

Extraction of lipids from waste biomass using compressed solvents: Kinetic and thermodynamic aspects

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Received: July 11, 2019; revised:, 2019

Traditional oil extraction involves organic solvents and represents both health and environmental concerns; besides, the large spend of these solvents is costly. Thus, safer alternative methods of extractions arouse interest. Supercritical fluid extraction (SFE), pressurized liquid extraction (PLE) and gas-expanded liquid (GXL) extraction can be applied to a full range of matrices. This paper aimed to briefly discuss some aspects related to the oil extraction from different biomasses using scCO₂ + organic solvents extraction technique in semi-batch scheme and highlight some kinetic and thermodynamic aspects of this promising extraction strategy.

Key words: Biomass oil extraction, high-pressure, supercritical CO₂, co-solvent, GXL extraction.

INTRODUCTION

Application of organic solvents for liquid extraction purposes brings risks to the environment and public health. Therefore, alternative extraction processes that might link high yield to economic viability are of great interest. Recently, pressurized liquid extraction (PLE), gas-expanded liquid (GXL) extraction, and supercritical fluid extraction (SFE) gained attention due to their green appeal. These extraction methods have as main advantages the elimination of large amounts of solvent, high selectivity, and the facilitated separation between solvent and solute. [1–3].

The SFE has been applied to several plant matrices, reducing the need for downstream process steps, by eliminating the solvent from the extracts, and providing flexibility in process conditions with the addition of different co-solvents to modulate selectivity and yield [4,5]. In this matter, supercritical carbon dioxide plays an important role due to its mild critical point conditions, around 31 °C and 74 bar, furthermore, it is an inexpensive, highly available, non-flammable, and non-toxic gas [6]. Another extraction technique that arises interest is the pressurized liquid extraction, in which higher temperatures are achieved, elevating the solubility of oils in the solvent and lowering the viscosity and the surface tension, leading to shorter extraction times and lower solvent spent compared to batch extraction process [7].

Gas-expanded liquid (GXL) extraction represents a transition between the SFE and the PLE. In this technique, a compressible gas is blended into the extraction liquid, reducing mass transfer effects by lowering the viscosity and

increasing the density of the solvent. For safety and economic reasons, it is usual to perform carbon dioxide-expanded liquids (CXL) extraction modulating the pressure and CO₂ amount to achieve better solvation properties. In comparison with the use of scCO₂, the main advantage of CXL is related to the possibility of applying lower pressure operations and, when compared to PLE, the solvent usage is reduced [8,9].

Oil extraction from spent coffee grounds was investigated by Couto *et al.* [12] at various conditions, between 40 and 55 °C, and 15 and 30 MPa. After 3h of extraction, the highest yield of 15.4 % was obtained at 25.0 MPa and 50 °C, corresponding to 85 % of the total oil content of spent coffee grounds. The use of 6.5 wt% ethanol in scCO₂ extraction system reduced the extraction time to roughly one third and diminished the solvent usage to acquire a 12.9% extraction yield. Andrade *et al.* [13] studied the extraction of spent coffee grounds at 40, 50 and 60 °C and 10 to 30 MPa during 2.5 h, and reported a maximum yield of 10.5 % with scCO₂ only, and 15 % in the presence of ethanol as co-solvent at otherwise identical conditions.

Extraction of rice bran lipids was performed by Sparks *et al.* [14], using pressurized liquid propane and supercritical carbon dioxide. The maximal yield of oil achieved by them using scCO₂ was 0.222 kg per kg of rice bran for conditions of 45°C and 35 MPa, and the maximal yield achieved with propane was 0.224 kg per kg of rice bran at 0.76 MPa and ambient temperature. These results correspond to approximately 85% of the total oil content on the raw material.

Soares *et al.* [15] compared the extraction of rice bran oil using scCO₂ (at 40 to 80 °C and 150 to 250

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bar) and compressed liquefied petroleum gas (at 20 to 40 °C and 5 to 25 bar). Those authors found little differences in yields between both methods. The highest yield in scCO₂ was 12.62 wt%, at 40 °C ad 250 bar, whereas for PLE the highest yield was 12.07 wt%, at the same temperature and 25 bar. Furthermore, the PLE extraction showed good results in terms of solvent and time spent, decreasing the solvent/feed mass by a factor of 30 and the extraction time by a factor of 15.

