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Simulation of supercritical water–hydrocarbon mixing in a cylindrical tee at intermediate Reynolds number: Formulation, numerical method and laminar mixing

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ABSTRACT

The objective of this work is to study the flow dynamics and mixing of supercritical water and a model hydrocarbon (*n*-decane), under fully miscible conditions, in a small scale cylindrical tee mixer (pipe ID = 2.4 mm), at an intermediate inlet *Reynolds number* of 500 using 3-D CFD simulations. A Peng–Robinson EoS with standard van der Waals mixing rules is employed to model the near-critical thermodynamics with the mixture binary interaction parameter obtained from a Predictive Peng–Robinson EoS using group contribution theory (PPR78). The *n*-decane stream is introduced at the colder temperature of 700 K to ensure operation above the Upper Critical Solution Temperature (UCST, 632 K) of the water *n*-decane system while the water stream enters at a higher temperature of 800 K. Under these conditions, the flow in the tee mixer remains laminar and steady-state is reached. Mixing occurs predominantly due to the circulating action of a counter-rotating vortex pair (CVP) in the body of the hydrocarbon jet entering from the top. This CVP is formed due to the reorientation of the streamwise vorticity pre-existing within the hydrocarbon jet as it flows down the vertical pipe of the tee junction. The advective transport is further assisted by a secondary flow of water from the bottom stream, around the hydrocarbon jet, toward the space vacated near the top of the downstream pipe section by the downward motion of the HC jet. The CVP becomes progressively weaker due to vorticity diffusion as it is advected downstream and beyond 10–12 diameter lengths downstream of the mixing joint, transport is mainly controlled by molecular diffusion. It was found that the variations of density and transport properties with temperature do not have a significant impact on the flow and mixing dynamics for a $\Delta T = 100$ K between the two streams. Local cooling of the fluid mixture was also observed in the mixing of water and *n*-decane streams entering at the same temperature (initially isothermal). This cooling effect is due to the diffusion of species along a gradient in their partial enthalpy in the mixture. Such gradients in species partial enthalpies are non-zero under near-critical conditions even for initially isothermal flows due to the non-ideality of the fluid mixture under these conditions. This local heating/cooling effect at near-critical conditions could give rise to unexpected formation of phases when operating close to critical points.

1. Introduction

Characterizing the mixing dynamics in a realistic reactor geometry is crucial to be able to estimate conversion rates and product distributions of the supercritical water upgrading and desulfurization (SCWUDS) process. The present study is focused on a cylindrical tee reactor geometry shown in Fig. 1. Flow in a cylindrical tee mixer exhibits a variety of flow features likely to be encountered in any general reactor.

Dreher et al. [1] performed CFD simulations of mixing of two streams in a rectangular cross-section opposed-flow tee micromixer with channel width of 300 μm for *Re* up to 1000. They were able to observe the transition of the flow regime from laminar flow for $Re < 10$ to steady engulfment flow for $10 < Re < 240$ (the two fluid streams swap to the opposite side) to periodically fluctuating flow for $240 < Re < 500$ and finally to chaotic flow for $Re < 500$ (turbulence). Hoffmann et al. [2] experimentally characterized the flow and mixing in a rectangular opposed-flow tee micromixer and also observed the flow transition from the straight laminar to engulfment flow regime. Correia et al. [3] numerically investigated the mixing in opposed-flow micromixers with a tortuous downstream flow channel and found an unsymmetrical downstream channel configuration results in slightly better mixing than a symmetric

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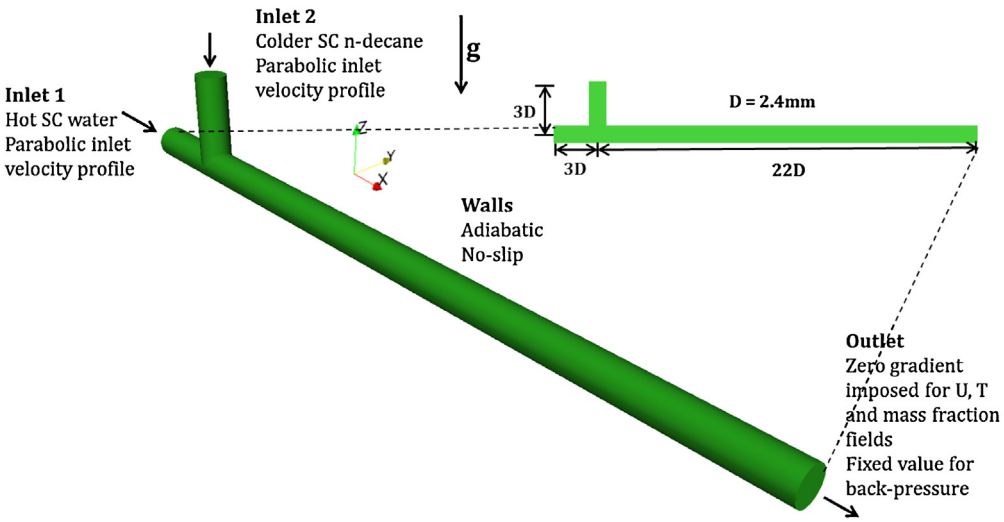

Fig. 1. Cylindrical tee mixer geometry and boundary conditions.

configuration. Though these studies focus on the laminar to transition flow regimes which are of interest to us in the preliminary small-scale tests of SCWDS, they study mixing of two streams of the same fluid in rectangular opposed-flow tees.

