

# Controlled production of food emulsion using microfluidics

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## ABSTRACT

Microfluidic technology has recently been applied to the formation of controlled particulate structures, such as emulsion droplets, foams, encapsulates and gel particles. While these types of particles are typical of many foodstuffs, production of foods with microfluidics is not really possible, due to the low throughput of typical microfluidic devices, as well as the general use of model materials. Here we present Microfluidic technology applied to the production of monodisperse emulsion using food ingredients. In particular, we investigate the effect of surfactants and microdevice geometry on drop size and robust production regimes. The asymptotic minimum drop size is bigger in flow focusing geometries than in Psi and Pi junction geometries, decreasing with the addition of surfactant. Several production patterns were identified and only one of which is useful to produce monodispersed emulsion. The influence of surfactant is noted as the boundaries between the various production regions vary.

**Keywords:** microfluidic, emulsion, monodispersity, food.

## 1 INTRODUCTION

Microfluidic applications are numerous, ranging from bio-technology to pure chemistry [1-4]. Emulsification sector is also benefiting from microfluidics. Emulsions can be found in the pharmaceutical and chemistry industry as well as in cosmetics or foods. Many food products are based in oil in water emulsions (salad dressings, cream, beverages) or water in oil (butter, margarine) and foams (ice cream). The demonstrated capability of microfluidic to control emulsion characteristics is pledged to have a deep impact in this industry. Emulsion properties are determined by the mean size and size distribution of its droplets. As microfluidic technology allows the production of emulsions drop by drop under controlled conditions, [5,6], the monodispersity of the emulsion is considerably increased and thus emulsion properties can be modified.

Microfluidics studies the behaviour and manipulation of fluids in the microscale. There is a great variety of microfluidic devices (microdevices) but all of them involve the treatment of small quantities of fluid through small, micron scale, channels and/or cavities. Different approaches about how to manipulate the fluids have led to a wide range of microdevices concepts and geometries: flow focusing [7, 8], T junctions [9] and microchannel emulsification [10] among others.

The objectives of this study were to apply microfluidic technology to a foods context, to assess the scope it can provide to robust monodispersed emulsion production, i.e. to conditions for which small changes in processing parameters do not affect drop production or size. Drop size and production regimes were analyzed as well as the surfactant influence over them. Asymptotic minimum sizes were found for all geometries studied. Boundaries between different production regimes were identified. The addition of surfactant affects both the drop size and the regimes. It decreases the minimum drop size achievable and it changes noticeably the boundaries between the various production regimes.

## 2 MATERIALS AND METHODS

Emulsions were prepared with the following materials. Deionised water, sunflower oil from 3663 Food service, UK, filtered through 5 $\mu$ m pore size Acrodisc filter, and surfactant Admul WOL 1403 (Polyglycerol polyricinoleate E476) from Kerry Bioscience, The Netherlands.

To obtain the emulsion the two liquids to become the continuous and disperse phases are introduced separately in the microdevice. The surfactant is dissolved in the oil phase. The water and oil phase are pumped into the microdevice using Genie Pumps from Kent Scientific Corporation, US. The emulsion is produced in the microdevice and is collected afterwards. The process is followed via Redlake microscope camera, of 500 frames per second and both photographs and movies are taken to analyse drop size via image analysis.

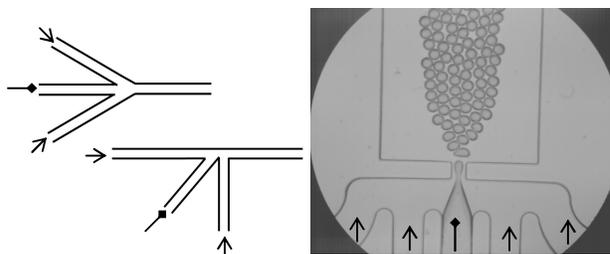


Figure 1: Microdevice geometries, from left to right: Psi junction, Pi junction and double flow focusing. Continuous phase:  $\rightarrow$ , disperse phase:  $\rightarrow$

The geometries used in this study are flow focusing, Psi junction and Pi junction. For a Psi and flow focusing the break up follows mainly an elongation mechanism [11] while the Pi presents a combination of elongation and

shear. Channels widths for these geometries were 100 $\mu\text{m}$ . A 100 $\mu\text{m}$  aperture width double flow focusing was used with two fluids. The devices were made of hydrophobic materials to produce water in sunflower oil emulsions.

