J. of Supercritical Fluids 109 (2016) 109–123

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Computational study of organic solvent–CO_2 mixing in convective supercritical environment under laminar conditions: Impact of enthalpy of mixing

José Sierra-Pallares[a,*], Ashwin Raghavan[b], Ahmed F. Ghoniem[b]

[a] Energy Engineering and Fluid Mechanics Department, University of Valladolid, Paseo del Cauce 59, 47011 Valladolid, Spain
[b] Reacting Gas Dynamics Laboratory, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, 02139 MA, USA

ARTICLE INFO

Article history:
Received 2 July 2015
Received in revised form 6 November 2015
Accepted 7 November 2015
Available online 22 November 2015

Keywords:
Mixing
CFD
Two-phase flow
Supercritical fluids
Equations of state
Supercritical antisolvent

ABSTRACT

Mixing under supercritical conditions plays an important role in a number of industrial processes including the selective separation or fractionation of certain species from oils or hydrocarbons and determining the final particle size distribution and product quality in supercritical nanoparticle synthesis routes. This paper presents a computational study of mixing in supercritical antisolvent systems in which the enthalpy of mixing is finite. In particular we focus on the mixing of an ethanol droplet immersed in a carbon dioxide stream near and far above the critical point using computational fluid dynamics (CFD) code coupled to the Peng–Robinson equation of state and appropriate mixing rules. The result of mixing is investigated under different process conditions: immediately above, above and far above the mixture critical point, all under laminar flow conditions. We show how mixing is far from being isothermal due to the large enthalpy of mixing and that significant spatially distributed temperature deviations can result. In particular, the mass and heat transfer in the droplet boundary layer exhibit large temperature gradients. Besides, this local heating/cooling may be responsible for the onset of a two-phase flow under the conditions studied; a phenomenon revealed experimentally in recent studies. Two different modes of mixing between the droplet and free stream, called "deformation" and "stripping", are observed for the cases under study. The mixing pattern depends on the Reynolds number and significant droplet deformation is observed as the convective velocity is increased and the vorticity forming in the boundary layer between the droplet and the flow accumulates in the wake region. Our results confirm previous observations, highlighting the fact that mixing is a crucial step in nanoparticle precipitation under supercritical conditions (supercritical particle synthesis, rapid expansion of supercritical solutions, supercritical antisolvent processes, etc.) due to its effect on particle size and morphology.

1. Introduction

Supercritical fluid conditions are becoming more important in industrial applications such as: nanoparticle production, oil upgrade, bio-oil production, high pressure combustion, etc., and the use of fluids at operating conditions above the critical pressure is expected to grow significantly. The unique environment they provide, in terms of transport characteristics and chemical reactions, and the opportunity to tune up the process conditions by varying pressure and temperature constitute a very interesting framework for different branches of science and engineering. Fluid flow around and above the supercritical pressure is therefore key to these technologies.

During the last fifteen years substantial efforts have been directed toward understanding these flows. It is well known that fluids above the critical pressure behave very differently than under normal conditions [1]. Some recent experimental investigations were reported by Segal and Polikhov [2] and Roy and Segal [3] regarding transcritical injection of round jets. Both studies indicate that the liquid break-up and atomization mechanisms that prevail at subcritical pressure are no longer observed under supercritical pressures because the surface tension and latent enthalpy of vaporization vanish, and there is no evidence of droplet formation. These flows feature "comb-like" structures at the edge of the dense stream, a pattern that is not observed under subcritical pressures. The geometry of the flow is reminiscent of a variable density turbulent gas stream.

* Corresponding author.
E-mail address: jsierra@eii.uva.es (J. Sierra-Pallares).

http://dx.doi.org/10.1016/j.supflu.2015.11.007
0896-8446/

The problem of modeling supercritical pressure fluid flow systems has been tackled using computational fluid dynamics (CFD). Bellan's group [1,4–6] studied the problem using direct numerical simulations (DNS) focusing mainly on nitrogen–heptane and oxygen–hydrogen mixtures with the aim of producing dataset in order to derive models for large eddy simulation (LES) of supercritical flows. Studies by Yang's group [7,8], aimed at testing classical LES turbulence closures against available experimental data. The performance of classical LES models was found to be quite encouraging in the description of cryogenic round jets of nitrogen. Meng and Yang also performed direct simulation of oxygen droplets in hydrogen streams at supercritical pressures [9,10]. Detailed flow structures and transport phenomena were examined, revealing various key mechanisms underlying droplet vaporization in a supercritical forced convective environment. Besides, correlations of droplet lifetime and drag coefficient were established in terms of fluid properties, pressure, and free-stream Reynolds number.

In addition to the efforts developed by the Mechanical Engineering and the Aeronautics communities, there has also been an emerging interest and research from the Chemical Engineering community, since supercritical flows are important in different application in this field, such as nanoparticle synthesis [11,12], destruction of organic waste [13], and desulfurization and upgrade of crude oil [14,15]. Analytical and computational analyses of the processes are very useful for the interpretation of experimental results and the design of new experiments and hence, fluid flow simulation is becoming more and more important. A methodology employed to tackle these types of flows is the Reynolds Averaged Navier Stokes approach. Sierra-Pallares et al. [16] performed an assessment of turbulence models to determine the best choice for simulating supercritical reactors at fully miscible conditions. The Realizable k–ϵ model showed the better performance. This model was also used to predict the local mean age of the fluid inside a carbon dioxide reactor with good agreement with the available experimental data. Regarding supercritical water oxidation applications, Narayanan et al. [17] have developed CFD simulations of methanol oxidation in supercritical water, using an eddy dissipation model. Sierra-Pallares et al. [18] proposed a mixing model adequate to high pressure conditions that significantly improves the prediction of the flame temperature.

