

ROTATING MEMBRANE EMULSIFICATION FOR PRODUCING UNIFORM EMULSION

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Abstract

A versatile and high capacity membrane emulsification system which utilises a rotating membrane for the precision manufacture of uniform emulsions droplet was investigated. Single emulsions were produced with a very low viscosity of paraffin wax, Tween 20 and carbomer as dispersed phase, emulsifier and stabilizer, respectively. Emulsion droplets in the range of 138 μm to 305 μm with coefficient of variation (CV) ranging from 9% to 29% were obtained. The methodology allows control of droplet production through adjustment of system operating parameters (membrane type, rotation speed, dispersed phase flux) to influence the average droplet size and droplet uniformity.

Keywords : *Emulsion, membrane emulsification, rotating membrane, stainless steel membrane, uniform droplet.*

1. Introduction

An emulsion is a colloidal dispersion of a single type of liquid droplets in another different liquid continuous medium. Sometimes it can take the form of multiphase system of two or more immiscible liquid with one liquid dispersed another. Emulsions play an important role in food, pharmaceutical, cosmetics as well as many chemical industries. The conventional methods of emulsion production are generally based on rotor stator system (for example stirring vessel, colloid mill and tooth disc homogenizer) and high pressure homogenizer (such as jet dispersion system). These processes use droplet break-up mechanisms to form the emulsions. Therefore they are usually coupled with considerable energy input and high shear rates (Schröder and Schubert, 1999). In addition, conventional processes also have

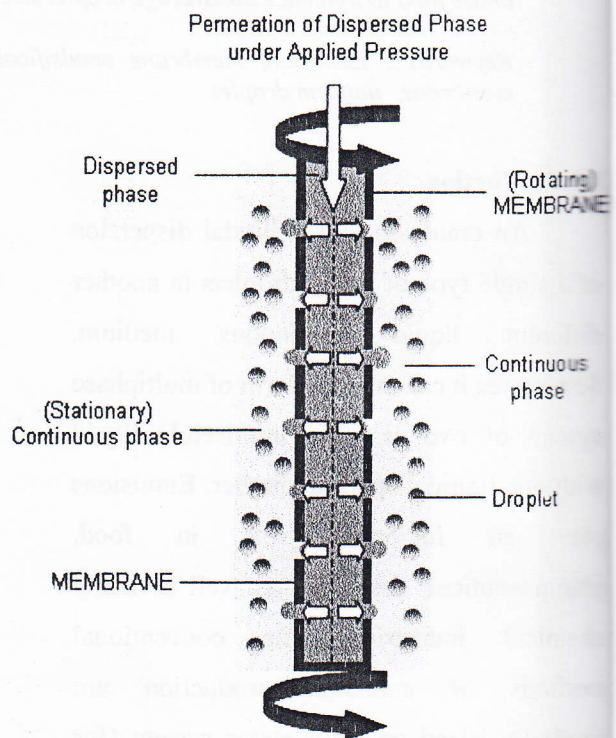
limitation in droplet size and droplet size distribution control, as well as equipment reproducibility. Furthermore, inefficiencies in the used of energy and variations in batch-to-batch products and different manufacturing methods can be significant disadvantages (Williams, 2001 and Williams, et al., 1998).

Membrane emulsification is a technique utilizing the principle of generating droplets 'drop-by-drop' to produce emulsion droplets exhibiting more uniform properties (Williams, 2001). Membrane emulsification involves using a low pressure to force the disperse phase to permeate a membrane into a flowing or moving continuous phase. By using this method, the size and size distribution of droplets can be carefully controlled through the selection of porous membrane, efflux rate of discontinuous phase and the nature of any

cross flow of the continuous fluid, etc (Peng and Williams, 1998). Consequently, the membrane emulsification processes often result in production of narrow droplets size distribution (Charcosset, 2004, Joscelyne and Trägådth, 2000) and potential to produce monodispersity emulsions (Abrahamse, et al., 2004). In addition, the apparent shear stress used in this equipment can be lower than the conventional homogenisation process (Charcosset, 2004, Abrahamse, et al., 2004). Membrane emulsification also generally require a lower energy input ($10^4 - 10^6 \text{ J/m}^3$) compared with the conventional emulsification ($10^6 - 10^9 \text{ J/m}^3$) (Charcosset, 2004, Joscelyne and Trägådth, 2000, Abrahamse, et al., 2004). Moreover, it is reported that membrane emulsification has a lower surfactant requirement (Joscelyne and Trägådth, 2000).