### 3 RESULTS AND DISCUSSION

#### 3.1 Drop size

Study of control and reproducibility of drop size for the same flow rates was carried out for Psi, Pi junction and flow focusing geometries. For these three geometries, drop size decreases with increasing flow rate of the continuous phase and an asymptotic minimum size is observed. For flow focusing geometry of aperture width 100 $\mu\text{m}$ , the minimum size is 80% of the aperture width. For the Psi and Pi geometries the minimum size achieved is about half of the channel width. The asymptotic minimum size can be decreased with the addition of 4% of surfactant. Following this procedure we were able to reduce the minimum asymptotic size by a 50% (see figure 2). Note, however, that at higher concentrations of surfactant the monodispersity is lost and either polydispersity or parallel flow of the liquids appears.

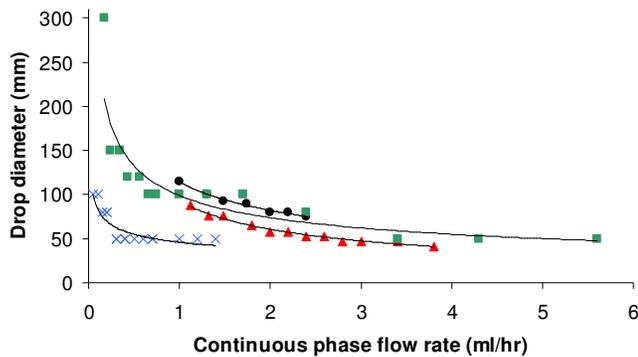


Figure 2: Asymptotic drop size for different geometries. ● Flow focusing, no surfactant, ▲ Flow focusing 4% of Admul Wol in continuous phase, ■ Pi junction no surfactant, X Psi junction no surfactant.

The following results have been obtained using a hydrophobic double flow focusing geometry of 100  $\mu\text{m}$  width. Two different cases, surfactant in the system and no surfactant added have been analysed. In figure 3 below drop volume has been drawn against the flow rate divided by the interfacial tension  $Q/\sigma$ , a value proportional to the capillary number  $Ca = \mu v/\sigma$ , where  $\mu$  is viscosity,  $v$  velocity and  $\sigma$  interfacial tension. We have not used the capillary number  $Ca$ , as viscosity was not changed. It can be seen that there is a clear continuity between the 2 cases. For small capillary numbers the drop size achievable is bigger than for larger capillary numbers.

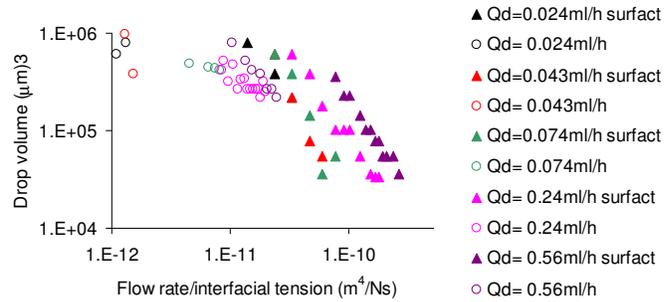


Figure 3: Drop volume dependence with  $Q/\sigma$ . ▲ Surfactant added, ○ no surfactant added.

For low value of disperse phase flow rate,  $Q_d$ , drop size is only dependent on the continuous phase flow rate,  $Q_c$ , and not on  $Q_d$ . For high values of  $Q_d$  drop size depends on the flow rate ratio  $Q_c/Q_d$ . Figure 4 represents drop size versus flow rate ratio  $Q_c/Q_d$  (b) and drop size versus  $Q_c/Q_d^0$ , where  $Q_d^0 = 0.24\text{ml/h}$  (a). The data shown correspond to a system with surfactant added. From figure 3a, we can see that for values of  $Q_d < 0.24\text{ml/h}$  drop size does not depend on dispersed phase flow rate, hence all curves collapse onto  $D = m(Q_c/Q_d^0)^{-0.5}$ , where  $Q_d^0 = 0.24\text{ml/h}$  and  $m \sim 130\mu\text{m}$ . On the other hand, for values of  $Q_d$  above 0.24ml/h, drop size becomes independent of  $Q_d$  and can be fitted by a law of the form  $D = n(Q_c/Q_d)^{-0.8}$   $n \sim 180\mu\text{m}$ , see figure 3b. This difference probably relates to a difference in the break up mechanism.

