on the order of seconds. Schröder and Schubert reported the dynamic interfacial tension between vegetable oil and water containing Tween20 at 0.1 wt% or 2.0 wt% [19]. The interfacial tension decreased steeply within one second, and then decreased slowly with time. This result suggests that Tween20 molecules can rapidly cover a newly created oil-water interface. When a droplet is just generated at stage iii, the surfaces near the pinch-off point of the neck would be only partially covered by Tween20 molecules. The surfaces are considered to be sufficiently covered by Tween20 molecules within several seconds, which prevents coalescence between the droplet and the advancing disk at stage iv.

3.2 Effect of the flow rate of the continuous phase

3.2.1 Flow state of the continuous phase

To investigate the effect of \( Q_c \), MC emulsification using WMS3 chips was conducted while varying \( Q_c \) between 50.0 mL h\(^{-1}\) and 1,000 mL h\(^{-1}\). \( Q_d \) was fixed at 1.0 mL h\(^{-1}\) during the emulsification. The flow state of the cross-flowing continuous phase was evaluated as follows. The average continuous-phase velocity \( (U_{c,av}) \) was estimated by

\[
U_{c,av} = \frac{Q_c}{A_{ch}} \tag{2}
\]

where \( U_{c,av} \) is the average continuous-phase velocity, and \( A_{ch} \) is the cross-sectional area of the flow channel with a 1.0-mm height over the top of the chip. \( U_{c,av} \) values in this section fell between 0.9 mm s\(^{-1}\) and 17.4 mm s\(^{-1}\).

Following this, the Reynolds number of the cross-flowing continuous phase \( (Re_c) \) was calculated by

\[
Re_c = \frac{\rho_c U_{c,av} d_{eq,ch}}{\eta_c} = \frac{\rho_c U_{c,av} (4A_{ch}/L_{ch})}{\eta_c} \tag{3}
\]

where \( \rho_c \) is the continuous-phase density, \( d_{eq,ch} \) is the equivalent diameter of the channel for flowing the continuous phase, \( L_{ch} \) is the wetted perimeter of the channel, and \( \eta_c \) is the continuous-phase viscosity. The calculated \( Re_c \) values, which ranged from 1.4 to 27.7, suggest that the cross-flowing continuous phase was a laminar state.

3.2.2 Results

Figure 7 illustrates the effect of \( Q_c \) on the diameter of the produced large droplets. The resultant droplet diameter \( (d_{dr}) \) for WMS3-1 remained almost constant in the \( Q_c \) range investigated here, which is similar to the previous MC emulsification results for generating soybean oil droplets with \( d_{av} \) of \( \sim 30 \mu m \) and \( \sim 50 \mu m \) [11,15]. \( d_{dr} \) values for WMS3-2 and -3 were also unchanged in \( Q_c \) ranges below the critical values \( (500 \text{ mL h}^{-1} \text{ for WMS3-2 and } 400 \text{ mL h}^{-1} \text{ for WMS3-3}) \) but decreased somewhat in the \( Q_c \) ranges above the critical values. \( d_{dr} \) values at a maximum \( Q_c \) of 1,000 mL h\(^{-1}\) were about 5 \( \mu m \) lower than those at a control \( Q_c \) of 50 mL h\(^{-1}\). In other words, the droplet volume decreased by up to 12% over the critical \( Q_c \). Thus, the cross-flowing continuous phase was found to be a factor affecting the droplet size when large droplets with \( d_{dr} \) of \( > 100 \mu m \) are generated at high \( Q_c \). Large droplets with broader size distributions might be generated via an MC array with \( Q_c \) above the critical value, which is due to the parabolic distribution of the continuous-phase velocity over the chip surface. However, the critical \( Q_c \) values were sufficiently high to appropriately sweep away the droplets from the outlet of an MC array; therefore, uniform large droplets can be collected from the module by applying \( Q_c \) below the critical value.

