

USING CFD SIMULATIONS TO ESTIMATE PROPERTIES OF A SUPERCRITICAL BINARY MIXTURE

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Computational Fluid Dynamics (CFD) has proven to be a powerful tool to numerically solve the fluid-flow equations so it gives a further insight into the flow pattern of contacting equipment. There has been a fast growing in the study of applications in fluid flow and heat and mass transfer.

In this work, a prediction of the physical properties of a near-critical or supercritical binary mixture is obtained via CFD simulations in a 2D pipe flow model. Near-critical or supercritical CO₂ was chosen as circulating fluid; in order to obtain a composition profile, a mass flux of toluene was imposed through the pipe walls. In order to impose near-critical or supercritical conditions to the fluid, Peng Robinson equation of state was imposed to the CFD model through a C++ subroutine compiled within the solver CFD code.

Navier-Stokes equations together with Peng Robinson EOS and species transport and diffusion model are solved using a commercially available finite volume-element code (Fluent 6.2 solver). Fluid is taken to be compressible, Newtonian and in laminar flow regime.

INTRODUCTION

Supercritical fluid extraction (SFE) processes have been lately successfully applied as an alternative to conventional separation methods in the chemical, food, pharmaceutical, biochemical and environmental industries. Supercritical fluids have been proven to be more efficient extractants than most commonly employed liquid solvents [1]. Very recently Computational Fluid Dynamics (CFD) has been found to be a very useful tool in the understanding and optimization of such complex processes [2].

Determination of the basic properties is essential to get accurate results through CFD simulation. The aim of this work is to compare and contrast different methods of determining viscosity and density of a mixture at low pressure, near critical pressure and supercritical pressure, and verify the numerical error got when the method is implemented in CFD software. In order to do so, the most relevant methods have been tested one against the other and compared with the results got implementing them into a commercial CFD Software (Fluent 6.2). The mixture selected is CO₂-toluene, due to the fact that CO₂ is a wide applied supercritical extractor and toluene can be a good example of solute to be extracted.

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1. CFD MODEL & SOLVER

In order to study how the desired properties (density and viscosity) of the mixture are estimated by the software, a 2-dimensional cylinder of 5m length and 20cm diameter was created. From one side of the tube carbon dioxide (CO₂) in laminar flow regime was fed to the model. In order to impose a density gradient along the tube, a flux of 0.01 kg/s of toluene vapour was imposed through the pipe walls. The diffusion coefficient has been determined by the method of Hirschfelder-Bird-Spotz with the modification of Wilke-Lee **Erreur ! Source du renvoi introuvable.**]. Three temperatures (i.e. 298, 310 and 320K) and four pressures (i.e. 1, 60, 80 and 200 atm.) have been taken as study cases. For atmospheric pressure situations, Ideal Gas law was used to estimate density. For near-critical and supercritical conditions, Peng Robinson equation of state for density and Lucas method for viscosity were implemented through a C++ subroutine inside the CFD solver.

The under-relaxation factors for the pressure, density, body forces, momentum, C₇H₈ and energy have been set to 0.3, 1, 1, 0.7, 1 and 1 respectively. A discretization of 1st order until convergence was used as an initial solution for a 2nd order discretization. Continuity, velocity, energy and C₇H₈ residuals have been taken as convergence monitors.

For each of the simulations it has been recorded the C₇H₈ mass fraction, the density and the viscosity at the central axis of the tube. The numerical results obtained were compared against correlations and equations of state.

2. DENSITY ESTIMATION

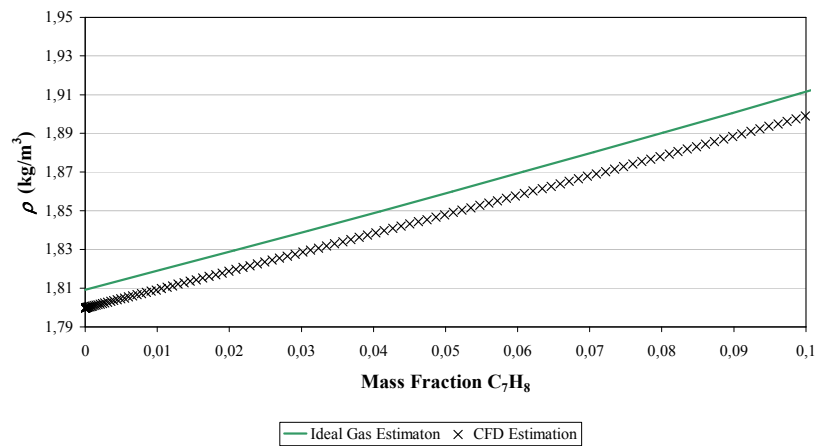
Low pressure density has been determined by ideal gas law for both of the pure components assuming the flow as incompressible. In such way the density is computed by the CFD solver as shown in Eq. 1.