This paper describes the development of a novel membrane emulsification system which utilises rotating tubular membranes to initiate droplet detachment. In this system, the necessary shear force needed to initiate droplet detachment was induced by the rotating membrane rather than flowing continuous phase in parallel to the longitudinal axis of the tubular membrane. Setting the membrane instead of the continuous phase in motion has a potential advantage of eliminating use of external pump to circulate the continuous phase in the system. This is particular useful when manufacturing coarse emulsion droplets or

fragile structured particulate products are required, as the delicate structure of the products can be easily destroyed during the circulation inside a pump. In addition, the rotating membrane emulsification reactor (RMR) method tends to reduce droplet coalescence and the likelihood of droplet adhesion, increase droplet production rate per pore, and control the residence time of the product independent of the emulsification rate. Figure 1 shows a schematic diagram of



the RMR.

Figure 1. Schematic drawing of the emulsions production by rotating membrane emulsification reactor (RMR)

The effect of dispersed phase flow rate on the droplet size and uniformity are discussed.

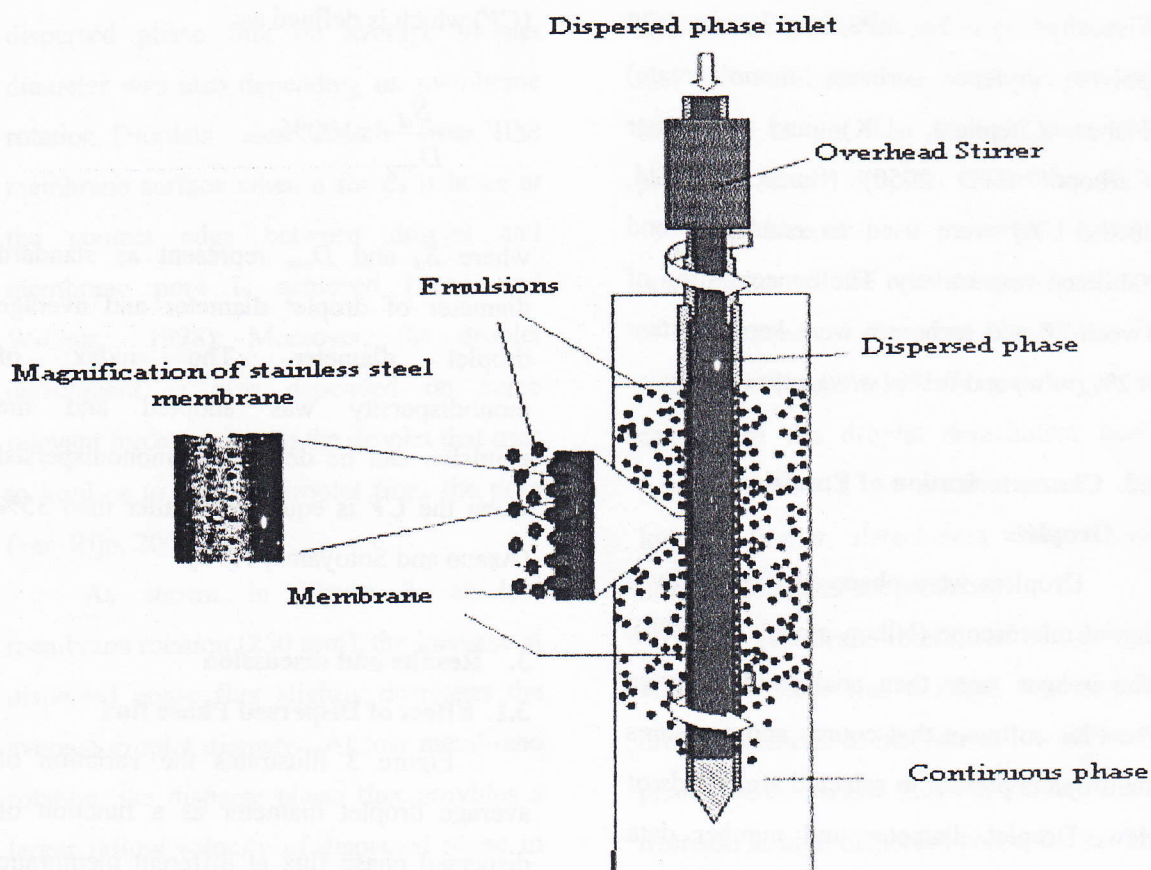


Figure 2. Schematic diagram of experimental arrangement using a tubular rotating membrane reactor (RMR) system

2. Experimental

2.1. Experimental Setup

A schematic diagram of rotating membrane emulsification reactor system is illustrated in Figure. 2.