Figure 8 depicts typical characteristics of droplets generated via an MC array (WMS3-2) at different \( Q_c \). Below the critical \( Q_c \), the expanding dispersed
phase did not move toward the downstream area of the cross-flowing continuous phase during droplet generation, and the generated droplets remained attached to the slot outlet (Fig. 8a). The reason for this was explained in an earlier section. Thus, droplet generation in the low $Q_c$ range was not affected by the cross-flowing continuous phase. Above the critical $Q_c$, a dispersed-phase droplet expanded without being affected by the cross-flowing continuous phase (top of Fig. 8b), whereas the expanding droplet began to tilt toward the downstream side just before the completion of droplet generation (middle of Fig. 8b). In addition, the generated droplet was rapidly swept away from the slot outlet by the cross-flowing continuous phase (bottom of Fig. 8b). The micrographs in Fig. 8b demonstrate that the cross-flowing continuous phase affected the droplet generation characteristics as well as the resultant droplet size in the high $Q_c$ range. The droplet generation characteristics depicted in Fig. 8 were also observed using WMS3–4. In contrast, when WMS3–1 was used, only the droplet generation characteristics depicted in Fig. 8a were observed irrespective of $Q_c$.

3.2.3 Discussion

The authors will discuss the forces acting on a dispersed-phase droplet that expands over a microslot. The drag force due to the cross-flowing continuous phase ($F_D$) is influenced by the local continuous-phase velocity. The continuous phase that flows in a laminar state in the channel has a parabolic velocity distribution, as illustrated in Fig. 9a. The continuous-phase velocity in this case has a maximum value at the center of the channel. The maximum continuous-phase velocity ($U_{c,\text{max}}$) in a laminar flow is assumed to be approximately twice $U_{c,\text{av}}$ [20]. The continuous-phase velocity at the center of the expanding droplets ($U_{c,\text{dr}}$) can be estimated using the following equation:

$$U_{c,\text{dr}} = U_{c,\text{max}} \left[1 - \frac{(h_{c,\text{ch}} - d_{dr})}{h_{c,\text{ch}}} \right]$$

Fig. 7 Effect of the flow rate of the continuous phase ($Q_c$) on the resultant droplet diameter ($d_{dr}$). $U_{c,\text{av}}$ is the average continuous-phase velocity in the top flow channel.

Fig. 8 Typical droplet detachment results using a WMS3–2 chip. The applied flow rates of the continuous phase were 400 mL h$^{-1}$ in (a) and 1000 mL h$^{-1}$ in (b). The continuous phase was forced to flow from top to bottom as designated by arrows. Adjacent micrographs in (b) have a time interval of $1/30$ s.
where $h_c$ is the channel height. The $U_{c,dr}$ values estimated using the data in this study are plotted in Fig. 9b. The $U_{c,dr}/U_{c,av}$ ratio was 0.29 for WMS3-1, 0.43 to 0.45 for WMS3-2, and 0.64 to 0.65 for WMS3-3, indicating that $U_{c,dr}$ greatly depended on $d_{dr}$ and was significantly lower than $U_{c,av}$. The cross-flowing continuous phase affected the droplet generation characteristics just before the completion of droplet generation, as demonstrated in Fig. 7. At the moment depicted in Fig. 10, $F_D$ can be given by

$$F_D = 3k_x \pi \eta_d d_{dr} U_{c,dr}(1 + (2/3) \kappa)/(1 + \kappa)$$

where $k_x$ (a wall-correction factor for a sphere) is 1.7, and $\kappa$ is the viscosity ratio of the continuous phase to the dispersed phase [20]. $F_D$ acts to promote droplet detachment from the slot outlet (Fig. 10). Figure 11a plots the $F_D$ values estimated using the data in this study and depends on $Q_c$ and the type of MC array, which also affect $d_{dr}$. At a given $Q_c$, WMS3-4 had the greatest $F_D$, exceeding $F_D$ for the other MC arrays by 5.0 to 5.3 times for WMS3-1 and 2.2 to 2.3 times for WMS3-2. $F_D$ at the critical $Q_c$ exceeded $F_D$ at the maximum $Q_c$ for WMS3-1, suggesting that the $F_D$ that acted during droplet generation using WMS3-1 was insufficient to cause droplet detachment.