Recently, Araújo [10] investigated the CXL extraction of oil from spent coffee grounds, and Juchen *et al.* [11] reported a study concerning SFE of rice bran lipids. Both applied a semi-batch process approach that provided similar yields as the traditional continuous process with lower solvent consumption.

Despite the different studies conducted for oil recovery from several raw materials, where the extraction efficiency and technical feasibility are demonstrated, the thermodynamic backgrounds and the kinetic aspects of this process are still in need of greater debate. Thus, this paper aims to present and discuss some aspects related to the extraction process using scCO₂ + organic solvents (ethanol specifically) in a semi-batch extraction system. For this purpose, two different study cases based on previous results obtained in our research group are used: spend coffee grounds [10] and rice bran [11] oil extraction in a semi-batch process approach.

SEMI-BATCH METHODOLOGY OF SUPERCRITICAL CO₂+SOLVENT EXTRACTION

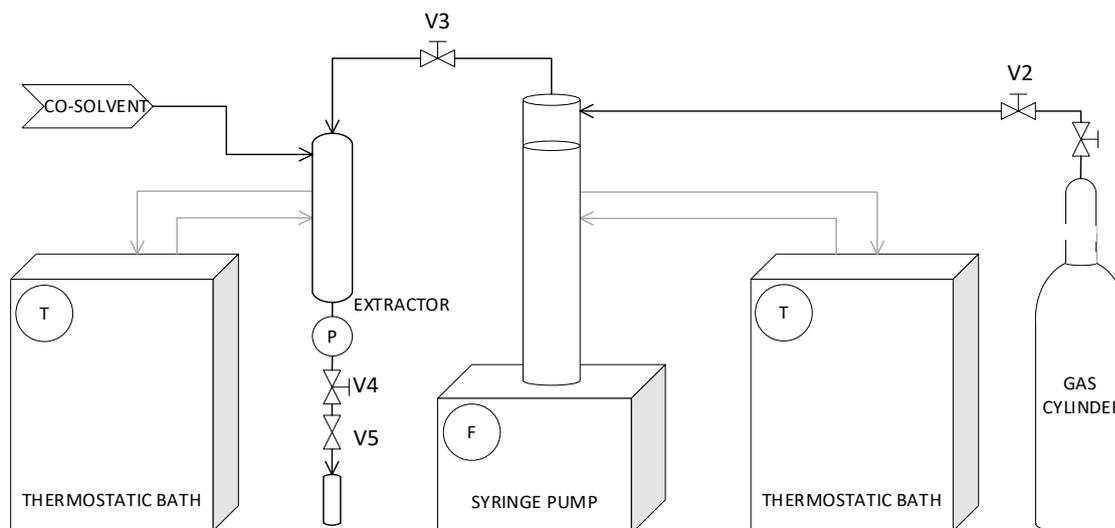


Fig. 1. Schematic diagram representing the laboratory scale unit used for semi-batch extraction using scCO₂ + ethanol mixture as solvent for oil extraction from waste raw materials.

beginning of the dynamic extraction step the solvent system is like a CXL and, after the ethanol is

A laboratory scale unit used for the semi-batch extraction with scCO₂ + organic solvent (in the present case, ethanol is used) mixtures is presented in Figure 1. The experimental setup basically consists of a jacketed extractor vessel with a thermostatic bath for temperature control; a syringe pump for CO₂ injection and pressure control during the extraction; a needle valve for the flow control; and pressure and temperature transducers and indicators. Also, an extra thermostatic bath is used for temperature control in the syringe pump jacket. More details about this extraction set up can be easily found in the literature [10,11,16].