The apparatus comprises a tubular stainless steel membrane tube (10 mm diameter x 85 mm effective length) connected with a digital overhead stirrer (IKA Eurostar) that allows the membrane to rotate inside a stationary glass cylinder (diameter 25 mm). The membrane pores were fabricated by laser drilling and arranged in cubic array having mean pore

size of 100 μm and pore-pore spacing of 500 μm . This resulted in a membrane surface porosity of 3%. The continuous phase volume was 100 ml and the rotational speed was varied ranging from 250 rpm – 1000 rpm. The dispersed phase was introduced inside the membrane tube by mean of a constant flow syringe pump with flow rate adjustable between 7-211 ml/hr.

2.2. Materials

In this work, the O/W emulsion has been prepared using very low viscosity of

paraffin wax (Fluka) as the disperse phase (viscosity ~ 5 mPa.s). Tween 20 (polyoxyethylene sorbitan monolaureate) (Fisher Chemical, UK) and carbomer (Carbopol ETD 2050) (Surfachem Ltd, Leeds, UK) were used as emulsifier and stabilizer, respectively. The concentration of Tween 20 and carbomer were kept constant at 2% (w/w) and 0.1% (w/w), respectively.

2.3. Characterization of Emulsion

Droplets

Droplets were observed directly by a digital microscope (Nikon model SMZ800). The images were then analyzed by Image Pro Plus software that counts and measures the droplets present in selected area fields of view. Droplet diameter and number data were used for determining droplet size

distribution as well as coefficient of variation (CV) which is defined as:

$$CV = \frac{S_d}{D_{avg}} \times 100\%$$

where S_d and D_{avg} represent as standard diameter of droplet diameter and average droplet diameter. The index of monodispersity was adopted and the emulsion can be defined as monodispersed when the CV is equal or smaller than 35% (Asano and Sotoyama, 1999).

3. Results and discussion

3.1. Effect of Dispersed Phase flux

Figure 3 illustrates the variation of average droplet diameter as a function of dispersed phase flux at different membrane rotation.