Besides $F_D$, an expanding dispersed-phase droplet (Fig. 10) was affected by the buoyancy force ($F_B$), the inertial force associated with the dispersed phase flowing out from an MC ($F_I$), the lift force due to the velocity gradient in a cross-flowing continuous phase, and $F_L$ is the interfacial tension force.

$$F_B = (\pi / 6)\eta_d^3 k \Delta \rho$$

$$F_I = (\pi / 3) \rho_d d_{MC}^2 U_{c,MC}^2$$

$$F_L = 0.761(\tau_w d_{dr}^2 \rho_d^{1/3} / \eta_d)$$

$$F_L = \pi d_{neck}^2 \gamma = \pi d_{MC}^2 \gamma$$

Fig. 9 (a) Schematic drawing of the profile of the cross-flowing continuous phase inside the flow channel during droplet generation. $h_{c,ch}$ is the channel height, $U_{c,dr}$ is the continuous-phase velocity at the center of an expanding droplet, and $U_{c,max}$ is the maximum continuous-phase velocity. (b) Effect of the flow rate of the continuous phase ($Q_c$) on $U_{c,dr}$. $U_{c,av}$ is the average continuous-phase velocity.

Fig. 10 Schematic drawing of the main forces acting on a dispersed-phase droplet that expands over a microslot under a cross-flowing continuous phase. $F_B$ is the buoyancy force, $F_D$ is the drag force caused by a cross-flowing continuous phase, $F_I$ is the inertial force exerted by a dispersed phase flowing out from an MC, $F_L$ is the lifting force caused by the velocity gradient in a cross-flowing continuous phase, and $F_J$ is the interfacial tension force.
The characteristic velocity of the dispersed phase flowing inside the MC, \( \tau_w \) is the wall-shear stress, and \( \gamma \) is the interfacial tension across the two phases [20]. Figure 11b plots the \( F_B \) and \( F_\gamma \) values estimated using the data in this study. For a given \( Q_c \) and MC array, the \( F_1 \) and \( F_L \) values were at least several orders of magnitude smaller than the \( F_D \) and \( F_B \) values, indicating that \( F_1 \) and \( F_L \) can be considered negligible. \( F_B \) was almost independent of \( Q_c \) but depended greatly on \( d_w \) (i.e., the type of MC arrays). The \( F_B \) ratio of WMS3-4 to the other MC arrays was 12.1 to 13.1 for WMS3-1 and 3.4 to 3.7 for WMS3-2. The \( F_D \) and \( F_B \) values were comparable at a \( Q_c \) of 50 mL h\(^{-1}\) (Fig. 11). \( F_D \) becomes greater than \( F_B \) as \( Q_c \) increases, with the \( F_D/F_B \) ratio reaching 33.8 for WMS3-1, 22.3 for WMS3-2, and 14.0 for WMS3-4. The \( F_D/F_B \) ratio at the critical \( Q_c \) was 10.7 for WMS3-2 and 6.9 for WMS3-4. A comparison between \( F_1 \) and \( F_B \) indicates that \( F_B \) is the major force acting to promote droplet detachment under the conditions applied here (except for \( Q_c \) of 50 mL h\(^{-1}\)). \( F_\gamma \) values, which ranged from \( 3.3 \times 10^{-7} \) N to \( 8.5 \times 10^{-7} \) N, were independent of \( Q_c \) but were dependent on the type of MC array. \( F_\gamma \) was at least one order of magnitude greater than \( F_D \) (Fig. 11). The \( (F_\gamma-F_B)/F_D \) values with \( Q_c \) at the critical value or higher were 68.7 to 37.0 for WMS3-2 and 64.9 to 26.8 for WMS3-4, and the smallest \( (F_\gamma-F_B)/F_D \) value for WMS3-1 was 53.5. Although \( F_\gamma \) was the greatest force acting on the expanding droplet, the effect of \( F_D \) became greater compared to the other forces as \( Q_c \) increased. From an analysis of the force balance at the moment depicted in Fig. 10, it is considered that \( F_B \) becomes effective in promoting pinch-off of the neck and droplet detachment for \( Q_c \) above the critical value, leading to the generation of smaller droplets.

