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# Influence of the plate-type continuous micro-separator dimensions on the efficiency of demulsification of oil-in-water emulsion

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ABSTRACT

The objective of this article is to find the optimal dimensions of rectangular plate-type micro-separators in order to enhance the continuous separation of immiscible liquids. The main structure of the separators contains two plates: a hydrophobic (PTFE) upper plate and a hydrophilic (stainless steel) bottom plate which formed the contact surfaces for the fluids in the channel. The devices have two outlets, one for the aqueous phase and the other for the organic phase enabling the continuous separation and withdrawal of the separated phases. Demulsification has been carried out using Shellsol/water emulsion in the presence of a non-ionic surfactant (Tween 80). The separation efficiency is investigated as a function of micro-separator sizes, channel depths, flow rates and plate configurations. The major parameter that controls the destabilization mechanism is the ratio between the droplet size and the channel depth. When the size of the dispersed droplets remains smaller than the height of the separator (channel depths: 25–100 μm), creaming is the main demulsification mechanism. Creaming refers to the migration of the dispersed phase of an emulsion, under the influence of buoyancy. The particles float upwards and rise to the top due to the difference in the densities of the particles and the medium. The separation efficiency depends mainly on the residence time of the liquid/liquid mixture in the device regardless of the separator dimensions and channel heights. The separation rate is limited by the removal of the cream layer, formed at the top of the upper plate, from the separator. When the size of the dispersed droplets is larger than the depth of the separator (channel height of 9 μm), the separation performance and mechanism become different. The coalescence of the dispersed droplets occurs by passing through the device. The comparison of the data corresponding to creaming and coalescence phenomena emphasizes that the coalescence greatly enhance and accelerate the separation action. The phase separation in the micro-coalescer takes place considerably faster than in the micro-separators.



*Keywords:* Demulsification; Micro-separation devices; Liquid/liquid separation; Oil in water emulsion; Coalescence; Creaming

## 1. Introduction

In many chemical processes, efficient removal of a dispersed oil phase from a continuous water phase is highly desirable. Currently, there are several available methods, including filtration, membrane separation, gravity or centrifugal settling, chemical demulsification, pH adjustment, heat treatment, and electrostatic demulsification (Lissant, 1983; Sun et al., 1998; Eow and Ghadiri, 2002; Jeelani and Windhab, 2009; Roques-Carmes et al., 2011). The slow rate at which liquids may be separated in such operations has important consequences in many commercial operations (Akay et al., 2012). Thus, there is a wide scope for developing new devices for separating dispersed oil from aqueous solutions.

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Due to increased process intensification, offered by micro-reaction technology, more traditional pilot-scale reactor systems and pilot plant systems may be replaced, at least in some cases, by smaller, faster responding, more flexible mini-plants with reduced capital and operating costs (Commenge et al., 2002; Charpentier, 2005; Mills et al., 2007). Moreover, the micro-reactors appear as efficient tools for the transition from batch operations to continuous processes (Lomel et al., 2006). Features unique to micro-reactors include laminar flow, short molecular diffusion distances, large specific interfacial areas, excellent heat transfer characteristics associated with precise control and manipulation of flows (Ehrfeld et al., 2000). With this huge increase of applications of micro-reactors, there is a growing demand for micro-structured separation devices (Stone et al., 2004). In micro-scale extraction processes, it is relatively easy to create dispersion by using micromixers, but separation of immiscible liquids remains a challenge. In addition, new ways of separation need to be developed, because in these small devices capillary forces dominate.

In recent years, a number of different micro-structured phase separators and coalescers have been proposed (Chan et al., 2008; Gaakeer et al., 2012). For example, Wengeler et al. (2006) described a microhydrocyclone for liquid/liquid separation which utilizes the difference in densities of the two phases. Another option is to use hydrophobic membranes (Kralj et al., 2007). The narrow openings (diameter: 1 μm) in the hydrophobic membrane provide large capillary forces to block the aqueous phase. The membrane is capable to separate slugs of hexane from water at a maximum flow rate of 1.2 mL/min (Assmann and von Rohr, 2011). Recently, it has been shown that plate-type micro-separators constitute an attractive technology for rapid separation (Okubo et al., 2004; Kolehmainen and Turunen, 2007; Gaakeer et al., 2012). The separation principle utilizes the surface tension between the two liquids and the wetting properties of the inner surfaces of the micro-device. The system consists of a micro-channel in which the inner walls are modified to produce hydrophilic/hydrophobic surfaces. Okubo et al. (2004) showed experimentally the occurrence of droplets coalescence inside a plate-type device with channel height of 5–12 μm and residence time of several tenths of seconds. They demonstrated that the oil droplets coalescence, in the presence of surfactants, can only take place when the size of the dispersed droplets is larger than the depth of the micro-separator. More recently, Kolehmainen and Turunen (2007) used the same kind of plate-type device to produce the coalescence of the oil droplets. However, the channel depth was larger (100–200 μm) but they do not work with surfactant to stabilize the O/W emulsions.