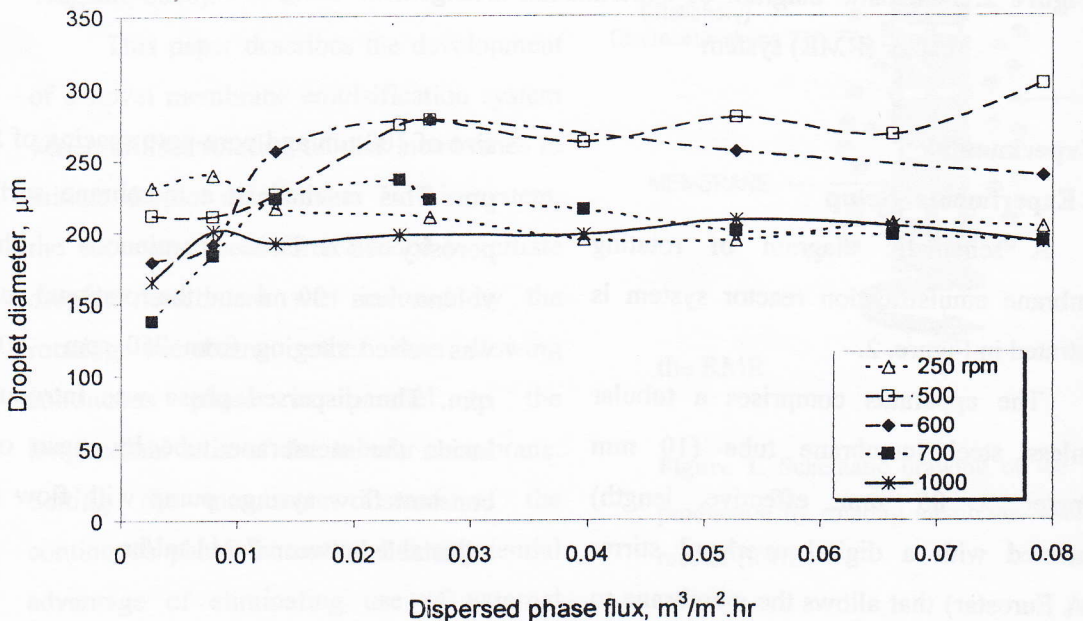


Figure 3. Effect of dispersed phase flow flux on average droplet diameter

The figure indicates that the effect of dispersed phase flux on average droplet diameter was also depending on membrane rotation. Droplets can detach from the membrane surface when a forces balance at the contact edge between droplet and membrane pore is achieved (Peng and Williams, 1998). Moreover, the droplet detachment is also depended on some relevant forces acting on the droplet that tries to hold or to remove droplet from the pore (van-Rijn, 2004)

As shown in Figure 3, at low membrane rotation (250 rpm), the increase in dispersed phase flux slightly decreases the average droplet diameter. At low membrane rotation, the disperse phase flux provides a larger inflow velocity of dispersed phase in the neck. In this condition, a Bernoulli under-pressure drop as defined in equation (2) that arises as a result of necking process.

$$\Delta P_{BN} = \frac{1}{2} \rho_D v_n^2$$

where ΔP_{BN} is Bernoulli pressure drop, ρ_D is density of dispersed phase and v_n is velocity of dispersed phase at neck. This pressure drop will counterbalance the viscous pressure contribution in the neck (ΔP_n) resulting in smaller droplets (van-Rijn, 2004).

On the other hand at 500 rpm, higher dispersed phase flux yields larger droplets diameter. At high dispersed phase flux, there are increased possibility droplets

coalescences at membrane surface. In addition, at higher dispersed phase flux, the rate of emulsifier to stabilize the new interfaces is not fast enough and hence produces larger droplets (Schröder et al., 1998). Moreover, a viscous pressure contribution will be resulted as consequence of the increase of dispersed phase flux. The pressure will maintain neck open longer and can retard the droplet detachment period (van-Rijn, 2004). As a consequence, with longer droplet detachment time, larger droplet diameters are produced.

At membrane rotation of 600 rpm and 700 rpm, there was a slight tendency for droplet diameter to increase at low dispersed phase fluxes (below $0.026 \text{ m}^3/\text{m}^2\text{hr}$) and to decrease at high dispersed phase fluxes. This is due to at high membrane rotation, there will be a droplet break up due to high shear stress and producing small droplet sizes. In addition, the possibility of droplet coalescence at high dispersed phase flux (2) is also reduced by the membrane rotation and hence the droplets detach at smaller size. Moreover, the presence of rotating will generate Taylor vortices on the membrane emulsification system. The action of Taylor vortices will help the emulsion droplets detaching from membrane pore and hence results on emulsion droplet at smaller diameter.

At high membrane rotation (1000 rpm), similar reason is also taking place. There was a minor effect on droplet size with

increased dispersed phase flux. In the membrane emulsification process, the droplets start to accelerate and move away with varying velocity at the end of the droplet growth stage. However, during detachment stage the connection between droplet and the pore through a neck still exists for a short period. Droplet will detach and the detachment period is finished when the connection is broken. The final droplet size can also be determined by the final droplet volume at moment it breaks away. Hence with the definition, the volume of droplet can be estimated by equation (3).

$$V_f = V_g + Qt_d$$

where V_f is the volume of final droplet, V_g is the volume of growth side droplet, Q is the dispersed phased flux and t_d is the duration of detachment period (Peng and Williams, 1998). According to equation (3), at 1000 rpm is perhaps the net effect condition for droplet volume increases. When the membrane rotation is increased, the droplet detachment period is decreased and reduces the differences between final droplet volume and the growth droplet volume.

3.2. Product Characterisation of O/W emulsion

Some micrographic images of O/W emulsion are presented in Fig. 4 and Fig. 5. Figure 4 shows typical images of O/W emulsion at low dispersed phase flux ($0.0079 \text{ m}^3/\text{m}^2\text{hr}$).

