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Contribution of Computational Fluid Dynamics and Thermodynamics to the development of supercritical carbon dioxide extraction processes

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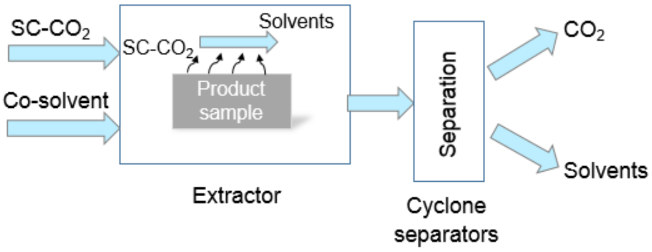
ABSTRACT

In supercritical CO_2 extraction process , there are two essential steps: the extraction step in the extractor where the SC-CO_2 allows the solvent or extract removal from product structure and the separation step which consists of the separation of CO_2-solvents or CO_2-extract in a cascade of cyclone separators downstream the extractor. Cyclone separators are separation devices that use the centrifugal and gravity forces to remove liquid phase from flue gases.



Two supercritical extraction processes are studied here: organogels supercritical drying for aerogels production and supercritical extraction of polar compounds from natural products.

Concerning the first process, the organogel is prepared by an aminoacid-type organogelator with aromatic solvents such as tetralin or toluene. The experimental results showed a good solvent recovery rate in the case of tetralin, exceeding 90% but an unsatisfactory separation for toluene with a yield below 65%. In order to understand the experimental results a thermodynamic study and a hydrodynamic study (CFD) of the mixture separation in the cyclones are carried out.

Supercritical extraction of polar compounds from natural products using a CO_2 + aqueous ethanol mixture as solvent requires a reliable knowledge of vapor-liquid equilibria of the carbon dioxide + ethanol + water system in order to size and optimize the extraction process. The purpose of this study is to select an appropriate thermodynamic model among the ones available in commercial process simulators based on its ability to reproduce the phase-equilibrium behavior of the CO_2 + ethanol + water system on the temperature, composition and pressure ranges of interest. This study highlighted that the optimal thermodynamic models for the application of interest have to be chosen among the VTPR, PSRK and MHV2-UNIFAC

EoS. Once identified a suitable thermodynamic model for the CO_2 + ethanol + water ternary system, it has been possible then to simulate the supercritical extraction process and to discuss how water influences the process efficiency.

INTRODUCTION

In supercritical CO_2 extraction process , there are two essential steps: the extraction step in the extractor where the SC-CO_2 allows the solvent or extract removal from product structure and the separation step which consists of the separation of CO_2-solvents or CO_2-extract in a cascade of cyclone separators downstream the extractor. Two supercritical extraction processes are studied here: organogels supercritical drying for aerogels production and supercritical extraction of polar compounds from natural products. An organogel is firstly prepared by synthesizing an aminoacid-type organogelator which is able to immobilize aromatic solvents such as tetralin or toluene. Ethanol is classically used as CO_2 co-solvent for the extraction of biomolecules from natural products. When dealing with natural products, water is systematically present and, if in excess, can has a role as a physical "barrier", reducing the mass transfer. In addition, water is slight soluble in supercritical carbon dioxide and can displaces the equilibrium towards the liquid phase, entailing a decrease of the process efficiency. Hereby, it is important to optimize the water content. In order to control and even optimize the supercritical extraction process of natural substances, a reliable knowledge of the vapor-liquid equilibrium (VLE) behavior of the CO_2 + ethanol + water ternary system is eventually required to optimize the ethanol / water / CO_2 ratio in order to promote the vapor instead of liquid formation and even to optimize the supercritical extraction process.

MATERIALS AND METHOD

1. Organogel drying : Experimental set-up [1]

Figure 1 shows a simplified scheme of the process used for supercritical drying of organogel. In an autoclave, a cylindrical organogel [2] sample is initially placed and a quantity of free solvent is added. The sample diameter is 3 cm and its thickness varied between 0.5 cm and 1.5 cm. A CO_2 stream, of mass flow rate ranging from 300 to 750 g/h, is blown around the sample. The temperature and pressure in the autoclave are set to 45 °C and 180 bar and to 45 °C and 90 bar for tetralin and toluene respectively.