### 3.3 Effect of the flow rate of dispersed phase

The effect of \( Q_d \) on the size and size distribution of the produced droplets was investigated using a WMS3-2 chip. \( Q_c \) was fixed at 50 mL h\(^{-1}\) during MC emulsification. As can be seen in Fig. 12, \( d_{av,dr} \) was somewhat influenced by \( Q_d \), ranging from 117.6 \( \mu \)m to 130.8 \( \mu \)m. Large oil droplets of a very narrow size distribution with CV below 2% were obtained at \( Q_d \) of 5 mL h\(^{-1}\) or less (Figs. 12 and 13a); however, further increase in \( Q_d \) caused an increase in the CV values of the resultant droplets. For \( Q_d \) above the critical value of 5.0 mL h\(^{-1}\), larger droplets were also generated, and the droplet size distribution became wider toward the larger-size area (Figs. 13b and 13c). The droplet-generation frequency per an MC emulsification chip \( (v_{chip}) \) at a given \( Q_d \) can be estimated by

\[
v_{chip} = \frac{Q_d}{V_{av,dr}}
\]

where \( V_{av,dr} \) is the average droplet volume. The \( v_{chip} \) at the critical \( Q_d \) was \( 5.0 \times 10^6 \) h\(^{-1}\), corresponding to 1.4\( \times 10^3 \) s\(^{-1}\). The droplet generation frequency from a given microslot in this case was calculated to be 0.67 s\(^{-1}\). The critical \( Q_d \) value is equal to a dispersed-phase flux \( (J_d) \) of 50 L m\(^{-2}\) h\(^{-1}\), which is of the same order of magnitude as the critical \( J_d \) of a previous MC emulsification chip (TMS1-3) used for producing monodisperse soybean oil-in-water emulsions with \( d_{av,dr} \) of 40 \( \mu \)m [13]. This \( J_d \)
value also indicates that uniform droplets are generated via an MC array with high efficiency. The results obtained in this section demonstrate that the WMS3-2 chip has sufficient capacity to generate uniform large droplets on a laboratory scale.

4. Conclusions

This paper has demonstrated that uniform large droplets with sizes as large as 180 μm and CV below 2% were stably produced using new MC emulsification chips with microfabricated asymmetric through holes. The size of the resultant large droplets was controlled by the cross-sectional size of the microslots. The results obtained in this study also clarified that it is necessary to consider the effect of $Q_c$ on the droplet size, especially for large droplets with sizes exceeding 100 μm. An analysis of the force balance during droplet generation suggests that the decrease in the resultant droplet size above a critical $Q_c$ may be attributed to the fact that $F_D$ becomes effective for promoting pinch-off of the neck and droplet detachment. One MC emulsification chip (WMS3-2) designed for this study was capable of producing uniform large droplets of vegetable oil with a maximum $J_d$ equivalent to that of a previous MC emulsification chip used for producing smaller droplets. Although the MC emulsification chip permits the laboratory-scale production of uniform large droplets, its scaling-up and parallelization must be performed to achieve practical-scale production.