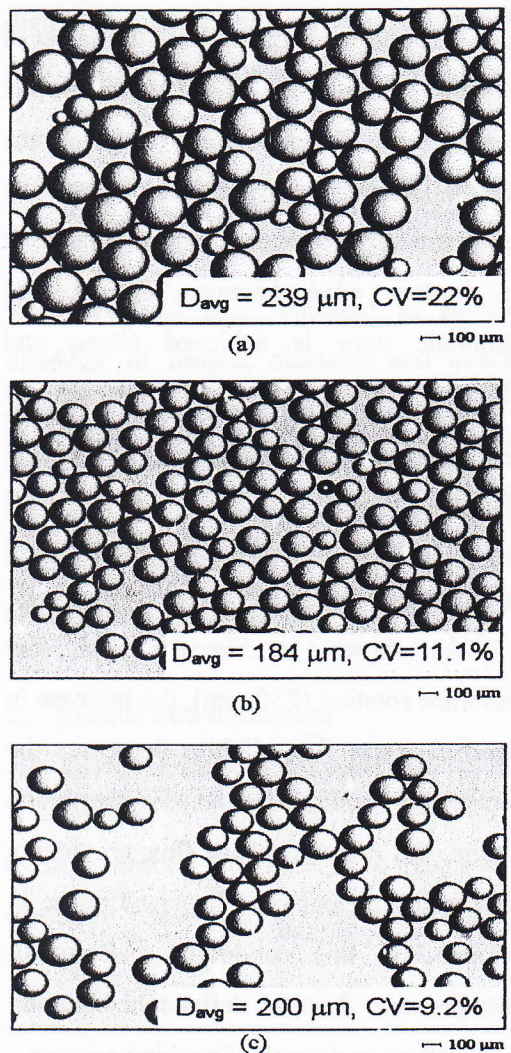
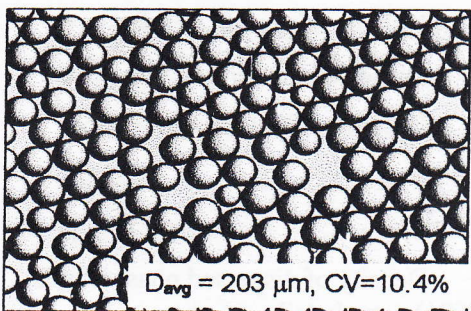


Figure 4 Microscopic images of O/W emulsion at low dispersed phase flux ($0.0079 \text{ m}^3/\text{m}^2 \cdot \text{hr}$). (a) 250 rpm, (b) 700 rpm, (c) 1000 rpm

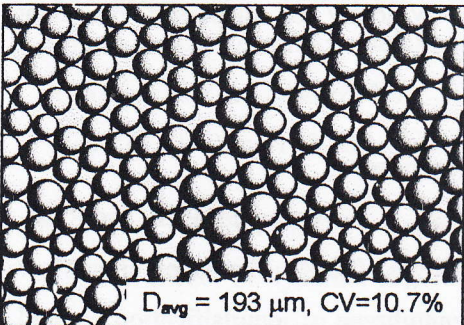
At low rotation rates, the droplet size and CV were much high, however it was still monodispersed. In contrast at 1000 rpm, the droplet size was smaller and the CV was the lowest. As the membrane was rotated, the shear stress of rotation will break up droplet formed at the membrane surface. Moreover, the rotation of membrane will increase the tangential drag force of the continuous phase thus reducing the growth time of droplets before detachment. As a result, droplets were

produced at smaller diameter. Moreover, a high rotation rate will also reduce the possibility of droplet coalescence emerging simultaneously from adjacent pores on the membrane. As a consequence, high rotation rate (1000 rpm) produced more monodispersed droplet size which is represented as low coefficient of variation (CV).

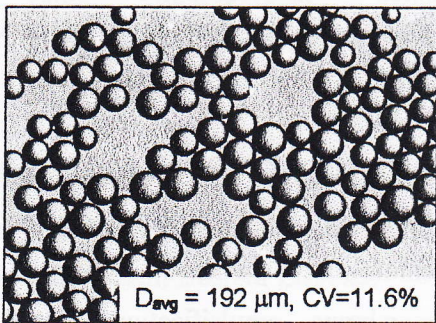
Figure 5 shows images of O/W emulsion at high dispersed phase flux ($0.079 \text{ m}^3/\text{m}^2 \text{ hr}$).



