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Numerical simulation of dripping and jetting in supercritical fluids/liquid micro coflows

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ABSTRACT

In this work, a two dimensional simulation of segmented micro coflows of CO_2 and water in micro-capillaries ($20 < T\ (^\circ C) < 50$ and $8 < p\ (MPa) < 16.5$) was carried out using a combination of the one-fluid model and the volume of fluid (VOF) method to describe the two-phase flow and a penalty method to account for the wetting property of the capillary walls. The computational work was validated by comparing numerical and experimental results in both the dripping and jetting regimes. The agreement of the calculated pressure difference across the droplet or jet interface with the Laplace–Young's law was assessed as supplementary criteria. The effects of CO_2/water interfacial tension ($5 < \sigma\ (mN\,m^{-1}) < 35$) and wall wettability (contact angle CO_2/wall varying from 0 to 180°) on the segmented water–supercritical CO_2 microflows were specially described. It was shown that switching the wall surface from hydrophilic to hydrophobic by tuning the contact angle allows for changing the droplet curvature so that the continuous water phase eventually undergoes a phase inversion resulting in water droplets/slugs formation in a continuous CO_2 phase.

1. Introduction

Over the past 15 years, the use of microfluidic devices in biology [1], chemistry [2] and materials science [3–5] has shown tremendous progresses. In particular, multiphase immiscible microflows have opened opportunities for generating controlled hydrodynamics structures (droplets, jets) allowing carrying out confined chemical reactions [4,6,7] or controlling reaction kinetics through reactivity at interfaces [8,9]. Droplets or jets are conventionally generated by mixing solutions through T-shape channel, flow focusing or coflow devices [10,11]. Recently, the design of microreactors withstanding high pressure and/or high temperature (typically up to 350 °C and 20 MPa) has driven the emergence of investigations with supercritical fluids [12–16], in which segmented or miscible flows can be created by manipulating flow rates or pressure. Supercritical fluids processes could largely benefit from the development of such microfluidic designs since droplets or jets are frequently encountered in materials synthesis or processing, like in the supercritical antisolvent process (SAS) [17–20] or in water–CO_2 microemulsions [21,22] for which the final materials characteristics are largely dependent on the initial hydrodynamic structures (size, polydispersity, *etc.*) [23,24]. Compared to macroscale approaches, the microfluidic generation and the subsequent confinement of such structures offer the opportunity to better control the droplets or jets uniformity, but also to perform *in situ* characterization [25], leading to advanced process mastering, as recently demonstrated for nanocrystals synthesis [26,27].

In microfluidics devices, the mechanisms of jets and droplets formation in both liquid–liquid and liquid–gas flows are largely studied [28,29]. The flow of immiscible fluids occurs generally in the form of segmented flow, where a disperse phase flowing in the center of the channel is segmented by a continuous liquid phase into distinct slugs. The continuous phase wets the wall so that the disperse elements are not in contact with the wall but fully surrounded by a liquid film. The transition from dripping to jetting and the droplets or jets size can be analytically determined by varying experimental parameters such as surface tension, viscosities and fluid velocities that are of peculiar importance in case of coflowing fluids [30,31]. Although these approaches are interesting for addressing the global behavior, numerical approaches [32] brings additional information such as velocity and pressure

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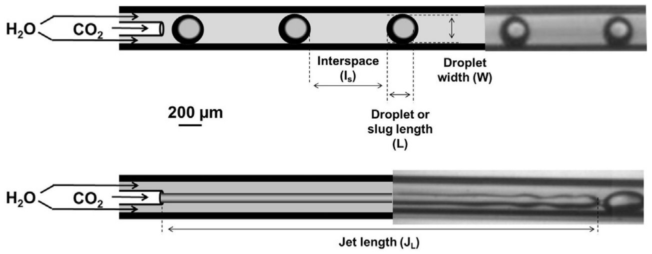

Fig. 1. Scheme of the general microcapillary-based coflowing configuration in the two regimes: (A) dripping or (B) jetting and additional relevant experimental and numerical geometrical parameters. The full set-up description can be found elsewhere [12].

gradient, profiles of surface tension and concentration that can be critical for the mixing of reagents as demonstrated for gas/liquid [33,34], liquid/liquid [35] microsystems or for supercritical/liquid macroscale process [36,37]. By predicting the flow behavior, simulations allow for reducing the experimental designs to the most valuable experiments.

The objective of this work is to develop a numerical approach for modeling the experimental observations of jets and drops generated by CO_2 and water micro coflows under high pressure conditions and high Reynolds numbers. This is a first step toward complete simulations of more complex processes, which could include various other physico-chemical phenomena (phase equilibria, chemical reactivity, nucleation and growth) occurring in real synthesis processes.

