MEASUREMENT OF BURITI OIL (*Mauritia Flexuosa*, Mart.) SOLUBILITY IN SUPERCRITICAL CARBON DIOXIDE

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Abstract: In this work, the solubility of buriti oil in supercritical CO_2 has been determined experimentally by the dynamic method. Experiments have been carried at pressures of 15, 20, 25, and 30 MPa, temperatures of 313, 323 and 333 K and solvent flow rate of Q_{CO2} = 10.6 L/min, using a high pressure vessel of 1000 cm^3, and a stainless steel cylinder of 22 cm^3, assembled within the high pressure vessel. The solubility was determined by computing the slope of the straight line *accumulated mass of condensates x accumulated mass of solvent*. Experimental results show that solubility of buriti oil increases with pressure at fixed temperature, showing a maximum of 4.85 gOil/kgCO_2 at 25 MPa and 333 K, and increases with increasing temperature at 25 MPa, which is in agreement not only with experimental data reported in the literature for the solubility of vegetable oils in supercritical carbon dioxide under the investigated state condition, but also with the solubility of buriti oil in supercritical carbon dioxide measured using a equilibrium cell by the static method at 25 MPa and 323 K, showing a deviation of 11.8 %. The experimental results corroborate on the sense that this methodology is suitable for measuring the solubility of vegetable oils in supercritical carbon dioxide.

Keywords: Solubility, supercritical carbon dioxide, vegetable oils, buriti.

1. Introduction

The dried pulp of the fruit buriti (*Mauritia flexuosa*, Mart.), a native occurring palm in the Amazon region, contains between 20-30 % (wt.) of a yellow-orange oil with the highest content of carotenes (~ 3600 ppm) in vegetable oils reported in the literature (França *et all*., 1999), a natural substance of special interest in the food and pharmaceutical industries.

Several methods to recover and enrich carotenes from the palm oil have been studied and developed recently. Among these esterification, transesterification followed by selective adsorption of the carotenes in packed columns and desorption by using organic solvents (Choo *et all*., 1991), esterification followed by distillation under high vacuum (Ooi *et all*., 1991), and adsorption in stirred tanks followed by supercritical desorption in packed columns using carbon dioxide as solvent (Raiol *et all*., 2000) are included.

Of special importance in fractionation and enriching of fat-soluble substances (e.g: carotenes, tocopherols, etc.) present in vegetable oils using supercritical fluids are phase equilibrium data, particularly in the gaseous phase known as solubility. Equilibrium solubility can be determined by the static or dynamic method (Sosová *et all*., 2001; Rodrigues *et all*.,

2005). Measurement of solubility by the dynamic method makes use of the extraction curve experiments. In this case, particularly for natural products including lipids, the dynamic solubility, also called operational solubility, is computed using the data of the integral extraction curve, and the solvent flow rate chosen must ensure that the solvent leaving the fixed bed must be saturated with the solute as reported in the literature (Sosová *et all*., 2001).

In the last two decades a number of works have been reported in the literature concerning vapor-liquid equilibrium data for binary systems triglycerides/supercritical CO_2, multi-compound systems vegetable oil/supercritical CO_2 as well the solubility of vegetable oils, pure and mixed triglycerides in supercritical CO_2. Among those, the solubility of pure triglycerides in supercritical CO_2 (Bamberger *et all*., 1988), the solubility of simple and mixed simple and mixed triacylglycerols (TAGs) in supercritical CO_2 (Nilsson and J.K. Hudson, 1993), vapor-liquid equilibrium of the binary system tricaprylin/supercritical CO_2 (C. Borch-Jensen and J. Mollerup, 1997), vapor-liquid equilibrium for the binary systems tristearin, tripalmitin, and triolein in Supercritical CO_2 (Weber *et all*., 1999), the solubility of oils from the seed of blackcurrant (*Ribes nigrum*) and grape-vine (*Vitis vinifera*) in supercritical CO_2 measured by the dynamic method (Sosová *et all*., 2001). vapor-liquid equilibrium of the pseudo-binary system buriti (*Mauritia flexuosa*) oil/supercritical CO_2 (Rüster *et all*., 2001), measured by the static method, vapor-liquid equilibrium of the pseudo-binary system Brazil nut (*Bertholletia excelsa*) oil/supercritical CO_2 (Rodrigues *et all*., 2001), S. G. Özkal, M. E. Yener and L. Bayındırlı, the solubility of apricot kernel oil in supercritical carbon dioxide (Özkal *et all*., 2005), the solubility of refined corn and sunflower seed oils, babassu (*Attalea funifera*) and ucuuba (*Virola sebifera*) fats in supercritical carbon dioxide (Soares *et all*., 2007) are included.