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Nomenclature

\( A_{ch} \) : cross-sectional area of flow channel, m\(^2\)

\( CV \) : coefficient of variation, –

\( d_{dr} \) : droplet diameter, m

\( d_{eq,ch} \) : average droplet diameter, m

\( d_{MC} \) : MC diameter, m

\( F_B \) : buoyancy force, N

\( F_D \) : drag force caused by a cross-flowing continuous phase, N

\( F_I \) : inertial force exerted by a dispersed phase flowing out from a MC, N

\( F_L \) : lifting force caused by the velocity gradient in a cross-flowing continuous phase, N

\( F_y \) : interfacial tension force, N

\( g \) : acceleration due to gravity [m s\(^{-2}\)]

\( h_{c,ch} \) : height of flow channel, m

\( h_{MC} \) : depth of circular MC, m

\( h_{slot} \) : depth of microslot, m

\( J_d \) : dispersed-phase flux, L m\(^{-2}\) h\(^{-1}\)

\( k_x \) : wall correction factor for a sphere, –

\( L_{ch} \) : wetted perimeter of flow channel, m

\( l_{MCs} \) : distance between two adjacent MCs, m

\( l_{rows} \) : distance between two rows, m

\( Q_c \) : flow rate of continuous phase, L h\(^{-1}\)

\( Q_d \) : flow rate of dispersed phase, L h\(^{-1}\)

\( Re_c \) : Reynolds number of cross-flowing continuous phase, –

\( U_{av,dr} \) : average continuous-phase velocity, m s\(^{-1}\)

\( U_{dr} \) : continuous-phase velocity at the center of an expanding droplet, m s\(^{-1}\)

\( U_{max,MC} \) : maximum continuous-phase velocity, m s\(^{-1}\)

\( U_{d,MC} \) : characteristic dispersed-phase velocity inside MC, m s\(^{-1}\)

\( w_{long} \) : longer width of microslot, m

\( w_{short} \) : shorter width of microslot, m

\( V_{av,ch} \) : average droplet volume, m\(^3\)

\( v_{chip} \) : droplet generation frequency per MC emulsification chip, h\(^{-1}\)

Greek symbols

\( \eta_c \) : continuous-phase viscosity, Pa s

\( \gamma \) : interfacial tension across two phases, N m\(^{-1}\)

\( \kappa \) : ratio of the viscosity of continuous phase to dispersed phase, –

\( \rho_c \) : continuous-phase density, kg m\(^{-3}\)

\( \Delta \rho \) : density difference between two phases, kg m\(^{-3}\)

\( \sigma \) : standard deviation, m

\( \tau_w \) : wall-shear stress, N

References

14) I. Kobayashi, K. Uemura, M. Nakajima; Formulation of


非対称微細貫通孔を用いたマイクロチャネル乳化によるラージ微小大豆油滴の製造特性

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連続相となる液体の中に分散しているラージ微小液滴（直径 50～100 μm）は、微粒子や微小カプセルを製造するための基材として食品産業、医薬品産業などでよく利用されている。サイズが均一な単分散微粒子・微小カプセルは、細胞・微生物の内包および微粒子・微小カプセルの内部で産出された生理活性物質の放出に有用な微小キャリアである。前述の微小材料のサイズ分布を基材となるラージ微小液滴のサイズ分布に大きな依存するため、単分散微粒子・微小カプセルを製造するには均一径ラージ微小液滴を利用することが必要である。

ラージ微小液滴の製造は、多重ノズルを用いて連続相の中に分散相を滴化させて行うのが一般的である。この手法では直径 200 μm 以上の均一径ラージ微小液滴を製造することが可能であるが、各々の液体の流量を精密に制御する必要がある之上、ノズルの並列化も容易ではない。また、回転翼乳化法よろばれる手法を用いて直径 100 μm 程度の均一径ラージ微小液滴を製造することも可能であるが、この手法で適用可能な素材は高粘性液体に限定される。

筆者らの研究グループは、独特な構造をもつ多数の並列微細液滴であるマイクロチャネル（MC）アイレを用いた MC 乳化を 1990 年代後半に提案した。MC 乳化では、MC アレイを介して分散相を圧入することで液滴径が精密に制御された均一径微小液滴を製造可能である。MC 乳化の液滴作製プロセスは極めてマイルドであり、なかかつ各々の液体の流量の影響も受けにくい。筆者らが最近開発した非対称貫通孔型 MC アレイは、均一径微小液滴を安定かつ高生産速度で製造可能な高性能 MC 乳化チップである。しかし、非対称貫通孔型 MC アレイを用いて製造可能な微小液滴の直径は 50 μm 未満に限定されている。そこで本研究では、新たに設計した非対称貫通孔型 MC アレイを用いた均一径ラージ微小液滴の製造を目的として種々の検討を行った。