The first conditions simulated here correspond typically to the hydrodynamics encountered in a segmented microflow synthesis process. Then, the numerical approach is used to anticipate the effects of a given parameter on the flow characteristics. We focus on predicting the effect of interfacial forces on the flow, first by changing the surface tension – a parameter usually modified by adding surfactant to the fluid, and secondly by changing the wetting properties of the external capillary wall, which is more difficultly done by surface modifications, but which can occur as well during an experiment by the adhesion of reagents or synthetized particles with walls.

2. Experimental

2.1. Experimental set up

The capillary-based set-up was previously described elsewhere [12]. Briefly, the microsystem consisted of two silica capillaries inserted in one another. CO_2 and water were injected separately with high pressure syringe pumps (ISCO Teledyne 100 DM) generating a coflow (jet, drops or slugs) at the contacting point, as described in the general system configurations in both dripping and jetting regimes (Fig. 1). Pressure was controlled thanks to a back pressure regulator (JASCO BP2080) placed downstream the microsystem, while the entire set-up was immersed in a water bath for controlling temperature. Optical characterizations were performed with a high speed camera (Phantom V 9.1) connected to binocular microscope (Zeiss Stemi 2000-C). The inner diameters of internal and external capillaries were 100 and 250 µm, respectively (the external diameter of the internal capillary was 200 µm).

2.2. Determination of the relevant experimental parameters

The velocities at the desired operating conditions cannot be simply derived from the flow rates provided by the pumps since the fluids within the syringe reservoirs of the pumps are not at the same temperature than that of the microsystem, inducing density variations and therefore fluid expansions. In this work, conditions for the water and CO_2 reservoir were 25 °C and 0 °C, respectively, whereas the investigated conditions in the capillaries were in the range 20–80 °C. Thanks to the ISCO pumps running principle, the two fluids can be pressurized within the reservoir at the same pressure than the desired operating pressure, *e.g.* between 8 and 16.5 MPa. The fluids velocities within the microcapillaries, v_{int} for CO_2 and v_{ext} for water, were calculated as:

$$V_{\text{int}} = \frac{Q_{\text{int pump}}}{S_{\text{int}}} \times \frac{\rho_{\text{int}\,p,T_0}}{\rho_{\text{int}\,p,T}}, \quad V_{\text{ext}} = \frac{Q_{\text{extpump}}}{S_{\text{ext}}} \times \frac{\rho_{\text{ext}\,p,T_0}}{\rho_{\text{ext}\,p,T}}$$

with $Q_{\text{int pump}}$ and $Q_{\text{ext pump}}$ the pump flowrates for the internal and the external fluid, respectively, S_{int} and S_{ext} the inner section of the internal and external capillary, $\rho_{\text{int}\,p,T_0}$ and $\rho_{\text{ext}\,p,T_0}$ the density of the inner and outer fluid in the pump reservoir and $\rho_{\text{int}\,p,T_0}$ and $\rho_{\text{ext}\,p,T_0}$ the density of the inner and outer fluids at the experimental conditions.

The parameters required for the calculation of the relevant non dimensional numbers and used in the numerical modeling were either obtained from the NIST thermophysical properties online tools [38] (densities and viscosities for both $scCO_2$ and water at various pressure and temperature) or directly measured experimentally (interfacial tension for the $scCO_2$/water systems were determined from the pendant drop method).

The experimental errors on velocities are mostly related to the flowrates accuracy. For the ISCO 100 DM pumps used in this work, the flowrate uncertainty was estimated at ±1 µL min^{-1}, which yielded to an experimental error of ~1 mm s^{-1} for velocity.

2.3. Microflows parameters

In this computational study, the numerical results were validated against experiments thanks to measurements provided by the images collected by the high speed camera (Fig. 1). The measured responses were:

- In case of dripping regime: the length (L) and width (W) of generated droplets or slugs and the interspace between droplets or slugs (I_s),
- In case of jetting regime: the jet length (J_L), and when droplets are formed by the jet breakup, their L, W and I_s.

The reported values were averaged from at least 50 pictures measurements. The uncertainty of L, W, I_s and J_L measurements came from the quality of the video collected during the experiments. Based on the pixel size and camera/binocular resolution and the averaged measurements, the overall error in a characteristic length was of ±20 µm.

3. Numerical section

Compressed CO_2 and water are the two fluids used in this work. In the range of investigated conditions, they are considered as immiscible fluids, so a two-phase flow has to be accounted for in the computational study. The two-phase flow was described by the one-fluid model [39] that was previously used for simulating a liquid jet breakup in pressurized CO_2 [37]. This one-fluid model considers each phase as fictitious domains that are merged into the global simulation domain. The boundary between the two fictitious domains was numerically tracked with an interface capturing method using a volume of fluid (VOF) approach [40]. This method has the advantage of being independent on the grid topology that is fixed and does not conform to the interface topology.