(a)



(b)



(c)

Figure 5. Microscopic images of O/W emulsion at high dispersed phase flux ($0.079 \text{ m}^3/\text{m}^2 \text{ hr}$). (a) 250 rpm, (b) 700 rpm, (c) 1000 rpm

The images show that regardless the rotation speed, there was no significance difference in CV. This demonstrates that at high dispersed phase flux, the droplet will detach faster than at low dispersed phase flux. As a consequence, the possibility of droplet coalescence at adjacent pore will be prevented and this would serve to maintain a low value for the CV.

Particle size distributions of images for Figure 4 and 5 are presented in Figure 6 and Figure 7, respectively.

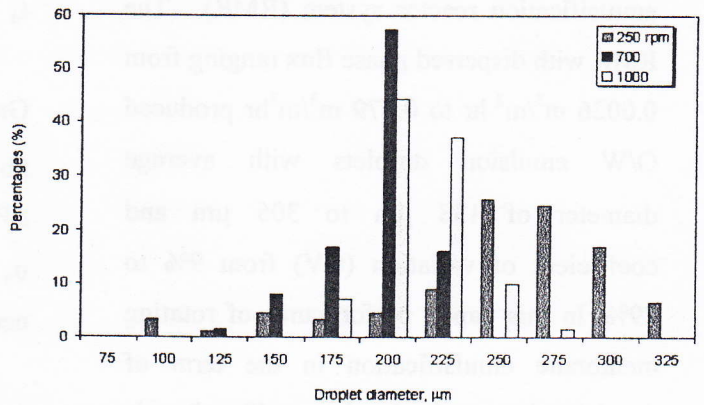


Figure 6. Particle size distribution of emulsion droplets at dispersed phase of $0.0079 \text{ m}^3/\text{m}^2 \text{ hr}$ at various membrane rotation rates

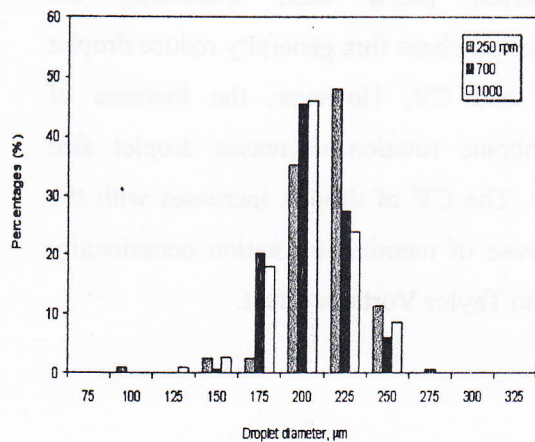


Figure 7. Particle size distribution of emulsion droplets at dispersed phase of $0.079 \text{ m}^3/\text{m}^2 \text{ hr}$ at various membrane rotation rates

As illustrated in Figure 6, the size distribution for rotation of 250 rpm exhibited a skewed distribution and unimodal distribution. Other size distributions are unimodal distribution with normal type population distribution. In Figure 7, all size distributions take the form of a unimodal distribution with normal type distribution.

4. Conclusion

Single (O/W) emulsions of very low viscosity paraffin oil have been produced successfully using a rotating membrane emulsification reactor system (RMR). The RMR with dispersed phase flux ranging from $0.0026 \text{ m}^3/\text{m}^2 \text{ hr}$ to $0.079 \text{ m}^3/\text{m}^2\text{hr}$ produced O/W emulsion droplets with average diameter of $138 \text{ }\mu\text{m}$ to $305 \text{ }\mu\text{m}$ and coefficient of variation (CV) from 9% to 29%. In this paper, performance of rotating membrane emulsification in the term of droplet size and droplet uniformity is influenced by membrane rotation rate and dispersed phase flux. Increasing the dispersed phase flux generally reduce droplet size and CV. However, the increase of membrane rotation decreases droplet size only. The CV of droplet increases with the increase of membrane rotation occasionally due to Taylor Vortices effect.

5. Acknowledgment

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6. Appendices

6.1. Nomenclature

CV	Coefficient of variation (%)
S_d	Standard deviation
D_{avg}	Average droplet diameter (μm)
V_f	Volume of final droplet
V_g	Volume of growth droplet
Q	Dispersed phase flow rate (m^3/s)
t_d	Duration of detachment period

Greek Letters

ρ_D	Density of dispersed phase (kg/L)
ΔP	Pressure Drop
u_n	Velocity of dispersed phase at neck

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