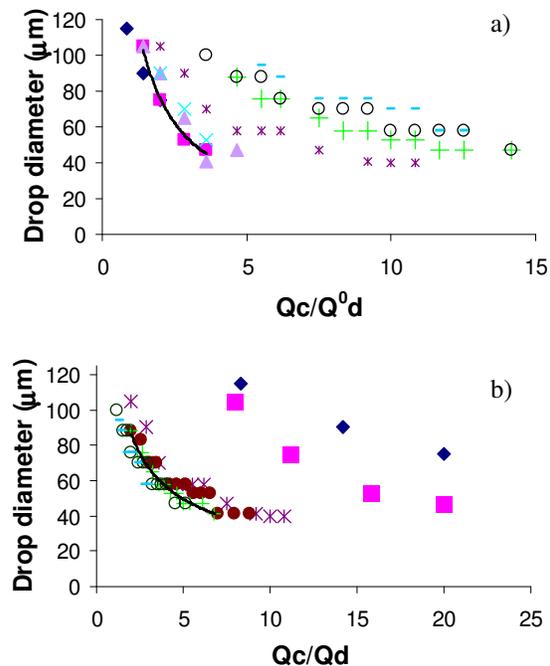


Figure 4: Drop diameter vs.  $Q_c/Q_d^0$  (a). Drop diameter versus  $Q_c/Q_d$ , (b).  $Q_d$  flow rates, in ml/h, are: ◆ 0.024, ■ 0.043, ▲ 0.074, x 0.1, \* 0.24, ● 0.43, + 0.56, ○ 0.74, - 1. 100 $\mu\text{m}$  flow focusing, surfactant added.

### 3.2 Production regimes

The production regime diagram is used to identify the various regions in which the flowing patterns are clearly differentiated one from another and whose boundaries are delimited by a drastic change of the behavior of the liquid threads.

We define dripping as the production regime in which drops are produced in a homogeneous and controllable way. The tip of the disperse phase produces drops one by one. On the other hand, a jetting regime shows a parallel flow of fluids that can lead occasionally to a break up but always in a non-controllable way.

Thus, we have identified the following five production regimes: 1) dripping production of stable monodispersed emulsion, the most desirable one, 2) dripping production of polydisperse emulsion, 3) dripping production of unstable monodispersed emulsion, that leads to polydispersity right after break up due to coalescence, 4) jetting, parallel flow of fluids with no break up and 5) jetting with no controllable occasional break up.

Hence, the main boundary between regimes lies between dripping regime and jetting regime. Experimentally, when looking for the jetting boundary each point of the boundary was determined by fixing the continuous phase flow rate while changing the dispersed phase flow. Figure 5 represents the boundaries for different microdevices. The dripping regime occurs above the boundary line for each geometry and the jetting regime below it. For different geometries with the same liquids, the  $Pi$  presents a larger dripping production range. A possible explanation can be the difference in mechanism of breakup. The  $Pi$  junction working with shear is more efficient at cutting the dispersed thread of liquid to produce drops than the elongation breakup mechanism of flow focusing.