$$\rho = \frac{P}{R \cdot T \cdot \sum \frac{y_i}{M_w}} \quad (1)$$

It was expected that for low pressure both methods would give similar results due to the low interaction forces between the molecules. The results obtained at the different temperatures tested (i.e. 298, 310 and 320K) are very similar to the ones shown in **Erreur ! Source du renvoi introuvable.**. From those results it has been checked that the numerical error of the CFD solver when applying the ideal gas law is neglectable.

In order to study high pressure situations, estimation of the mixture density has been checked at 60atm (pressure immediately below the critical point), at 80 atm (immediately above critical point) and at 200 atm (supercritical region). PR EOS implemented via user defined function together with a volume weighted mixing rule were imposed to the CFD solver. Results obtained were compared with those obtained for the mixture using PR EOS.

Figure 1. Density estimation at 298 K and 1 ATM



The results obtained for high pressure situations can be seen in Figures 2, 3 and 4. In general, for all situations simulated, it was noticed that despite the fact that the estimation done by the CFD solver (i.e volume weighted mixing rule) is close to the reference (PR) for low toluene mass fractions due to the good pure component density estimation, such a simple mixing rule is not able to predict the mixture critical point or phase changes as it does PR. This should not be an important issue because supercritical extractions are seldom run at conditions close to the critical point and phase changes are always avoided.

Figure 2. Density estimation at 320 K and 60 ATM

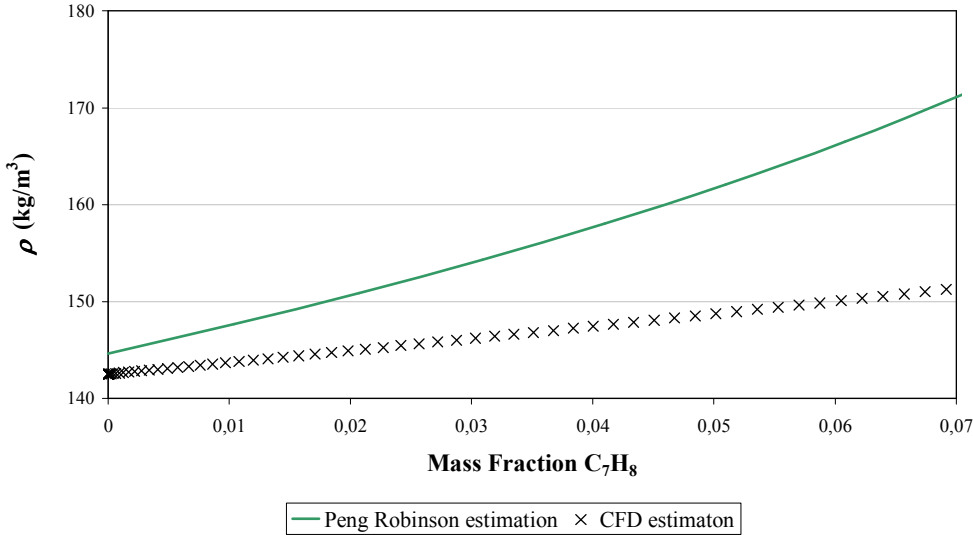


Figure 3. Density estimation at 320 K and 80 ATM.

