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OPTIMIZATION OF THE PROCESS OF CONCENTRATION OF VITAMIN E FROM DDSO USING SUPERCRITICAL CO_2

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Abstract - The objective of this work was the scientific development of concentration of vitamin E from deodorizer distillate of soybean oil (DDSO) using supercritical CO_2. Vitamins and sterols rare produced synthetically, but recently the interest in their extraction from natural sources has increased. Therefore, the motivation behind this work was to concentrate the tocopherols from deodorizer distillate of soybean oil, thereby increasing the value of this by-product, rich in fatty acids, sterols, tocopherols and squalene. The experimental step and the simulation of the process were done in a semi-batch mode using supercritical carbon dioxide. The operational conditions studied were temperatures of 40, 60 and 80ºC and pressures from 90 to 350 bar. The best results for concentration factor and efficiency and pressures were achieved in a continuous process where the operational variables were optimized.
Keywords: Soybean oil; Tocopherol; Supercritical CO_2; Process simulation.

INTRODUCTION

The main goal of this work was the scientific development of a process to concentrate the vitamin E from deodorizer distillate of soybean oil (DDSO) using supercritical carbon dioxide. Interest in this study was due to the large quantity of this by-product of which soybean production in Brazil, was 154 million of tons in 2002 (Hanna, 1999), and because this by-product is rich in valuable compounds, like fatty acids, tocopherols (vitamin E), sterols and squalene.

Vitamin E is a mixture of four isomers, α, β, γ and δ-tocopherol, and it is most frequently added to foods as an antioxidant. It is found in DDSO at percentages from 10 to 13%. Squalene, the principal hydrocarbon in DDSO, from 4 to 6%, is responsible for the biosynthesis of cholesterol. Fatty acids make up 70 to 80% of DDSO with linoleic acid representing the largest amount (40-50%) of this percentage. The process of refining soybean oil is composed of many steps, which prevents the use of the fatty acids in food, pharmaceutical and cosmetic industries. Sterols are another important class of valuable compounds that have many uses in the pharmaceutical industry and are currently imported in large quantities due to their capacity for cholesterol absorption. The most important are stigmasterol, ergosterol and sitosterol.

Because of the complexity of the raw material due to its many components, this work includes some steps like the experimental process to

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concentrate the vitamin E from DDSO, achievement of phase equilibrium between the components and the supercritical CO_2, the thermodynamic modeling of the phase equilibrium, the simulation of the process and the technical and economic analysis of the process.

Lee et al. and Brunner et al. (1991) studied respectively the solubility of DDSO in supercritical carbon dioxide and the concentration factors of the components related to tocopherols using a synthetic DDSO composed of the main components.

This work studies the experimental behavior of DDSO with CO_2 and the thermodynamic modeling and the simulation of the supercritical concentration process.

MATERIALS AND METHODS

Materials

The deodorizer distillate of soybean oil was obtained from CEVAL S.A. It was analyzed through gas chromatography coupled with mass spectroscopy and was found to contain 79% fatty acids, 11% tocopherols, 6% squalene and 4% sterols and esters.

The liquid CO_2 with a minimum purity of 99.9% was provided by AGA S.A. (Rio de Janeiro/Brazil).

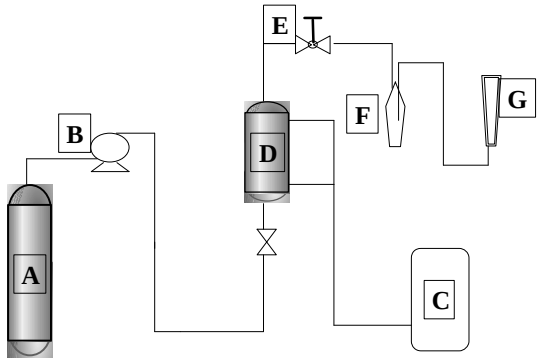
Chromatographic Conditions

The components were analyzed through high resolution gas chromatography (HRGC) coupled with mass spectroscopy (HRGC-MS). The components were identified using mass spectroscopy and compared with the standard specter and with the Wiley spectroscopy.

A gas chromatograph HP-5890 was utilized with an ionization detector (FID) and hydrogen as the gas (2 ml min^{-1}). The temperatures of the injector and detector were 270ºC and 300ºC, respectively. The mass spectroscopic analysis was done in HP5897A equipment, connected to an HP5880 gas chromatograph. The analysis was done in a column (L = 15 m, D_i = 0.25 mm and d_f = 0.25 μm).