A typical extraction run starts with loading the raw material into the extraction vessel and, after that adding the liquid co-solvent in a fixed co-solvent to raw material mass ratio. After that, the vessel is closed, the extraction temperature is set and CO₂ is injected using the syringe pump up to the desired pressure condition for the extraction. At this moment, the first step of the extraction process begins, named static extraction period. Usually, a period of 10 min to 90 min (depending on the raw material) is used. This static extraction step is needed to ensure that the system has reached the equilibrium conditions, in terms of solvent percolation into the raw material, and both thermal and mechanical stabilization. After this period, the dynamic extraction step is started by opening the flow control valve; then the compressed CO₂ passes throughout the extraction bed containing the sample, ethanol and CO₂ loaded into the extraction vessel. Thus, it is essential to highlight that at the

completely extracted from the vessel the process shifts to a process with pure supercritical CO₂-like

extraction. Hence, because the amount of liquid solvent (ethanol) in the extraction vessel is fixed there is a switch of the solvent system during the extraction.

DISCUSSION

In this section, two study cases are presented and discussed in terms of the overall performance of these extraction systems. The first case study is related to spent coffee grounds as presented by Araújo [10], and the second one is related to the rice bran oil extraction as presented by Juchen *et al.* [11]. Both authors evaluated the effects of the main process variables on oil extraction yield, such as pressure, temperature, confinement time and solvent to solids mass ratio. Also, both tested sequential extraction procedures in their works as an optimization strategy. After a brief presentation and discussion of the overall extraction curves of these two raw materials, some thermodynamic aspects considering the phase behavior and density of CO₂ + ethanol mixture are presented in relation to the conditions typically used in semi-batch scCO₂ + ethanol extraction procedure.

Case 1 – Oil extraction from spent coffee grounds

Araújo (2019) [10] evaluated the extraction of spent coffee grounds at 40 to 80 °C, 10 to 20 MPa, using scCO₂ and ethanol as co-solvent in a semi-batch GXL extraction. For comparative purposes, the oil extraction schemes in PLE and SFE (with scCO₂ only) were tested as well.

Figure 2 presents the overall extraction curves of different temperature and pressure conditions using an ethanol to biomass ratio of 2:1.

Figure 2 depicts little difference in the initial extraction rates among the studied conditions. At the same temperature, the lowest extraction pressure was always faster reaching the equilibrium, indicating that a highly packed bed may increase the mass transfer resistance. At 80 °C, the maximum yield at 10 MPa was almost four points percents lower than at 20 MPa. This dramatic effect probably happened due to a phase split of the solvent mixture (see discussion in the next section), which is coherent with the phase diagram further presented in Figure 10.

With pure scCO₂, the maximum extraction yield was insignificant, suggesting that the oil inside spent coffee grounds is scarcely available, and as expected its solubility in pure CO₂ was very low. However, as the ethanol to biomass ratio increases, the maximum yield tends to approach the one acquired using pure ethanol in a continuous flow scheme (PLE).

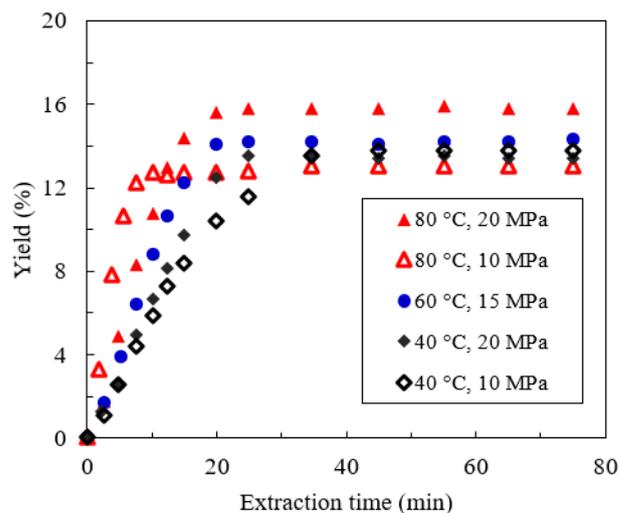


Fig. 2. Experimental overall extraction curves obtained by Araújo (2019) [10] for spent coffee grounds oil extraction with scCO₂+EtOH at ethanol to biomass ratio of 2:1.