Concerning nanoparticle synthesis at supercritical pressure conditions, the gas or supercritical antisolvent synthesis (GAS or SAS) process and its variants have received considerable interest because of the wide range of materials that can be micronized using these approaches. In the SAS process, there is a general agreement regarding the flow regimes observed when a liquid is injected into a vessel filled with a solvent at the supercritical state. Lengsfeld et al. [19] studied the evolution and disappearance of the liquid surface tension of immiscible, weakly miscible and miscible fluids injected in supercritical carbon dioxide to determine whether the liquid atomizes into droplets or evolves as a gaseous jet. They concluded that in the case of miscible fluids (i.e., at supercritical conditions), the surface tension vanishes before an appreciable jet break-up is obtained. Consequently, a gas-like jet is formed after the jet break-up. Dukhin et al. [20] found that jet break-up into droplets still takes place at pressures slightly above the mixture critical point. According to this research, due to the non-equilibrium conditions during mixing, a dynamic (transient) interfacial tension exist that decreases between the inlet of the liquid and its transformation to a gas-like mixture. They also observed that for pressures far above the mixture critical point, the solvent jet injected into supercritical CO_2 does not behave like an atomized or spray jet but a gas-like jet without any interface or formation of droplets. Reverchon et al. [21] investigated the injection of liquid acetone and dimethyl sulfoxide in a vessel containing carbon dioxide at operating conditions of 313 K in the pressure range between 6 and 16 MPa

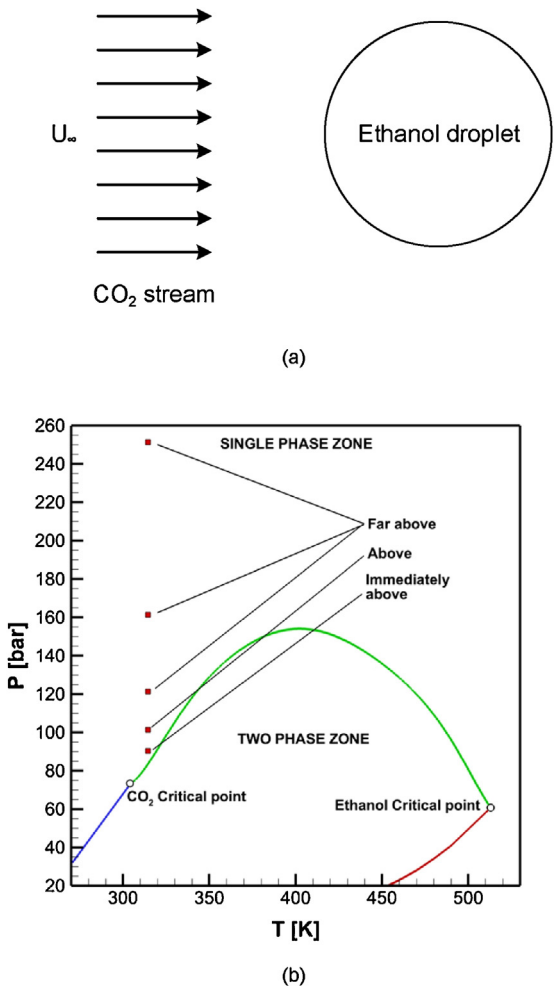

Fig. 1. (a) Simulation set-up; (b) Red squares show the initial conditions for the system under study localized in the phase diagram carbon dioxide–ethanol. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(relevant for SAS applications) using elastic light scattering. Their results showed, surprisingly, the establishment of two-phase mixing below and above the mixture critical point. Single-phase mixing was observed for acetone very near the mixture critical point. In the case of dimethyl sulfoxide, and at pressures significantly higher than the mixture critical point, a progressive transition was found to exist between multi-phase and single-phase mixing.

The explanation of this phenomenon is far from established. Reverchon et al. attributed this phenomenon to the operating pressure, the viscosity and the surface tension of the solvent, and developed a model that takes into account different time scales to explain their experimental results [22]. According to Dukhin et al. [20], excess molar enthalpies can be quite high under these conditions, hence thermal effects during this process have an effect on the phase separation path and must be considered in order to fully explain the process. Zahran et al. [23] supported this hypothesis. In their research, excess enthalpies of carbon dioxide–dimethyl sulfoxide mixture were measured, showing an exothermic behavior. These data were used to confirm the thermal effects in SAS experiments using enthalpy balances, showing the heating of few degrees Kelvin with regard to the injection temperature. Although, this was a rough estimate based on macroscale arguments, it pointed out the impact of excess enthalpy on the overall dynamics of the system.

Although the mixing between an organic stream and supercritical carbon dioxide (as antisolvent) has been studied using CFD,