In this work, the solubility of buriti oil in supercritical CO_2 has been determined experimentally by the dynamic method using a new methodology, and the experimental results compared with data available for the solubility of buriti oil in supercritical carbon dioxide measured by the static method.

2. Materials and Methods

2.1 *Materials* - Carbon dioxide with 99.95 % [vol/vol] purity was supplied by White Martins S.A (Belém-Pará-Brazil). The oil was obtained by exhaustive extraction of buriti pulp, dried for 24 hours at 333 K in order to remove water, using supercritical carbon dioxide as solvent using a SFE unit described elsewhere (França *et all*., 1999).

2.2 *Experimental Apparatus* – A schematic diagram of the high pressure apparatus used in this work is depicted in Figure 1. The unit consists of high pressure vessel of 1000 cm^3, adapted to be used as an equilibrium cell, a cylinder of 22 cm^3, a membrane compressor, which raises the pressure from 3 to 40 MPa, a carbon dioxide reservoir, a sampling system, a gas meter, and a control unit that displays the system temperature and pressure. The complete description of the high pressure unit can be found elsewhere (França *et all*., 1999).

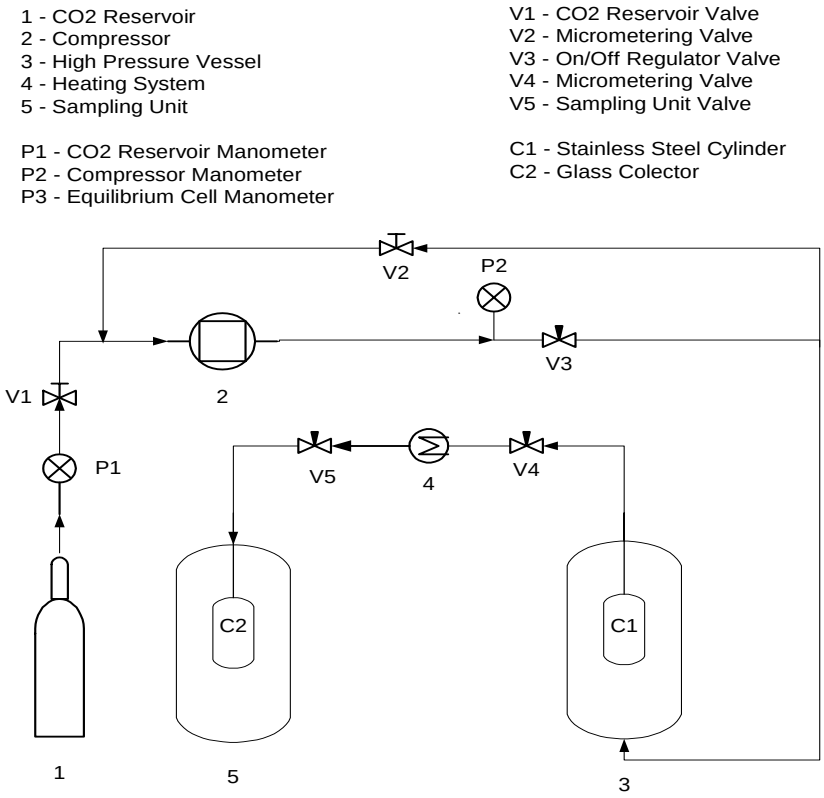
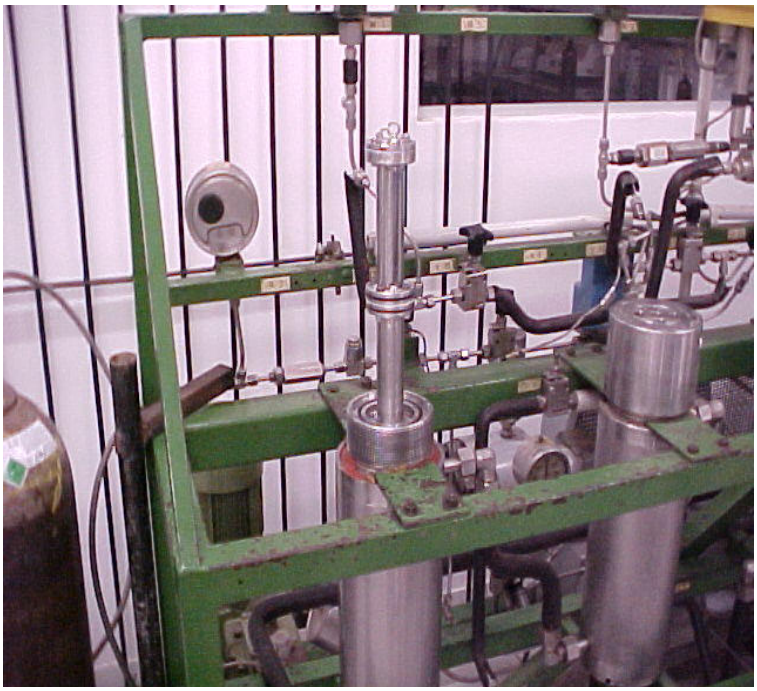