Figure 3 depicts the kinetic curves reported by Araújo (2019) [10] at 60 °C and 15 MPa with different co-solvent to biomass ratio and this revealed interesting trends from an optimization point of view. The initial extraction rate is higher at lower ethanol loadings, and the maximum yield is higher at higher ethanol loadings. Thus, sequential extractions using fresh ethanol injections can reduce the extraction time and both solvent and co-solvent consumptions to obtain the same final yield of a semi-batch CXL extraction.

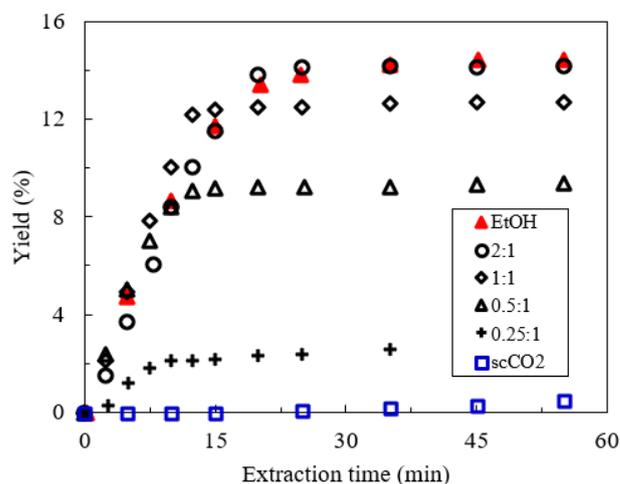


Fig. 3. Experimental overall extraction curves obtained by Araújo (2019) [10] for spent coffee grounds oil extraction with scCO₂+EtOH at different ethanol to biomass ratios in comparison to SFE with scCO₂ and PLE with ethanol.

Araújo (2019) [10] also evaluated a sequential extraction approach and the corresponding kinetic extraction curves are shown in Figure 4, in which, one can notice that the maximum yield obtained by sequential extraction, with ethanol to biomass ratio

of 0.5 to 1 is analog to the pure ethanol, and to the one acquired by a regular extraction with ethanol to biomass ratio of 2:1.

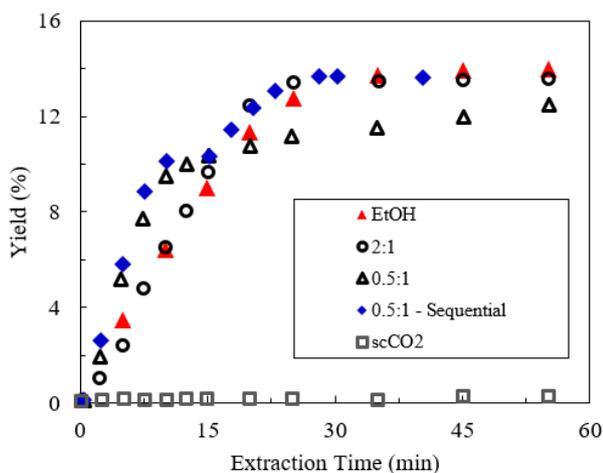


Fig. 4. Experimental overall extraction curves obtained by Araújo (2019) [10] for spent coffee grounds oil with $\text{scCO}_2 + \text{EtOH}$ at different ethanol to biomass ratios in comparison to SFE with scCO_2 and continuous PLE with ethanol, at 40 °C and 10 MPa. Comparison of one step with sequential extraction processes.

Case II – Oil extraction from rice bran

Juchen et al. (2019) [11] studied the oil extraction from rice bran at the same temperature and pressure conditions (40 to 80 °C and 10 to 20 MPa), comparing pure scCO_2 with $\text{scCO}_2 + \text{ethanol}$ as co-solvent in a semi-batch process, using ethanol to biomass ratios between 0:1 and 2:1.