Supercritical Extraction Process

The tocopherol was concentrate in a stainless steel extractor with a volume of 42 ml. The sampling was done using a micrometric valve (Whitey, model SS-31RS4) that despressurizes the system. A high pressure pump (Thermo Separation Products, Constametric 3200 P/F) was responsible for feeding in the solvent at a flow rate of 9.31ml/min. The flowsheet of the experimental apparatus used in the laboratory is shown in Figure 1.



A. cylinder of CO_2,
B. high pressure pump,
C. temperature-controlled water bath,
D. extractor,
E. micrometric valve,
F. raffinate,
G. gas meter.

Figure 1: Flowsheet of the experimental apparatus, where

a) Experimental Procedure

The extractor was fed with 23 g of DDSO and extraction did not occur until the temperature and pressure of the extractor had become stabilized. The high-pressure pump was responsible for the constant flow of solvent reaching the desired operational pressure. After the steady-state was reached, extractions were done at a time interval of 2 to 3 hours.

The operational conditions studied were temperatures of 40, 60 and 80ºC and pressures of 90,

100, 150 and 200 bar.

THERMODYNAMIC MODELING

A thermodynamic model including the cubic equation of state of Peng-Robinson (1976) with the mixing rules of van der Waals (quadratic) was used to correlate the phase equilibrium of the mainly binary systems CO_2-α-tocopherol, CO_2-linoleic acid and CO_2-squalene.

The critical properties of the components were predicted as suggested by Melo et al. (1996).

Table 1 shows the interaction parameters for the three binary systems. These parameters were estimated using experimental data for temperatures from 40 to 80ºC and represent the experimental conditions of temperature and pressure used in the simulation of the extraction process.

SIMULATION OF THE SEMI-CONTINUOUS PROCESS

Supercritical extraction in a semi-continuous mode was first studied and calculated by Melo (1997) using a different raw material. Separation is possible due to the difference in affinity between the mainly components and the supercritical solvent. Figure 2 shows the flowsheet of the equipment, making an analogy with batch distillation with one stage of equilibrium.

Two separation procedures were studied independently in order to show how the separation factor changes according to tocopherol content. Because of this, two ternary systems, were studied, CO_2-tocopherol-linoleic acid and CO_2-tocopherol-squalene.

The operational conditions used are those applied in the experimental section and higher pressures up to 350 bar were also used to predict the phase equilibrium behavior.

Table 1: Binary parameters of the systems studied

Systems	Kij	Lij
CO_2-tocopherol	0.10717	0.12360
CO_2-linoleic acid	0.07083	0.08850
CO_2-squalene	0.10972	0.11846

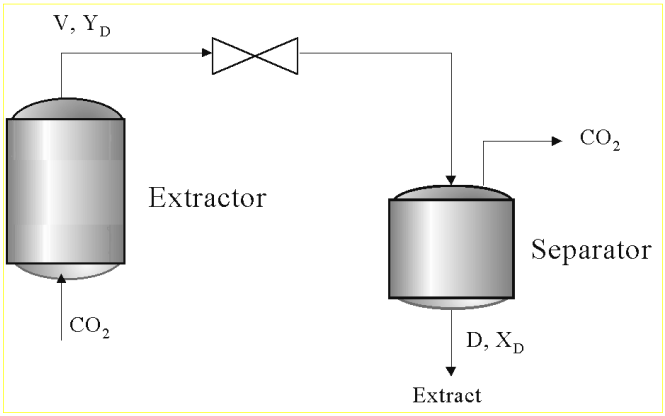


Figure 2: Flowsheet of the semi-continuous supercritical extraction process, where V is the vapor flow rate, D is the extract flow rate and x and y are the liquid and vapor mass fractions of the components

SIMULATION OF THE CONTINUOUS PROCESS

A continuous process to concentrate the vitamin E was simulated using the general flowsheet suggested by Sievers (1996). The results obtained in the simulation will be useful in proposing an industrial supercritical extraction process. Figure 3 shows a general flowsheet of the supercritical fluid extraction process in a continuous mode.

The procedure for this process is based on the feding of raw material into the extractor (E). The raw material contains the main components of the original deodorizer distillate of soybean oil. The supercritical fluid, carbon dioxide, initially passes through a compressor (C1) and a heat exchanger (W1) before entering the extractor to attain the same operational conditions. At this moment, the solvent and the raw material are come into contact and two phases are formed. The poor phase in solute is

discharged as a bottom product of the extractor and the rich phase in solute with the supercritical fluid passes through the valve (C2) and the heat exchanger (W2) to attain the operational conditions of the separator (S). This equipment operates at a lower pressure to reduce the affinity between the supercritical fluid and the solute. This behavior allows separation of the product as the bottom stream of the separator. The solvent flows out in the top stream of the separator to the compressor (C3) and heat exchanger (W4) to recover the initial operational conditions necessary for extraction.

