Jet breakup and droplet formation in near-critical regime of carbon dioxide–dichloromethane system

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ABSTRACT

The jet breakup and droplet formation mechanism of a liquid in the near-critical conditions of a solvent–antisolvent system is examined with high-speed visualization experiments and simulated using a front tracking/finite volume method. The size of droplets formed under varying system pressure at various jet breakup regimes is measured with a Global Sizing Velocimetry, using the shadow sizing method. A stainless steel nozzle with 0.25 mm I.D and 1.6 mm O.D was used in this study. Experiments were performed at fixed temperature of 35 °C and system pressure in the range from 61 to 76 bar in the near-critical regime of the DCM–CO_2. At the near mixture critical regime for DCM–CO_2 mixture, the miscibility between the two fluid phases increases and the interfacial tension diminishes. This phase behavior has important applications in particle formation using gas antisolvent (GAS) and supercritical antisolvent (SAS) processes. The jet breakup and droplet formation in the near-critical regime is strongly dependent on the changes in interface tension and velocity of the liquid phase. An understanding of the droplet formation and jet breakup behavior of DCM–CO_2 in this regime is useful in experimental design for particle fabrication using SAS method.

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1. Introduction

Particle formation is an important application of supercritical fluid technology (Jung and Perrut, 2001). Properties of supercritical fluids that favor particle formation include liquid-like density and gas-like viscosity (Richard and Dechamps, 2004). The well known techniques for particle formation using supercritical fluids include the rapid expansion of supercritical solutions (RESS) (Jung and Perrut, 2001; Richard and Dechamps, 2004; Tom and Debenedetti, 1991; Debenedetti et al., 1993) and the gas/supercritical antisolvent (GAS/SAS) processes (Jung and Perrut, 2001; Richard and Dechamps, 2004; Tom and Debenedetti, 1991; Randolph et al., 1993; Subramaniam et al., 1997; Chattopadhyay and Gupta, 2001a,b, 2002a–c; Reverchon et al., 2003; Henczka et al., 2005).

Carbon dioxide (CO_2) is used extensively as a supercritical fluid in particle fabrication and pharmaceutical applications, which is attributed to its desirable properties such as relatively accessible critical point at temperature of 31.1 °C and pressure at 73.8 bar,

abundance and its low toxicity (Jung and Perrut, 2001; Richard and Dechamps, 2004; Tom and Debenedetti, 1991). Since most organic solvents are miscible with CO_2 at supercritical conditions, a low residual solvent content can be easily achieved in the final product without extensive downstream purification to remove excess organic solvent (Ruchatz et al., 1997). In particular, the SAS process has been used in numerous studies for pharmaceutical products. In the SAS process, the substrate of interest is first dissolved in a suitable organic solvent. The organic solution is then injected into supercritical fluid which acts as an antisolvent by rapid mass transfer, resulting in precipitation of the substrate.

Several factors may affect the particle size and properties achieved from SAS process. This includes the phase behavior of the ternary mixture and the hydrodynamics of the solution injected into the supercritical phase. Considerable literature suggests that the controlling parameter for particle size in the SAS process is the rate of mass transfer (Reverchon et al., 2003; Henczka et al., 2005). This is influenced by both the spray hydrodynamics of the organic solution and thermodynamic properties of the supercritical fluid phase. Perez de Diego et al. (2005) reported the mechanism of particle formation in subcritical and supercritical regimes for precipitation from compressed antisolvent (PCA) process. The jet disintegration mechanism for operation in subcritical and supercritical conditions

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was different and hence particles properties were also different. The effect of flow rate on particle size in the subcritical regime was reported. Carretier et al. (2003) investigated the hydrodynamics of the SAS process by evaluating the macro and micromixing within the precipitation vessel.

It was observed that most studies on SAS were carried out in atomization of a gaseous plume mode in the turbulent jet regime (Carretier et al., 2003; Shekunov et al., 2001). Varying parameters such as nozzle diameter, solution flow rate, pressure and temperature have no significant effect on the size and size distribution of final particles obtained. Final particle size achieved is mainly dependent upon the extent of mixing between the organic solvent and CO_2 phases. Smaller and more uniform sized particles could be achieved using coaxial (Henczka et al., 2005) and ultrasonic nozzles (Randolph et al., 1993; Subramaniam et al., 1997) which provides better mixing between the two phases.

The dichloromethane (DCM)–CO_2 system is one of the most commonly used for fabrication of polymeric particles using SAS process (Perez de Diego et al., 2005; Gokhale et al., 2007; Obrzut et al., 2007), and the various flow regimes in the free jet of DCM in CO_2 have been reported (Kerst et al., 2000). DCM is a good solvent for Poly L lactide (PLA) and several other pharmaceutical compounds. The mixture critical pressure of DCM–CO_2 at 35 °C is 78 bar (Gokhale et al., 2007) with a composition between 1.0 and 1.9 mol% DCM in CO_2 (Reaves et al., 1998). In this work, the droplet formation and breakup of DCM jet in CO_2 is studied. By operating in the regime close to the mixture critical point (MCP) of DCM–CO_2 system, and with careful manipulation of the Reynolds number of the liquid phase, it is possible to achieve dripping or Rayleigh disintegration of droplets where more monodispersed droplets could be achieved. In the dripping mode, the droplet size is a very strong function of the interface tension between the two phases. In the Rayleigh disintegration mode or jetting mode, droplet size is approximately 1.5 times the jet diameter.