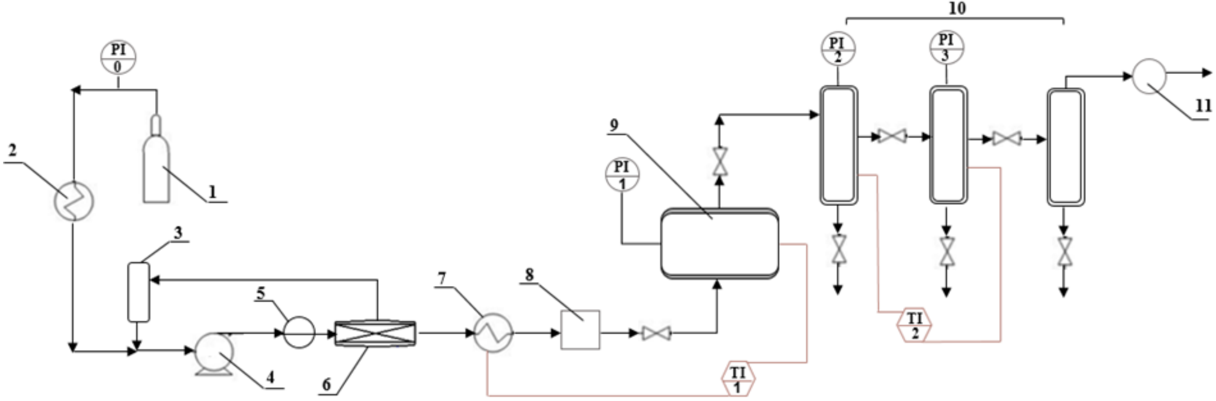


Figure 1. Scheme of the supercritical drying set-up: 1-CO_2 bottle; 2-cold exchanger;
3-CO_2 tank; 4-pump; 5- Damper, 6-back pressure regulator; 7-hot exchanger;
8-Coriolis mass flowmeter; 9-autoclave; 10- three cyclone separators;
11- Flowmeter, PI-pressure gauge, TI-thermostatic bath.

Every 15 minutes liquid solvent is recovered at the bottom of the separators and the collected quantity is weighed with $\pm$ 0.1 mg accuracy. The most amount of solvent is collected from the first separator and only a very small quantity in the two others. Furthermore, the flow rate and the pressures in the first two cyclones separators are reported.

2. Thermodynamic Modelling

2.1 Supercritical drying : CO_2/toluene and CO_2/tetraline

The experimental study showed that most of the solvent recovery was carried out in the first cyclone separator. For this reason, the thermodynamic and the CFD studies focuse on this separator. Hydrodynamic predictions showed that cyclone separators allow an efficient mechanical separation of the CO_2/toluene mixture [1] (figure 2). Thermodynamic investigations of the CO_2/solvent mixture are needed in order to explain the difference of the performance of cyclone separators when tetralin and toluene are used for producing aerogels.

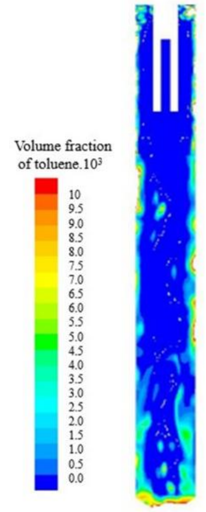


Figure 2. Distribution of toluene volume fraction at the central section vertical to the cyclone [1]

In the present study, the CO_2/solvent separation is modelled similarly as a simple theoretical stage. The expansion following the depressurization valve is generally considered as an isenthalpic (adiabatic) expansion at industrial scale. However since experiments were carried out on a laboratory scale unit and due to the small size of the valve, the expansion in the laboratory equipment can be reasonably assumed to be isothermal. For this reason, despite of the depressurization valve between the extractor and the first separator, the separation is considered as an isothermal flash.

Former Computational Fluid Dynamics (CFD) simulations performed on this separator showed that the pressure drop across the separator is lower than 35 Pa [1]. Because of this low value, the pressure is considered uniform throughout the separator. The first separator is modeled as a simple isothermal theoretical equilibrium stage. A simple flash drum was used to simulate this separator. Simulations were carried out using the PRO/II software, a steady state chemical-engineering process simulator.