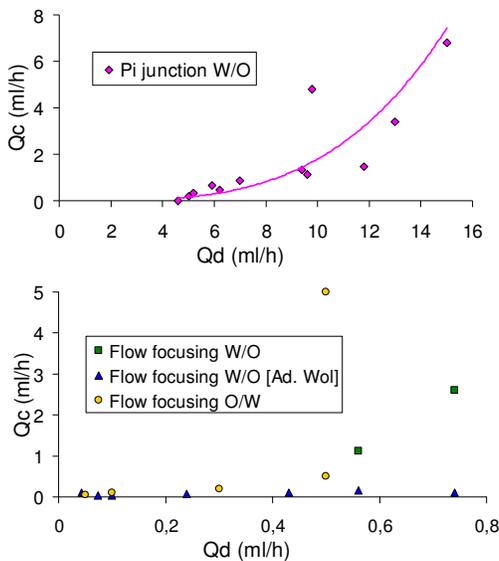


Figure 5: Jet boundary for  $Pi$  junction (up) and flow focusing (down). Dripping occurs above boundaries, jetting below.

The addition of surfactant to our systems provides several effects. Firstly, it favors the production of the emulsion by lowering the surface tension between the two liquids thus helping drop break up. It also modifies the wettability of the microdevice material by the fluids. As a result of the small dimensions of the devices used to produce the emulsion the influence of the surface and wetting is very important [12]. The hydrophobicity/hydrophilicity of the microdevice determines which kind of emulsion will be made inside of it. The material that wets the walls will become the continuous phase. If the liquid we want to be the continuous phase does not completely wet the wall the addition of a suitable surfactant can help. Finally, the surfactant will cover the produced drops and help to stabilise the emulsion against coalescence.

We measured two different flow diagrams to compare the effect of a surfactant in the continuous phase (see figures 6 and 7). The first diagram was done without any surfactant present in the system whereas in the second diagram the continuous phase has 4% of Admul Wol added. The fluids chosen were water as the dispersed phase and sunflower oil as the continuous phase. The microdevice used was the same in both cases, a double flow focusing geometry of  $100\mu\text{m}$  opening and hydrophobic, thus yielding water in oil emulsions.

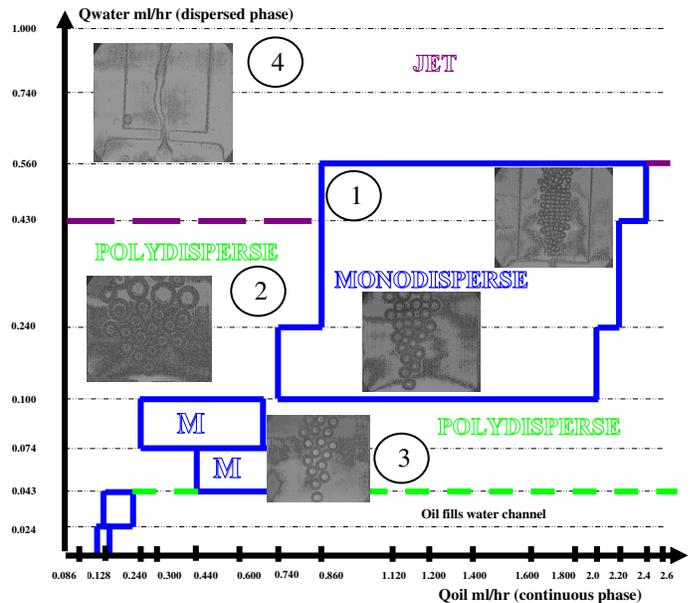


Figure 6: Surfactant free system. Flow regime diagram for flow focusing. Continuous line defines monodispersed boundary, dashed line defines polydisperse boundary.

In the centre of the diagrams the microdevice produces a monodisperse emulsion as can be seen in the diagrams below (1). On the left of this central region, where the dispersed phase flow rate is higher than the continuous phase

flow rate, there is a polydisperse emulsion zone (2). The production is thought to be monodisperse but coalesces immediately, hence losing monodispersity almost instantaneously. Finally the third region is on the right of the central monodisperse one (3). This region is also marked as polydisperse although, unlike the previous polydisperse region, within this region the microdevice is producing drops of different sizes. That is, coalescence does not account for the polydispersity in the emulsion. For a surfactant free system we also observe another zone. At higher flow rates the disperse phase does not allow the breakup of the thread and jetting appears (4).

For the system with surfactant added (figure 7) in the same high flow rate region we observe the growth of big drops that end in big blobs which break occasionally (5). In this later case the surfactant is aiding in the breakup but the low continuous flow rate does not allow regular drop production. The monodisperse production region is increased by almost 50% with the addition of surfactant.