The effect of pressure on maximum yield was positive, while the impact of increased extraction temperatures was highly negative on both extraction systems. By maintaining the temperature at 40 °C and the ethanol to biomass ratio at 1:1, the maximum yield increased from 16.26 % (10 MPa) to 25.48 % (20 MPa). On the other hand, maintaining the same ethanol to biomass ratio and the pressure at 10 MPa, the maximum yield decreased from 16.26 % to 2.60 % when temperature was increased from 40 to 80 °C. This effect may have happened because up to 27 MPa, the CO_2 density controls the extraction process, while over 27 MPa the vapor pressure of the oil components dominates the extraction process [17].

Figure 5 present the extraction kinetics obtained at different ethanol to biomass ratios and PLE extraction carried out continuously with pure ethanol at the same conditions, while Figure 6 shows a sequential run with ethanol to biomass ratio of 1:1. All the experiments were performed at 40 °C and 20 MPa.

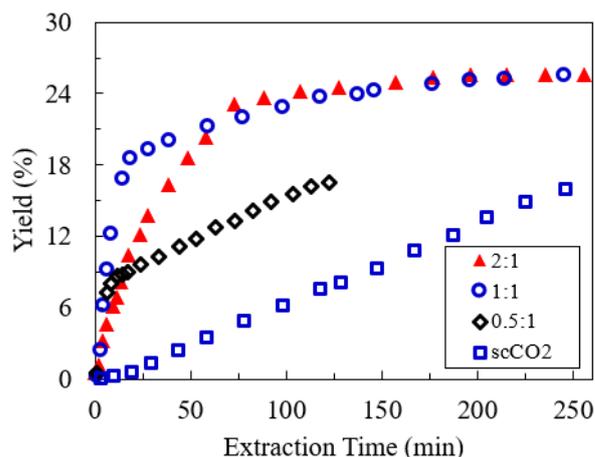


Fig. 5. Experimental overall extraction curves obtained by Juchen et al. (2019) [11] for spent coffee grounds oil extraction with $\text{scCO}_2 + \text{EtOH}$ at different ethanol to biomass ratios in comparison to SFE with scCO_2 and continuous PLE with ethanol, at 40 °C and 20 MPa.

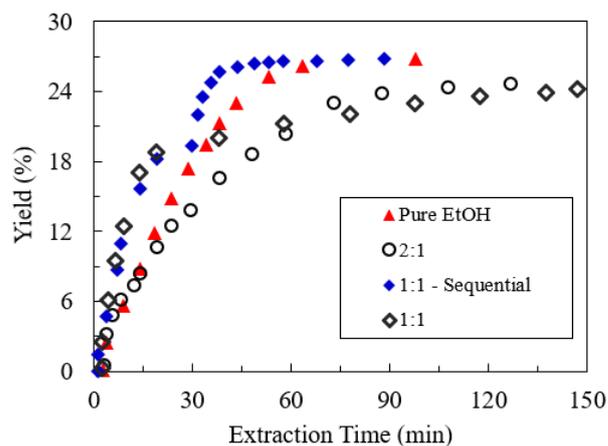


Fig. 6. Experimental overall extraction curves obtained by Juchen et al. (2019) [11] for rice bran oil extraction with $\text{scCO}_2 + \text{EtOH}$ at an ethanol to biomass ratio 1:1 and 2:1 in comparison to continuous PLE with ethanol, at 40 °C and 20 MPa. Comparison of one step with sequential extraction processes.

Figure 5 exhibits that the pure scCO_2 extraction was technically viable for lipid extraction from rice bran due to its higher availability in comparison to lipids from the spent coffee grounds. Also, the addition of ethanol as co-solvent increased the extraction rate. By contrast, Figure 6 demonstrates that PLE and sequential extraction provided similar results. However, the first spent 21.09 g EtOH/g biomass and the second spent only 2.12 g EtOH/g biomass.