The Peng-Robinson EoS (PR-EoS) has demonstrated its ability to manage high pressure fluid phase behavior and has shown simplicity and reliability for the class of compounds considered in this study. Therefore, the PR-EoS is implemented into the thermodynamic model of the separation process. For temperatures below 40 ° C including the separation temperature (20 ° C), no experimental data exists in the literature. The experimental bubble points for three temperatures covering the separation temperatures 10, 20 and 30°C were determined [3]. The CO_2/tetralin diagram was extended at these temperatures with the PR-EoS. In Figure 3 the experimental points and the theoretical curves are compared. The model represents satisfactorily the binary CO_2/tetralin mixture behavior at these temperatures. Despite the slight underestimation of bubble pressures and the overestimation of critical pressures, this model can however provide acceptable estimations of solubility in the liquid and gas phases in the pressure domain covered by the separation process.

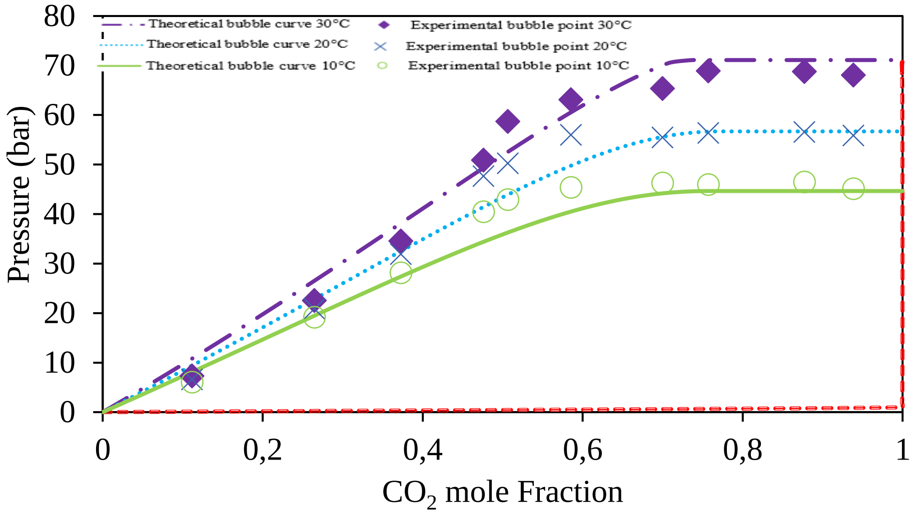


Figure. 3 Isothermal phase equilibrium diagrams of CO_2/tetralin at three temperatures

2.2 Supercritical carbon dioxide extraction: CO_2/Ethanol/Water

It is not an easy task to benchmark thermodynamic models based on previous works, as these models were all compared or calibrated on different datasets covering disparate domains of temperature and pressure. In addition, these models show generally an unsatisfactory correlation of phase-equilibrium data for the CO_2 + ethanol + water ternary system in the supercritical domain of pure CO_2. The first part of the present study aims at selecting an equation of state usable for correlating and even extrapolating, the vapor-liquid equilibrium behavior of the CO_2 + water + ethanol ternary system in the ranges of pressure and temperature usually considered in the supercritical extraction process. By using the thermodynamic model previously identified, it is discussed how the presence of water influences the efficiencies of the extraction and separation processes.

The thermodynamic models were chosen according to the selection method proposed by Hemptinne et al. [4], Sandler [5] and Aspen Plus® User Guide [6]. This methodology helped us to choose between two classes of models: non-predictive (all available for PRO/II software) and predictive (all available for Simulis thermodynamics software). Note that in this work, it is desired to benchmark predictive and non-predictive models available in commercial simulators without re-adjusting binary interaction parameters (BIP). The selection of the model will be based on its ability to reproduce the phase-equilibrium behavior of the CO_2 + ethanol + water system on the temperature, composition and pressure ranges of interest. Advantage will be given to predictive models because of their modularity (and in particular, the simplicity to generate the phase equilibrium behavior of systems made up of CO_2 + ethanol + water + other species, which is of particular interest for future studies).