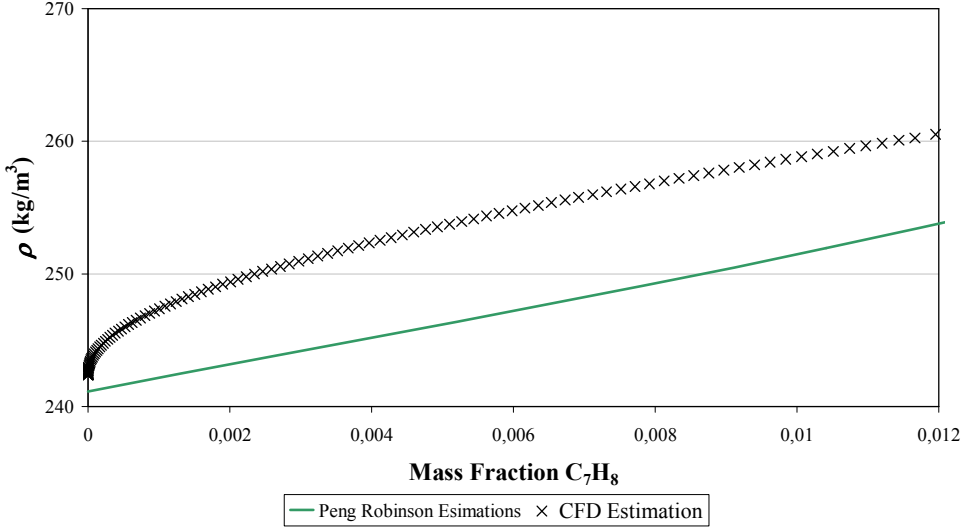
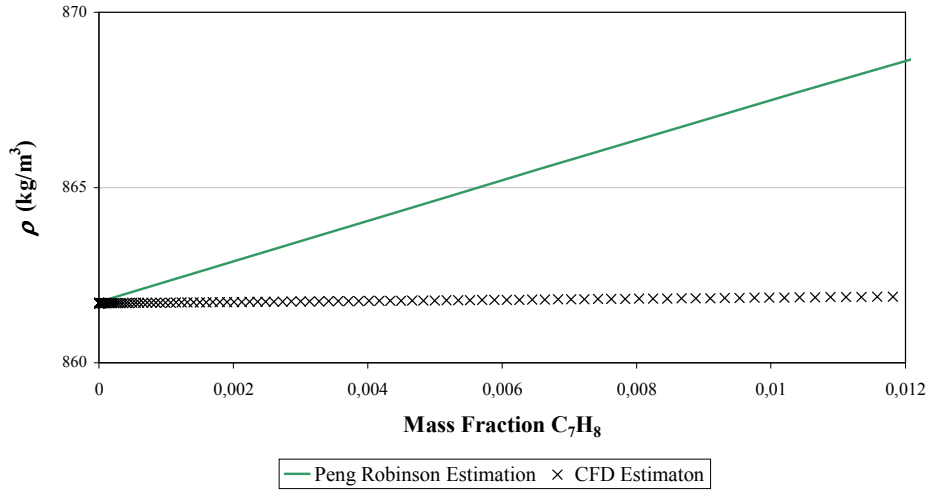


Figure 4. Density estimation at 310 K and 200 ATM.



For all cases analyzed the divergence between CFD estimated results and increases as the mass fraction of toluene increases. According to this, the greatest numerical errors obtained for the CFD simulations were located at the saturation point (equilibrium conditions at the specified pressure and temperature). Maximum error measured when estimating density was of 6.24%, which is an acceptable value.

At a pressure of 200atm, far away from the critical conditions, the results are again similar between the temperatures. As example, for a temperature of 310K the results are shown in **Erreur ! Source du renvoi introuvable.** It can be seen that despite having similar tendency to the one at 80atm, the error is smaller. It has been found for the temperatures checked that for mass fractions of toluene below the equilibrium conditions, the error is never bigger that 1.25%.

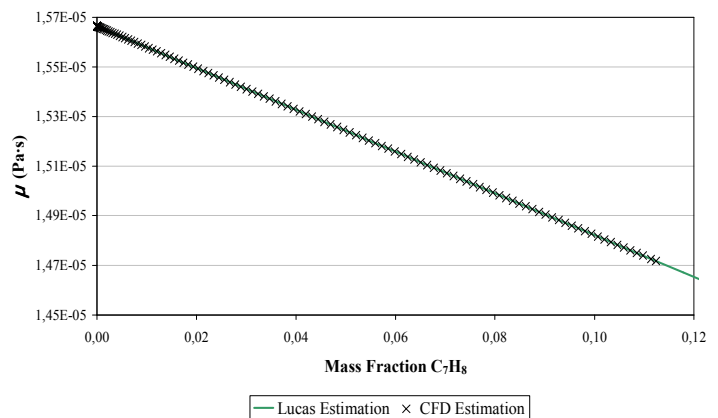
3. VISCOSITY ESTIMATIONS

To estimate the viscosity at low pressure the pure component viscosity has been calculated by the method of Lucas [4]. The mixing rule used was mass weighted mixing rule (see Eq.3).

$$\mu = \sum_i Y_i \cdot \mu_i \quad (3)$$

Results obtained with the CFD solver were compared against those obtained using Lucas Method for mixtures (see Fig. 5). The results are almost identical for the three temperatures tested. From the previous figure it can see that the calculations through CFD are exactly the same as the ones done with the contrast method, proving as done for the density that the CFD solver fits the results expected with the selected methods for comparison.

Figure 5. Viscosity estimation at 310 K and 1 ATM.