Some Thermodynamics Aspects

Since the thermodynamic behavior of the solvent mixture plays a vital role in both SFE and CXL, it is convenient to analyze the thermodynamic diagrams in terms of pressure-composition and density-composition at the operational conditions of semi-batch CXL extraction processes. However, the thermodynamic analysis essentially lays on the reliability of thermodynamic the models. Cubic equations of state are simple and computationally efficient thermodynamic models that have been used to predict the phase behavior of different systems involving CO₂ and short chain alcohols and esters [18–20], although it is well known that these models do not properly represent the volumetric properties of the liquid phase (for mixtures or pure compounds). On the other hand, the Cubic Plus Association (CPA) equation of state [21], which keeps the physical parts of a cubic equation of state and adds the association term of Statistical Association Fluid Theory (SAFT) as proposed by Chapman et al. [22] providing a better tool for predicting both phase equilibria and density of associating mixtures without demanding high computational cost when compared to original SAFT-EoS. Thus, in this work the Peng-Robinson equation of state (PR-EoS) was compared to CPA for predicting both phase behavior and density of CO₂ + ethanol mixtures (the system of interest for the study cases presented here).

Figure 7 depicts pressure-composition diagrams for CO₂ + ethanol at two different temperatures. Figure 8 and Figure 9 show density-composition diagrams for the same mixture. For all these analyses, values predicted by PR-EoS and CPA-EoS were compared to the experimental data.

All diagrams calculated via PR-EoS considered the binary interaction parameters adjusted and presented by Araújo et al. [23]. The pure components parameters of CPA EoS used in this work were: ethanol ($a_0 = 7.3110 \text{ bar}\cdot\text{L}^2\cdot\text{mol}^{-2}$, $b_0 = 0.0479 \text{ L}\cdot\text{mol}^{-1}$, $c_0 = 0.9200$, with one positive and one negative association site: $\varepsilon^{AiBi} = 207.64 \text{ bar}\cdot\text{L}\cdot\text{mol}^{-1}$ and $\beta^{AiBi} = 0.0160$) and CO₂ ($a_0 = 3.5256 \text{ bar}\cdot\text{L}^2\cdot\text{mol}^{-2}$, $b_0 = 0.0271 \text{ L}\cdot\text{mol}^{-1}$, $c_0 = 0.7119$, considered with two negative sites). Thus, CO₂ was considered non-self-associating but it able to make a cross association with ethanol due to the hydrogen bonds.

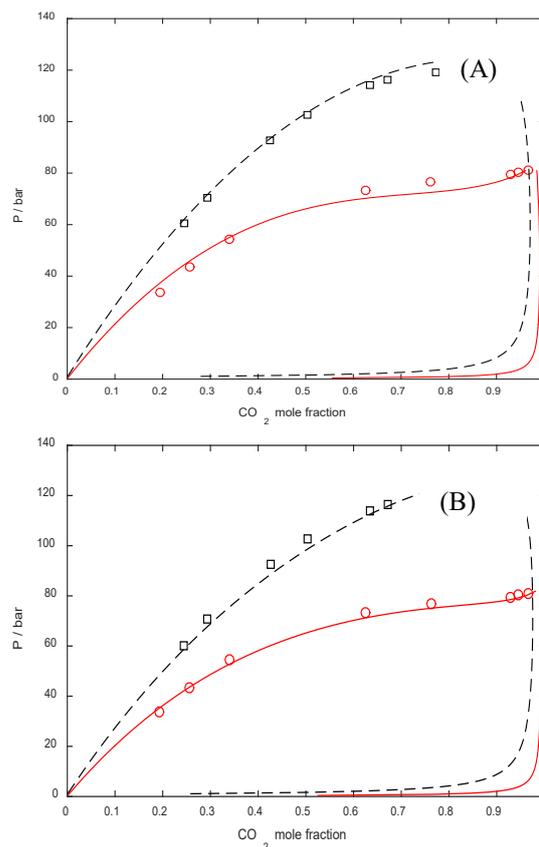


Fig. 7. Pressure-composition diagram for CO₂(1) + ethanol(2) at 313 K (red circle) and 343 K (black square). Comparison between **(A)** PR-EoS ($k_{12} = 0.065$, $l_{12} = -0.045$) and **(B)** CPA ($k_{12} = 0.035$, $l_{12} = -0.085$, cross-association parameters: $\varepsilon^{AiBj} = \varepsilon^{Ai}/2$ and $\beta^{AiBj} = \beta^{Ai}$, where Ai represents the association site of self-associating compound) predictions and experimental values [24].