2. Materials and methods

2.1. Materials

Compressed CO_2 (Air Liquide Paris, France) was purchased from Soxal (Singapore Oxygen Air Liquide Pte Ltd.). DCM (DS1432, HPLC grade) was purchased from Tedia (Fairfield, OH, USA). PLA was purchased from Sigma Aldrich (St. Louis, MO, USA).

2.2. Experimental setup and visualization

The experimental setup used in this study is shown in Fig. 1. Liquefied CO_2 (C1, Polyscience refrigerating circulator) was introduced into the high pressure vessel (HP, Jerguson 12-T-32, 70 cm^3) by means of a high pressure pump (P2, Jasco HPLC pump) to the required pressure. T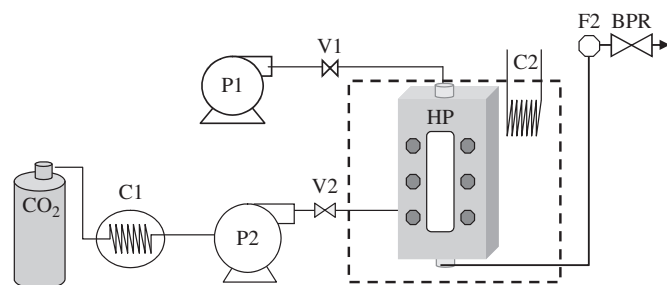he temperature in the vessel was controlled and maintained at 35 °C by use of a circulating heated water bath (C2, Polyscience 712 circulator). The system pressure used lies in the near-critical regime of DCM–CO_2 from 61 to 76 bar. The composition of the antisolvent phase in the vessel is maintained at 0–1% DCM in CO_2 at all times.

The high pressure vessel used in this study has two parallel borosilicate glass windows which allow visualization along the entire length of the vessel during the antisolvent process. High magnification images were captured with a digital SLR camera (D2H, Nikon, Japan) with a macro lens (105 mm Micro Nikkor, Nikon, Japan). High-speed camera was (FastCam PCI, Photron Inc., USA) used with the same macro lens to capture consecutive snapshots during the droplet formation process. The high-speed camera can capture images up to 2000 frames per second. Shadow sizing system (Dantec Dynamics, Denmark) is used for measurement of DCM droplet size during the SAS process. This system is equipped with a high sensitivity camera (Highsense MKII, Dantec Dynamics, Denmark) and is operated based on backlighting with laser light and image analysis software with an advanced edge detection algorithm (FlowManager PC, Dantec Dynamics, Denmark).

2.3. Numerical simulation

In order to aid the current investigation, numerical simulation was employed to study the formation process of the dripping mode and the Rayleigh disintegration mode. The two-fluid system consisting of a liquid jet emerging from a nozzle into a gaseous medium is modeled in this study. A two-dimensional (2D) axis-symmetric cylindrical-coordinate system was used, and the numerical simulation was done using a front tracking/finite volume method.

2.3.1. Front tracking/finite volume method

The recent development of a front tracking/finite volume method for multiphase flow simulation has provided a novel and robust method to treat the moving interface between two fluids with large density difference (Unverdi and Tryggvason, 1992; Hua and Lou, 2007). In this study, the front tracking/finite volume method proposed by Hua and Lou (2007) is modified to take into account the changes in the surface tension when the MCP of the DCM–CO_2 system is approached. In this method, a stationary fixed background mesh is used throughout the whole computational domain, and a set of adaptive front mesh is used to mark the moving interface. Only one set of the momentum and continuity equations is solved in the whole computational domain by treating the different phases as one single fluid with variable material properties. The distributions of physical properties such as density and viscosity are calculated according to the position of the interface and the property difference between two fluid phases. The physical properties of the bulk phases of DCM and CO_2 (at 35 °C) used in this study are summarized in Table 1. The surface tension stress is computed on the front mesh and then distributed to the fixed background mesh through the use of a dirac-delta like distribution function as a body force term in the momentum equation. The position of the interface is advected explicitly with the velocity interpolated from the flow field on the

Fig. 1. Experimental setup. P1, P2: pumps for the polymer solution and liquified CO_2, respectively. HP: high pressure vessel. C1, C2: temperature controllers. BPR: back pressure regulator. F2: flowrate regulator. Temperature of the setup for droplet and particle formation studies was fixed at 35 °C.

Table 1
Summary for physical parameters of CO_2 and DCM at 35 °C

DCM properties at 35 °C			
Density, ρ_L (kg m^{-3})			1289
Viscosity, μ_L (Pa s)			3.7×10^{-4}

	61 bar	71 bar	76 bar
CO_2 properties at 35 °C			
Density, ρ_G (kg m^{-3})	160	220	270
Viscosity, μ_G (Pa s)	2.81×10^{-4}	3.83×10^{-4}	4.24×10^{-4}
Interfacial tension coefficient, σ (N m^{-1})	5.359×10^{-3}	2.230×10^{-3}	1.126×10^{-3}