Some of the results obtained for the estimation of viscosity in high pressure situations can be seen in Figures 6 and 7. As happened with density, for all cases analyzed the divergence between CFD estimated results and increases as the mass fraction of toluene increases.

According to this, the greatest numerical errors obtained for the CFD simulations were located at the saturation point (equilibrium conditions at the specified pressure and temperature). Measured errors were lower than 10 %, which is an acceptable range.

Figure 6. Viscosity estimation at 298 K and 60 ATM.

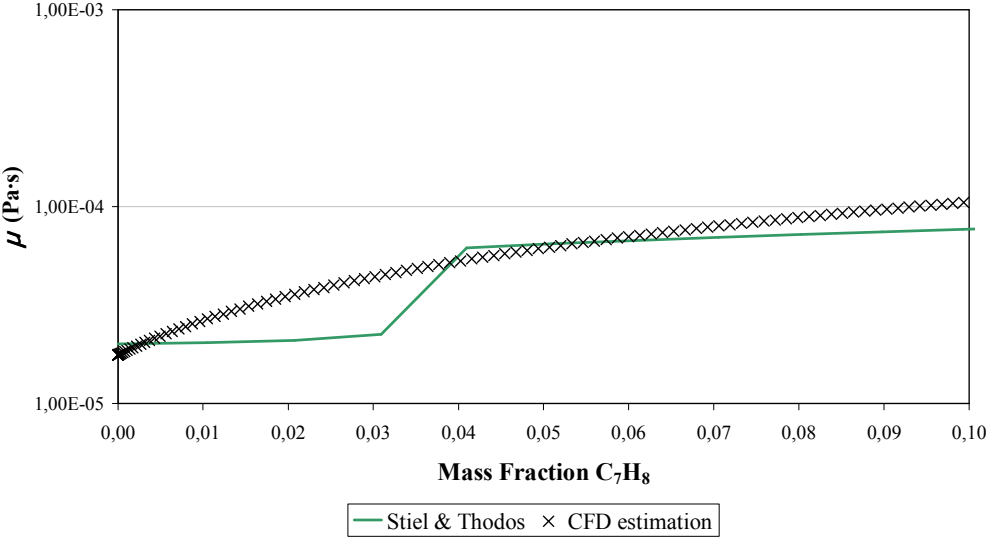
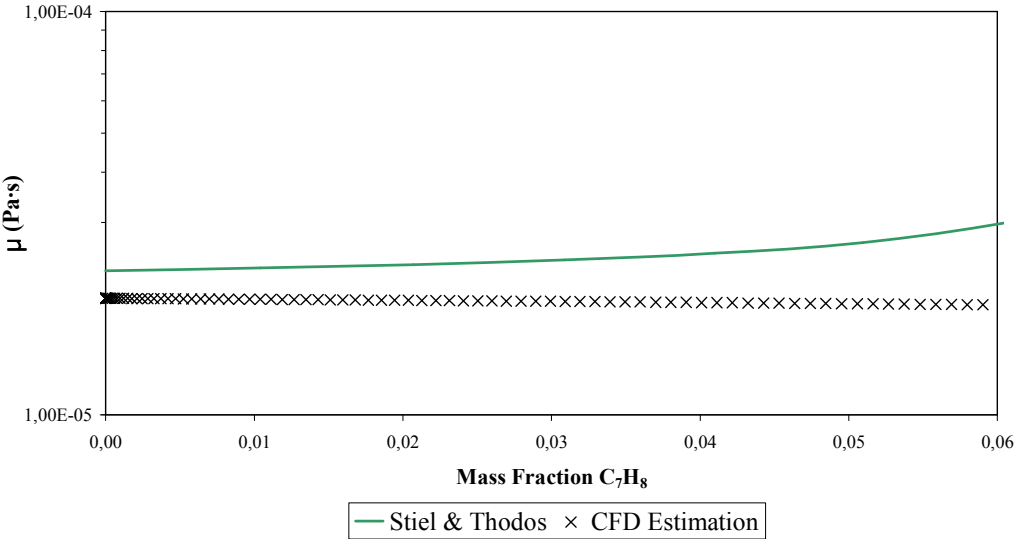


Figure 7. Viscosity estimation at 320 K and 80 ATM



CONCLUSIONS

Properties estimation methods for pure components implemented into the CFD solver via user defined functions (C++ subroutines) combined with pre-defined mixing rules proves to be a good method for estimating properties of supercritical mixtures. For all cases analysed, a good agreement between CFD estimations and correlations was obtained. Measured error was never superior than 10 %, which is an acceptable range.

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