The PRO/II software (Schneider Electric) was used to generate phase diagrams calculated from the two equations of state SRK (Soave-Redlich-Kwong) and PR (Peng-Robinson) combined with the following mixing rules: Panagiotopoulos-Reid (SRKP and PRP), modified Panagiotopoulos-Reid (SRKM and PRM) and Huron-Vidal-NRTL (SRKH and PRH). The *Simulis thermodynamics* software (ProSim) was used to generate phase diagrams using the following models: MHV2-UNIFAC PR or SRK, PSRK, VTPR and GC-PPC-SAFT. Thermodynamic data were obtained from the Detherm Database (Dechema) according to the selected operating conditions.

Once selected on the basis of their capacity to model VLE data of binary system, the following models: MHV2-UNIFAC PR or SRK, VTPR and PSRK, were benchmarked through their ability to predict ternary phase equilibrium data for the CO_2 + ethanol + water system. Although the VTPR model is not fully satisfactory regarding the modelling of the ethanol + H_2O binary system, it has been still considered for this final selection step as it was developed in particular to improve the prediction of supercritical data [7].

Despite the CO_2 + ethanol + water system is considered as especially difficult to model from a thermodynamic view point, the MHV2-UNIFAC (SRK or PR), VTPR and PSRK models can rather accurately reproduce its experimental phase behavior, at different operating temperatures and pressures of interest. Nevertheless, for all four models, a discrepancy between model predictions and experimental bubble and dew point data is observed near the critical point ($0.2 < x_{CO2} < 0.6$), as illustrated in figure 4. The modeling of the ternary system at the selected temperatures and pressures highlights a similar level of accuracy for all four models.

It should be noticed that regardless of the model used, the presence of a very small amount of water promotes the formation of a two-phase system.