単結晶シリコン製の非対称貫通孔型 MC アレイは、WMS3 チップ（表面サイズ 24-mm 四方）の中央部（10-mm 四方）に開口されている。非対称貫通孔型 MC アレイには、マイクロスロット（出口側）と円形マイクロホール（入口側）が連結された均一サイズの非対称貫通孔型 MC が集積されている。本研究では、マイクロホールの直径とマイクロスロットの短辺が 20～50 μm の三種類の非対称貫通孔型 MC アレイを用いた。MC 乳化実験では分散相として精製大豆油を用い、連続相として Tween20 水溶液（1.0 wt%）を用いた。本研究で用いた実験装置は、WMS3 チップを搭載したモジュール、シンジンボン、顕微鏡観察システムから構成される。液滴作製実験は、非対称貫通孔型 MC アレイを介して分散相を連続相領域に圧入させて行った。なお、分散相と連続相の供給流量はそれぞれ 1.0～12.0 mL h⁻¹ と 0～1000 mL h⁻¹ の範囲内で制御した。

三種類の WMS3 チップを用いて液滴作製を試みた結果、平均液滴径が 75.1～178.5 μm で変動係数が 2% 未満の均一径ラージ微小液滴を製造できることを示された。製造されたラージ微小液滴のサイズは MC 断面のサイズに依存することがわかった。作製後のラージ微小液滴はマイクロスロットの出口に一時的に留まり、その後マイクロスロットを通過した分散相に押し出される形で離脱した。この時、ラージ微小液滴と分散相の接触による合体観察されなかった。

次に、連続相流量（Qc）の影響について検討を行った。連続相の流れ状態については、算出したレイノルズ数が最大で 27.7 であったことより層流であることが示唆された。平均液滴径が 100 μm より大くなる WMS3 チップの場合では、Qc が臨界値を超えた範囲において液滴径が縮小していくことが明らかとなった。一方、平均液滴径が 75 μm 程度となる WMS3 チップの場合では、液滴径は本研究で適用した範囲では Qc に依存せず、液滴径が 30 μm 程度になる既存の貫通孔型 MC アレイと同様の傾向を示した。製造されたラージ微小液滴は，
$Q_e$が臨界値より低くても問題なく回収できることが確認されており、平均液滴径が100μmより大きい均一径ラージ微小液滴を連続的に製造することは可能であっ
た。マイクロスロットの出口から膨張した分散相液滴
の中心部における連続相流量は、$Q_e$が同一の場合では
液滴サイズの増大に伴って増加することが示唆された。
上述の分散相液滴に作用する力のバランスについて検
討したところ、液滴作製に関与する主な力は液滴作
製を促進する連続相流れに起因する抗力($F_D$)と浮力
($F_B$)ならびに液滴作製($F_a$)を抑制する界面張力であ
ることが示された。また、$Q_e$が臨界値を超えた範囲に
おいて液滴径が縮小した結果は、$Q_e$の増大に対して比
例的に増大する$F_B$の影響によるものであると考察され
た。
さらに、分散相流量($Q_d$)の影響についても検討を行っ
た。$Q_d$が5.0 mL h$^{-1}$以下の場合では、変動係数が2%
未満の均一径ラージ微小液滴（平均液滴径117.6～
130.8μm）を製造できた。$Q_d$が臨界値より大きい場合
では明確に大きな液滴の作製を観察され、液滴径分布
もラージサイズ側が拡がる結果となった。上述の臨界
$Q_d$値は50 L m$^{-2}$ h$^{-1}$の分散相流束に相当し、微小液滴
（直径40μm）の製造に用いられる既存の貫通孔型MC
アレイと同等の高い生産能力を有していることが示さ
れた。