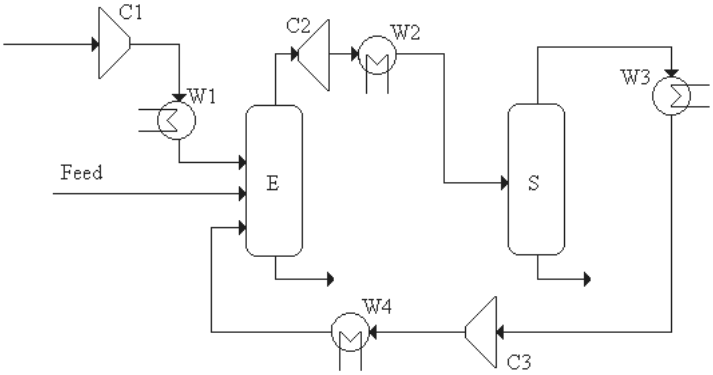


Figure 3: Process proposed by Sievers (1996) for the extraction of natural products making the recycle of the solvent (CO_2)

RESULTS AND DISCUSSION

Although many different operational conditions were studied, only the most significant results obtained in the experimental and simulation steps are discussed.

The experimental extraction curves for pressure of 150 bar and a temperature of 40ºC are presented. The results of the simulations are presented for all the operational conditions studied.

The simulation results were compared with the experimental ones for efficiency of the process (E), defined as the ratio of the extracted to the initial mass, and to the concentration factor (FC), defined as the ratio of the distribution coefficients for each component.

Figure 4 shows the extraction curve as a function of operation time at 150 bar for all the temperatures studied. In this case, the highest efficiency occurs at 40ºC. At 60 and 80ºC, the amount extracted was lower than at 40ºC, as also observed by Brunner et al. (1991).

Table 2 shows the experimental efficiencies of the process for all the temperatures studied at 150 bar. This table illustrates that the efficiencies decrease with the increase in temperature. This is due to the reduction in density of the solvent that decreases the solvent power of the carbon dioxide.

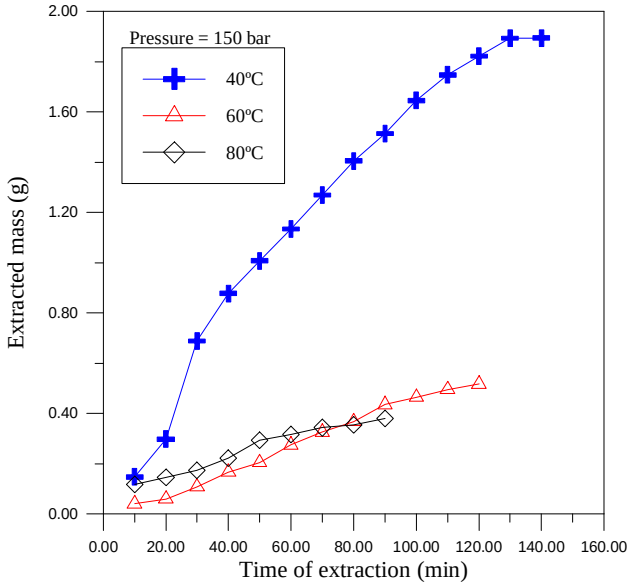


Figure 4: Extracted mass as a function of operation time at 150 bar

Table 2: Experimental efficiencies at 150 bar for all the temperatures studied

T (ºC)	Efficiency (%)
40	69.74
60	12.80
80	10.13

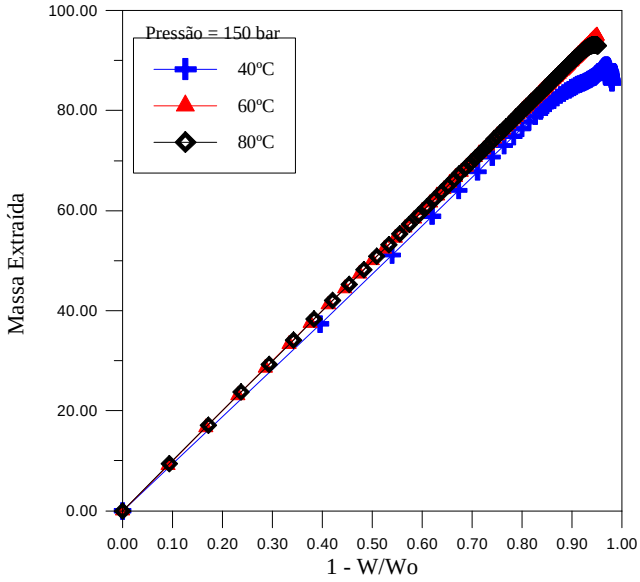


Figure 5: Extracted mass as a function of residual mass inside the extractor for the CO_2-tocopherol-linoleic acid ternary system for the three temperatures at 150 bar.