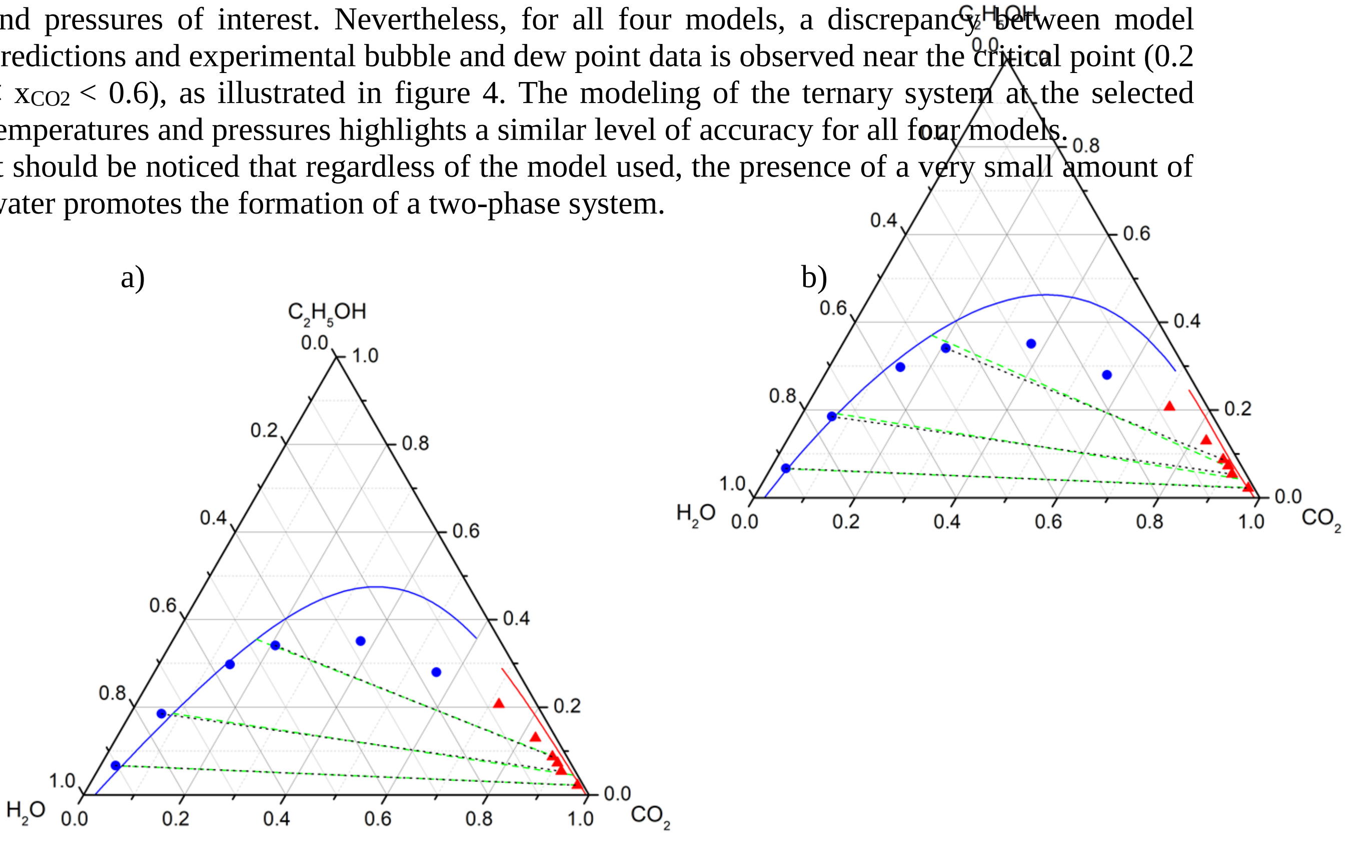


Figure 4. Ternary diagram of CO_2 + EtOH + water at 333K and 142 bar.
Experiment: (●) Liquid phase; (▲) Vapor phase [8,9].
(—) Predictions from the (a) SRK-MHV2-UNIFAC, (b) PSRK.
Tie line: (·······) model prediction (this tie-line was calculated at the temperature and pressure of the diagram, for an overall composition equal to the average of the experimental bubble and dew point compositions); (----) Experimental tie-line.

RESULTS

1. Organogels supercritical drying for aerogels production: solvent recovery and drying.

The experimental results showed a good solvent recovery rate in the case of tetralin, exceeding 90%, but an unsatisfactory separation for toluene with a yield below 65% (table 1).

Table 1. Comparison of theoretical and experimental solvent recovery rates (20 ° C and 50 bar)

Solvent	z_{sol} (%)	Experimental recovery rate SRR (%)	Theoretical recovery rate $\widehat{SRR}$ (%)	Relative difference (%)
Toluene	0.29	25.20	34.1	26.10
	0.32	47.47	40.4	17.50
	0.33	39.85	42.24	5.66
	0.51	50.55	63.1	19.89
	0.55	59.33	66.2	10.38
	0.59	62.50	68.56	8.84
	0.65	63.58	71.57	11.17
Tetralin	0.26	85.93	95.19	9.73
	0.27	94.10	95.37	1.33
	0.29	94.40	95.69	1.35
	0.36	98.39	96.54	1.92
	0.41	96.53	96.96	0.44
	0.43	96.60	97.10	0.51
	0.46	98.94	97.30	1.69

The proposed thermodynamic model is introduced in the PRO/II software and a single flash drum is used to simulate the separation of the CO_2/solvent mixture. For both solvents, the theoretical recovery rate matches the experimental rate within a relative discrepancy ranging from 0.5 to 26%. It is thus observed that a single flash drum modelled using the PR-EoS with temperature-dependent k_{ij} reasonably explained the unsatisfactory performances that were observed with toluene as solvent and the good recovery in the case of tetralin. Figure 5 illustrates the variation of the obtained theoretical solvent recovery rate (SRR) as a function of solvent concentration for both tetralin and toluene.

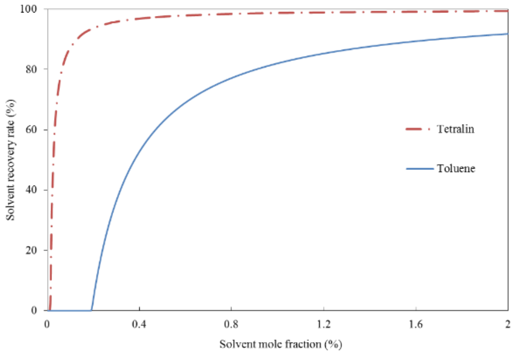


Figure. 5 Theoretical solvent recovery rate as a function of the solvent inlet composition at $T = 20\,^{\circ}C$ and $P = 50\ bar$

Simulations with different inlet compositions, pressures and temperatures show us that the optimum solvent recovery conditions would then be 56 bar and 19.5 ° C. These conditions are very close to the operating conditions. Thus, it is necessary to control accurately both process pressure and temperature along with CO_2 flow rate to ensure high yield of solvent recovery for both toluene and tetralin.