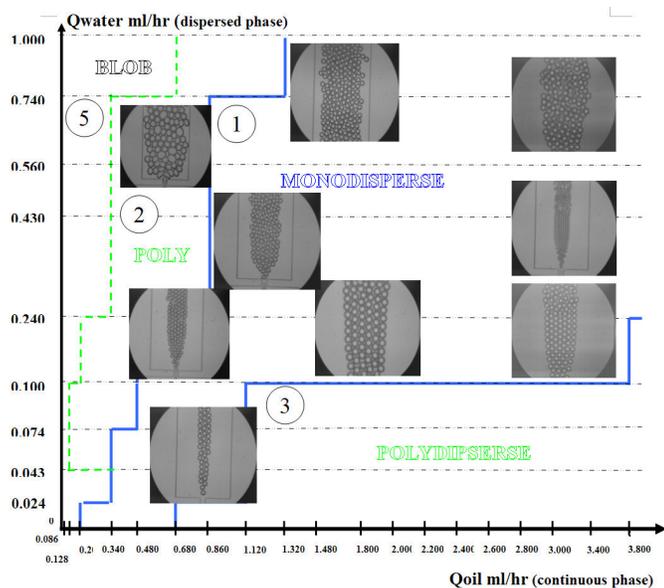


Figure 7: Flow regime diagram for flow focusing. Water in sunflower oil with surfactant. Continuous line defines monodispersed boundary, dashed line defines polydisperse boundary.

## CONCLUSION

In this paper we have presented the use of microfluidics to form drops of water in sunflower oil. Emulsion production has been analyzed focusing on influence of geometry and surfactant on production regimes and drop size control.

Drop size is proportional to channel width in Psi and Pi junction and to the aperture for a flow focusing one. Drop size decreases when adding surfactant.

A relationship between the magnitude  $Q/\sigma$  related with the capillary number and drop volume, where  $Q$  is the flow

rate of the continuous phase and  $\sigma$  is the interfacial tension has been shown.

Both polydisperse and monodisperse emulsions can be obtained with microfluidic devices. The flow diagrams show which flow conditions can achieve robust, stable in time and reproducible, production of monodispersed emulsion.

The boundary between jetting and drop production regimes is different for each geometry. Most noticeable is the increase of the drop production region for a Pi junction as compared to a flow focusing geometry. The larger amount of shear in Pi compared to flow focusing allows extending the drop production regime.

Surfactant is used in high concentration to help wetting and to stabilize the emulsion obtained. With this high concentration the region of monodispersion increases by 50% as compared to the case without surfactant. It also provides a better control of drop size at high flow rates of the continuous phase. However, too much surfactant leads to a no drop production condition.

This study has helped to understand how microfluidic technology can be applied to the production of food grade emulsions. Different geometries of single microdevices have been analyzed and robustness and reproducibility have been tested.

## REFERENCES

- [1] S. A. Khan et al. *Langmuir* 20, 8604, 2004
- [2] Z. Nie. *J. Am. Chem. Soc.* 127 (22), 8058, 2005
- [3] S. Okushima et al. *Langmuir* 20 (23), 9905, 2004.
- [4] A. S. Utada et al. *Science* 308, 537, 2005.
- [5] S. Sugiura et al. *J. of chem. Eng. Japan*, 34, (6), 757, 2001.
- [6] Q. Xu et al. *App. Phys. Lett.*, 85, 17, 3726, 2004.
- [7] A. M. Gañan-Calvo and J. M. Gordillo, *Phys. Rev. Lett.* 87, (27), 274501. 2001.
- [8] Anna et al. *Applied Physics Letters*, 82, 3, 364, 2003.
- [9] T. Thorsen et al. *Phys. Rev. Lett* 86, (18), 4163, 2001.
- [10] I. Kobayashi et al. *Food Sci. Technol. Res.* 5 (4), 350, 1999.
- [11] H. A. Stone et al. *Annu. Rev. Fluid Mech.* (36), 15, 2004.
- [12] R. Dreyfus et al. *Phys. Rev. Lett.* 90, 14, 144505, 2003.