In order to increase the feasibility of the micro-process, it is recommended to take under consideration the reasonable smallest dimension for the unit. The difficult fabrication of micro- or nano-separators and the high-pressure drops can become a serious drawback. We then propose to introduce plate-type rectangular micro-separators with the following typical characteristic dimensions: length (60 and 530 mm), width (21 and 16 mm) and heights ranging between 9 and 100 μm. The size of the internal channels is more adapted to future industrial implementation and more particularly for the numbering-up of these devices in order to cope with large volumetric flow rates.

In this paper, plate-type micro-separators are designed, constructed and tested. This study focuses on the separation of Shellsol/water emulsion in the presence of a non-ionic surfactant. The micro-separator sizes, channel depths, flow rates and plate configurations are varied. The relationship between the separation performances and the destabilization mechanism is enlightened. The described results provide useful guidelines for the design of liquid/liquid micro-separators.

## 2. Materials and methods

### 2.1. *Emulsion preparation and characterization*

The organic phase (further indicated as the oil phase, O) was Shellsol D60 provided by Shell Chemicals. It was a mineral spirit type hydrocarbon solvent which contained paraffins, naphthenes and aromatics compounds. The aqueous phase (further indicated as the water phase, W) was tri-distilled water (Milli-Q System, Millipore) containing 1% (w/w) sodium chloride to set the electrical conductivity. The non-ionic surfactant, Tween 80 (Aldrich), was dissolved in the aqueous phase and used at a fixed concentration of 4% (w/w) with respect to the amount of water.

The emulsions were formulated at laboratory scale in a 500 mL laboratory vessel. An O/W premix was prepared by adding progressively the oil phase to the aqueous continuous phase and stirred for 2 min with a magnetic stirrer. Then, the homogenization of the emulsion was carried out on a Ultra Turrax T25 dispersion unit for 2 min at 2000 rpm.

Droplet size was determined by laser diffraction granulometry with a Mastersizer 2000 instrument (Malvern Instrument, Malvern, UK) at 20 °C. However, our apparatus had a large "dead" volume before reaching the measurement cell. Consequently, for the measurement, the emulsion was diluted with distilled water in the granulometer cell under gentle stirring to have a sufficient amount of solution inside the setup. The data were analyzed to obtain the hydrodynamic diameter and size distribution in each emulsion at the inlet and the outlets of the separators.

The stability of the O/W emulsions on storage (in the absence of the micro-separator) was investigated. For creaming rate experiments, the height of clear liquid/turbid liquid interface in test-tubes was monitored visually over time. A volume of 50 mL of each emulsion was poured into polyethylene bottles of rectangular cross-section, which were capped. The stability against coalescence was studied by redispersion experiments. After two days of storage in the absence of stirring, the emulsion was redispersed by stirring with a magnetic stirrer. The droplet size distribution of the redispersed emulsion was then evaluated. The coalescence is an irreversible process. If coalescence was the driving force for instability, the size of the redispersed droplets was expected to increase.

### 2.2. *Characterization of the plate materials of the micro-separators*

The main structure of the separators contained two plates. The materials of the plates were PTFE and stainless steel. Interfacial effects become dominant and crucial when the length scale is reduced to the micrometer scale. The different wetting properties of the fluid/wall interfaces are extremely important in determining whether demulsification occurred. The contact angles correlate the ability of a fluid to wet the surface and spread on it.

The contact angle measurements ($\theta$) were performed using a Dataphysics OCA-20 measuring device (Dataphysics Instruments GmbH, Filderstadt, Germany). For that purpose, a liquid drop ($V = 5\ \mu L$) was deposited, at 20 °C, on the surface and

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