Figures 8 and 9 present the evolution of the mixture density when the CO₂ fraction increases and make clear that, even though both evaluated EoS were equivalent to reproduce the phase equilibrium data for density predictions the CPA-EoS showed to be more suitable for the studied system, as expected. It is also possible to notice that, at all evaluated conditions, there is a region that the mixture becomes denser than the pure ethanol as the CO₂ fraction increases. This occurs owing to the capacity of the liquid of comporting the gas phase. At higher CO₂ fractions, however, the mixture density tends to the density of the pure CO₂.

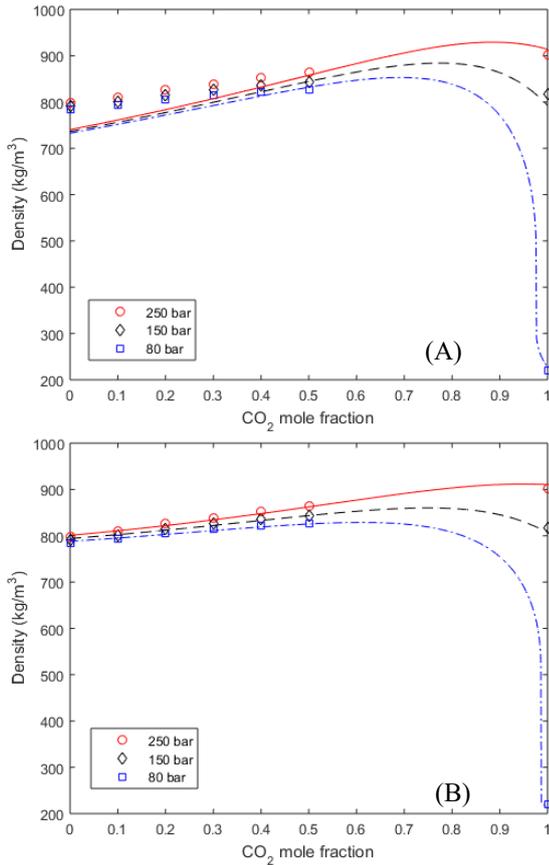


Fig. 8. Density-composition diagram for CO₂(1) + ethanol(2) at 308 K and different pressures. Comparison between (A) PR-EoS ($k_{12} = 0.065$, $l_{12} = -0.045$) and (B) CPA ($k_{12} = 0.035$, $l_{12} = -0.085$, cross-association parameters: $\varepsilon^{AiBj} = \varepsilon^{Ai}/2$ and $\beta^{AiBj} = \beta^{Ai}$, where Ai represents the association site of self-associating compound) predictions and experimental values (Ref1. [25]). Pure ethanol and CO₂ were obtained from (Ref. 3 [26,27]) and (Ref. 2 [28]), respectively.

Finally, in Figure 10, one can notice the extraction pathway going from the most concentrated in ethanol condition to the condition where there is only CO₂ (right side). At lower pressures, below 150 bar, may occur phase partition of the mixture, which is undesirable to extraction processes due to additional mass transfer resistance among phases and the reduced particle contact with one of the solvents since the vapor phase is high concentrated in CO₂. Also, the vapor phase density is much lesser dense than the liquid phase and presenting much lower solvent power when compared to the respective liquid phase in equilibrium. Therefore, the knowledge of phase envelopes of the mixtures supercritical CO₂ plus the organic solvent used for semi-batch extraction at high pressure conditions is an important issue and it must be considered for setting the operational conditions for this technique.