Mixing of hot and cold water in cylindrical mixing tees (similar geometry to ours) at high *Re* has been extensively studied in the nuclear industry community using the Large Eddy Simulation (LES) and Unsteady Reynolds Averaged Navier–Stokes (URANS) methodologies. Large Eddy Simulations were performed by Kuczaj et al. [4,5], Jayaraju et al. [6], Westin et al. [7] and Odemark et al. [8] for very high *Re* (∼150,000). They were all able to obtain satisfactory agreement with the experimental results of Andersson et al. [9] using appropriate mesh resolutions, inlet boundary conditions and sub-grid scale models. Frank et al. [10] and Merzari et al. [11] performed URANS of the same flow but were unable to capture the transient behavior as well as the LES calculations. The focus of all these studies was mainly to validate LES and URANS as viable predictive techniques for the prediction of thermal fluctuations in tee junctions in the nuclear industry. As such, they did not investigate the laminar to turbulent transition in cylindrical tee mixers. A discussion of the flow structures in a cylindrical tee mixer and their evolution is also lacking in these works.

The peculiar variations of thermodynamic and transport properties near the critical point can be expected to affect the flow and mixing dynamics. Cubic equations of state which can capture real-fluid thermodynamics have been formulated by Peng at al.[12] (Peng–Robinson EoS) and Soave et al.[13] (Redlich–Kwong–Soave EoS). These equations of state are the most widely used in numerical simulations of real-fluid flows due to their simplicity of implementation and effectiveness in capturing near-critical variations of fluid densities and specific heats (especially for hydrocarbons). The variations of viscosity and thermal conductivity of fluids and fluid mixtures near the critical point can be modeled using the correlations developed by Chung et al. [14] for a large number of substances and a wide range of temperature–pressure conditions. Liu et al. [15,16] and Silva et al. [17] have developed expressions for the variation of mass diffusivities with temperature and pressure of substances in dense non-ideal mixtures based on the hard-sphere Lennard–Jones model. Section 3 outlines the procedure adopted in this study to model the near-critical thermodynamic behavior and transport property variations of the water-HC system.

Miller et al. [18] performed Direct Numerical Simulations (DNS) of a supercritical heptane–nitrogen temporal mixing layer (both two and three dimensional) using a Peng–Robinson EoS to model the near-critical thermodynamic behavior and studied the effect of density stratification across the shear layer on the transition to turbulence. Okong'o et al. performed a similar DNS of a supercritical liquid oxygen/hydrogen three dimensional mixing layer [19] and observed a similar effect of the density stratification causing a suppression of the transition to turbulence. They investigated this effect by looking at the vorticity budget. The effects of the free-stream density ratio on the evolution of incompressible, high *Reynolds* and *Froude* number, confined mixing layer was investigated numerically by Soteriou et al. [20]. They found that a non-unity density ratio alters the flow characteristics significantly, influencing the entrainment patterns by means of baroclinic generation of vorticity.

Zong et al. [21] have performed the LES of a two-dimensional cryogenic supercritical nitrogen jet at high *Re* and studied the spatial and temporal evolution of the jet for different ambient pressures which lead to varying amounts of density stratification. Their findings seem consistent with previous results of Miller et al. [18] and Okong'o et al. [19] regarding the effect of density stratification leading to the suppression of shear layer transition to turbulence. A similar study of the dynamics of cryogenic nitrogen jets at supercritical pressures was performed by Kim et al. [22] using a RANS framework with a k–ϵ turbulence model and a presumed probability–density function for the conserved scalars. Park [23] performed a series of RANS and LES simulations of a cryogenic liquid nitrogen jet with a variety of turbulence models and three different equations of state (ideal gas, P–R and SRK) and found that the choice of an appropriate real-fluid EoS is more important in capturing the flow and mixing dynamics than the choice of turbulence models. Schmitt et al. [24] analyzed the behavior of a nitrogen coaxial shear jet under supercritical pressures through LES and experiments and investigated the effect of externally imposed acoustic perturbations on the jet mixing efficiency.

Narayanan et al. [25] simulated a supercritical water oxidation (SCWO) hydrothermal flame of methanol using RANS and an eddy dissipation combustion model with single-step kinetics. They were successful in obtaining a fair agreement with their experiments for the flame position but over-predicted the flame temperature. Sierra-Pallares et al. [26] have also simulated hydrothermal flames in SCWO of methanol using an eddy dissipation concept along with a micro-mixing model and were able to predict flame structure and temperature to a fair degree of accuracy. Kim et al. [27] validated