2. Influence of water in extraction process

Once a suitable thermodynamic model for the CO_2 + ethanol + water ternary system has been identified, the simulation of the extraction and separation process can be carried out.

The operating condition values (pressure, temperature, amount of ethanol, water and CO_2) used for the process simulation are similar to the experimental conditions used in our laboratory.

- Two levels of pressure were studied: 110 bar and 220 bar;
- Three levels of temperature were considered: 293.15 K, 313.15 K and 333.15 K.
- The starting water content in the material was 10 wt%, 25 wt% and 50 wt%, considering a dry-mass of 8 grams. We also considered that all the water present in the material was totally free to simplify the calculation;
- The mass of CO_2 introduced in each "step" was fixed by the average of all the experiments carried out in the studied installation (87.8 g, i.e. 2 mol).
- The volume of ethanol was 0 mL, 20 mL and 40 mL (the entire volume of ethanol is already present inside the extractor at the beginning of the process).

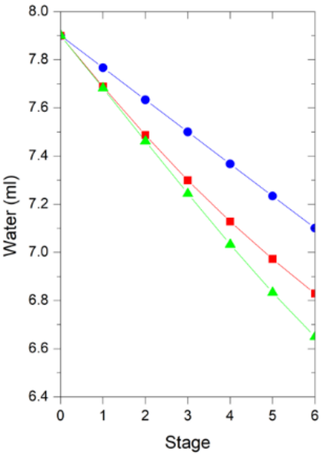
In order to simulate the process where CO_2 flows continuously through the extractor, a sequential approach is used: successive steps for which equilibrium is reached are considered. [10]. After each sequence, the gaseous phase present in the extractor is pushed out by pure CO_2 and exits towards separator 1. At each step, vapor and liquid composition as well as the amount of both phases are evaluated considering that the extractor behaves as a diphasic flash separator. Using this procedure, continuous extraction process was simulated considering the number of steps to remove all ethanol present in the extractor (6 equilibrium steps in most cases). The amount of water and ethanol previously present in the liquid phase is considered to remain in the extractor. The simulation of extraction process was performed using Simulis thermodynamics software (ProSim) considering the following assumptions:

- Mechanical dispersion of ethanol or water is not considered (entrainment of ethanol or water not solubilized by the CO2 flow reducing the extract recovery);
- The SRK-MHV2-UNIFAC model is well adapted to the description of the thermodynamics of the CO_2 + ethanol + water mixture.

Figure 6 presents the evolution of remaining ethanol (a) and water (b) in the extractor for the different steps.

a)

b)



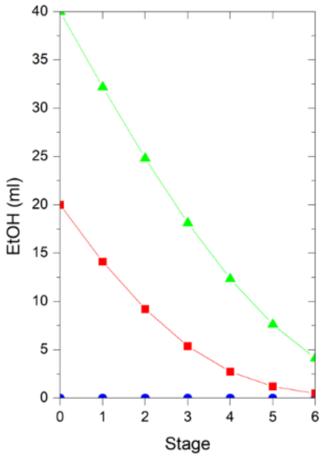


Figure 6. (a) Residual ethanol and (b) residual water at 313.15 K, 110 bar and 50% water. Ethanol initial volume (●) 0 ml, (■) 20 ml and (▲) 40 ml. Correlated with SRK-MHV2-UNIFAC.

It can be observed that:

- an increase of initial ethanol amount enhances water removal from the extractor,
- for a given pressure (220 bar) and temperature (313.15 K) an increase of water content (from 10 wt% to 50 wt%) leads to a decrease of ethanol removal rate,
- both water and ethanol are removed faster from the extractor when temperature increases,
- an increase of pressure (from 110 bar to 220 bar) enhances water and ethanol removal.

It can also be observed that water or ethanol promotes the formation of a biphasic system and displaces the equilibrium towards the liquid phase. Moreover, ethanol enhances water solubility in carbon dioxide due to strong hydrogen bonding associations between molecules.

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