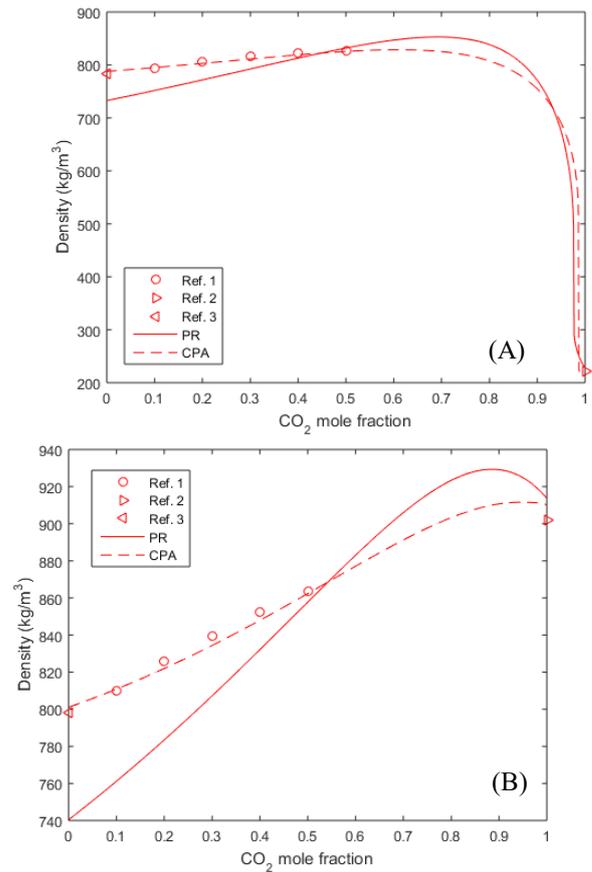


Fig. 9. Density-composition diagrams at 308 K and different pressures: 70 bar (A) and 250 bar (B) comparing both PR and CPA models. Using the following parameters: PR-EoS ($k_{12} = 0.065$, $l_{12} = -0.045$) and CPA ($k_{12} = 0.035$, $l_{12} = -0.085$, cross-association parameters: $\varepsilon^{AiBj} = \varepsilon^{Ai}/2$ and $\beta^{AiBj} = \beta^{Ai}$, where Ai represents the association site of self-associating compound) predictions and experimental values (Ref1. [25]). Pure ethanol and CO₂ were obtained from (Ref. 3 [26,27]) and (Ref. 2 [28]), respectively.

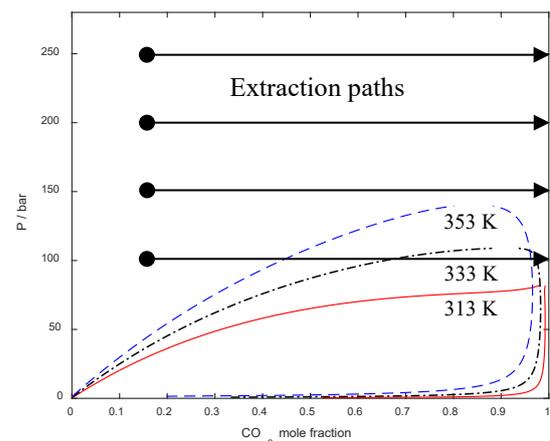


Fig. 10. Projection of extraction paths in a pressure-composition diagram for the CO₂ + ethanol system, at typical extraction conditions of temperature (313 to 353 K) and pressure (100 to 250 bar). Lines represent the phase envelopes predicted using CPA EoS.

CONCLUSION

This study highlighted and discussed some kinetic and thermodynamic aspects of results previously reported by the Research Group through a semi-batch GXL extraction strategy of rice bran and spent coffee grounds oil. Even though the matrices presented different structural characteristics, with the rice bran oil much more available than the spent coffee grounds oil, the semi-batch GXL extraction was shown as a promising extraction process, primarily when sequential extractions are performed. The thermodynamic behavior of the solvent mixture was debated at different extraction conditions, and some trends observed on the kinetic curves could be justified and predicted through this type of analysis. Additionally, it was demonstrated that CPA-EoS has a better prediction capacity for the density of the studied systems than the PR-EoS.

Acknowledgements: The authors thank the CNPq (305393/2016-2) and Fundação Araucária for providing financial support and scholarships to our graduate students and post-docs. This work was also financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brazil (CAPES) – Finance Code 001 and CAPES (Brazilian Agencies) for financial support and scholarships.

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