Figure 1: Experimental apparatus used to measure the solubility of buriti oil by the dynamic method.

2.3 *Experimental Procedure* – All the equilibrium experiments were carried out using 20 grams of buriti oil. The oil was placed inside a stainless steel cylinder of 22 cm³ depicted in Photography 1. The cylinder has 02 (two) flanges, whereas 03 (three) slices of filter paper between 02 (two) external stainless steel screens of mesh 200# were placed in order to avoid the oil to spread outside the cylinder. Afterwards it was assembled within the high pressure vessel as depicted in Photography 2. The carbon dioxide was recycled in a closed loop for at least for 05 (five) hours, by closing valves V_4 and V_5, and opening valves V_1, V_2, and V_3 (micrometer/recycle valve), in order to maintain the system pressure constant as well as to saturate carbon dioxide until equilibrium was reached. Afterwards, valves V_4 and V_5 were open and the flow rate was set low (10 g_{CO2}/min). The low flow rate makes it possible the fresh carbon dioxide that enters the high pressure vessel to achieve equilibrium within the sampling intervals of time. Samples from the gaseous phase were taken every 05 (five) minutes by opening valves V_4 and V_5. This experimental arrangement functions identical to a buffer autoclave on a static equilibrium cells. The condensed phase was weighted by gravimetric method. The CO_2 released into the atmosphere was measured using a gas flow meter. Since, ambient pressure and temperature are measured at gas meter inlet, the density of carbon dioxide cam be computed using the bender equation of state. The solubility is computed by plotting the cumulative mass of oil as a function of time or cumulative mass of

carbon dioxide and taking the slope of the straight line using the equation below. The slope represents the amount of oil dissolved in the gas phase which is defined as gaseous solubility.

Photography 1: Stainless steel cylinder of 22 cm².



Photography 2: Assemble used to measure the solubility by the dynamic method.

3. Results and Discussion

The experimental results obtained in this work are shown in Figures 2 and 3 and the data compared with experiments for the solubility of buriti oil in supercritical carbon dioxide measured in an equilibrium cell by the static method at 25 MPa and 323 K in Table 1. In all the experiments, the accumulated mass of buriti oil versus time shows a linear behavior, that is, the slope is constant, which is a measure for the solubility of burit oil in the gaseous phase.

3.1 Influence of Pressure – The influence of system pressure on the solubility of buriti oil in supercritical carbon dioxide is shown in Figure 1. The results show that solubility increases as system pressure increases, until the pressure crossover, with a maximum at 25 MPa, showing a retrograde behavior. This is in agreement with experimental data concerning the solubility of vegetable oils in supercritical CO_2 (França *et all*., 1999).

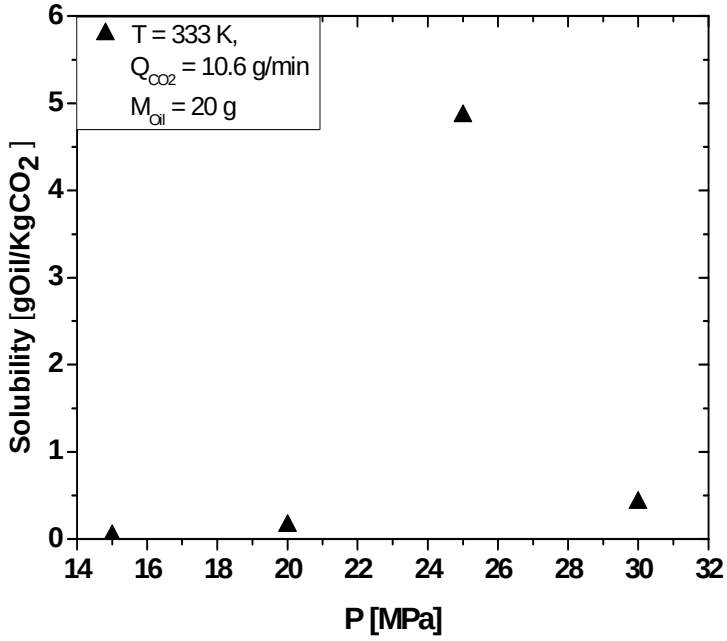


Figure 2: Solubility behavior of buriti oil in supercritical CO_2 as a function of pressure.

3.1 Influence of Temperature – The influence of temperature on the solubility of buriti oil in supercritical carbon dioxide is shown in Figure 3. The results show that solubility increases as temperature increases. In general, the solubility of vegetable oils in supercritical carbon dioxide increases with increasing solvent power, which is a function of solvent density, the density depends on the state conditions (T, P), on the other hand, temperature has a strong effect on vapor pressure, thus those effects compete, showing in this case that the temperature effect overcame the density.

Table 1 shows the computed values for the solubility of buriti oil in supercritical carbon dioxide with the respective R-Square, a measure for the quality of experimental data, showing a minimum of 0.88559 at 30 MPa. This is due to the fact that the solubility of vegetable oils in

supercritical carbon dioxide at pressures above the crossover pressure has the order of magnitude 10^{-1} g_{Oil}/kg_{CO2}, thus causing uncertainly on the experimental measurements. Table 1 makes also a comparison between experimental data obtained in this work with data available for the solubility of buriti oil in supercritical carbon dioxide measured by the static method at 25 MPa and 323 K (Rüster *et all*., 2001), which is in good agreement.

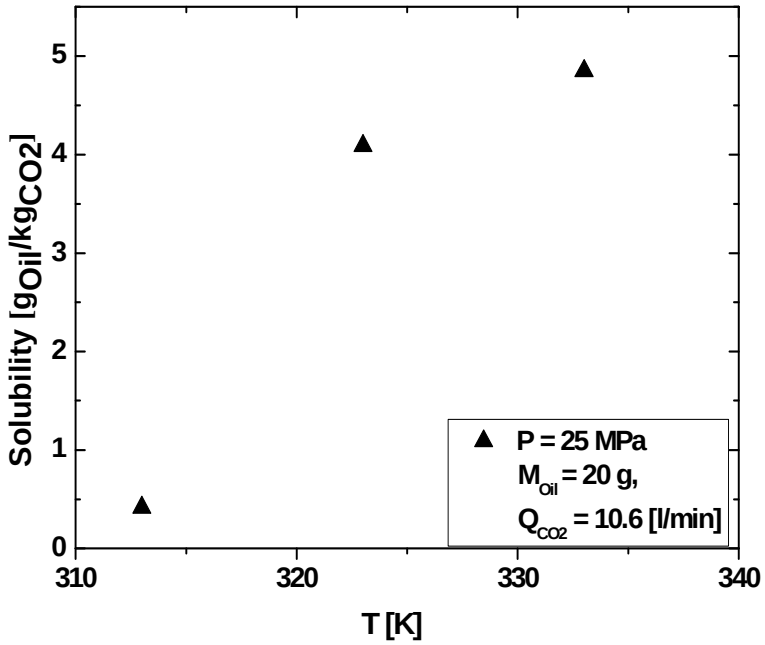


Figure 3: Solubility behavior of buriti oil in supercritical CO_2 as a function of temperature.

Table 1: Experimental data computed for the solubility of buriti oil in supercritical carbon dioxide.

References	T [K]	P [MPa]	Solubility [g_{Oil}/kg_{Co2}]	R-Square [-]
This work	333	15	$3.3434*10^{-2}$	0.98629
	333	20	$1.5234*10^{-1}$	0.91204
	333	25	4.85	0.99981
	333	30	$4.1520*10^{-1}$	0.88559
	313	25	$4.1548*10^{-1}$	0.91743
	323	25	4.09	0.98308
(Rüster *et all*., 2001)	323	25	4.6400	

4. Conclusions

The experimental results show that solubility of buriti oil in supercritical CO_2 increases as system pressure increases, until the pressure crossover, showing a retrograde behavior at

333K, and increases with increasing temperature at 25MPa. The dynamic method proposed in this work is suitable for measuring the solubility of vegetable oils in supercritical CO_2.

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