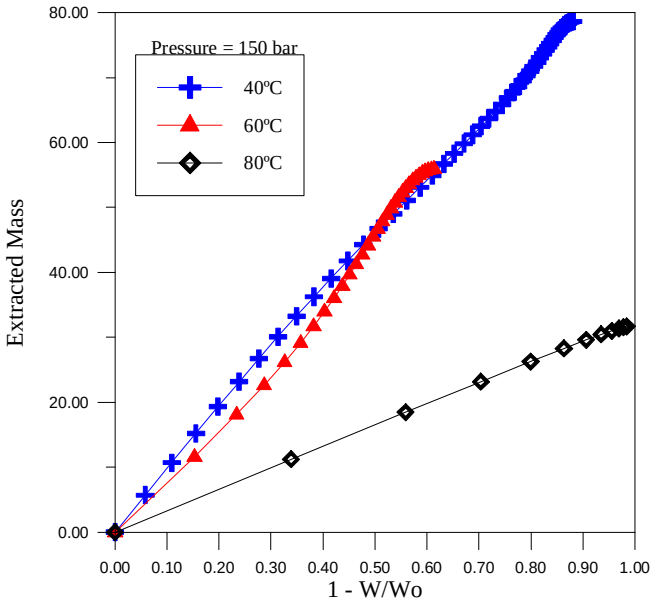


Figure 6: Extracted mass in function of the residual mass inside the extractor for the CO_2-tocopherol-squalene ternary system for the three temperatures at 150 bar

The semi-continuous process was simulated under operational conditions that were the same as those of the experimental step and using higher pressures up to 350 bar to explore the behavior of the mixture.

Figures 5 and 6, as Figure 4, show the extracted mass for the three temperatures studied at 150 bar, respectively for the tocopherol-linoleic acid and tocopherol-squalene separations. The same behavior was observed when analyzing the experimental results in relation to efficiency with almost no effect for the separation of tocopherol and linoleic acid.

Besides the Figures 5 and 6, the results of the simulations are presented for all the temperatures varying the pressure from 90 to 350 bar for the two systems studied, tocopherol-linoleic acid and tocopherol-squalene. Figures 7, 8 and 9 show results of the simulations of separation of tocopherol and squalene and Figures 10, 11 and 12, of tocopherol and linoleic acid, where W is the liquid quantity inside the extractor, Wo is the liquid quantity at the beginning of extraction and 1-W/Wo is the residual mass inside the extractor at any time during extraction.

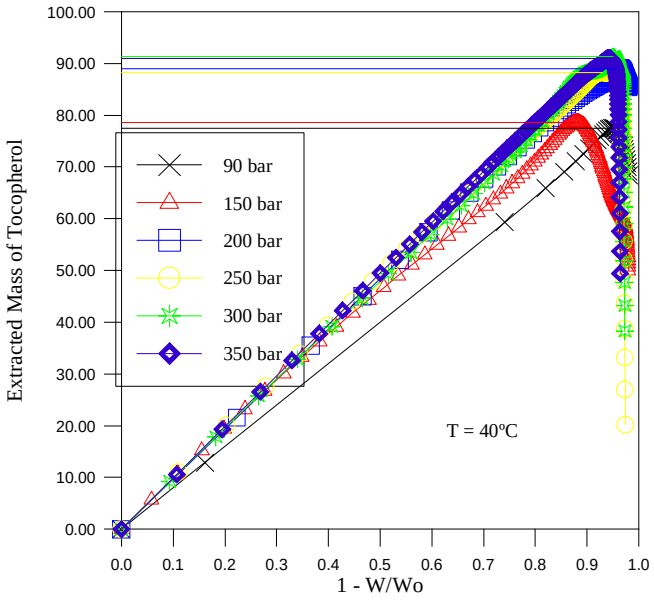


Figure 7: Variation of the mass of tocopherol extracted with the fraction of DDSO extracted (1-W/Wo) at 40°C and pressures of 90, 150, 200, 250, 300 and 350 bar for the CO_2-tocopherol-squalene system

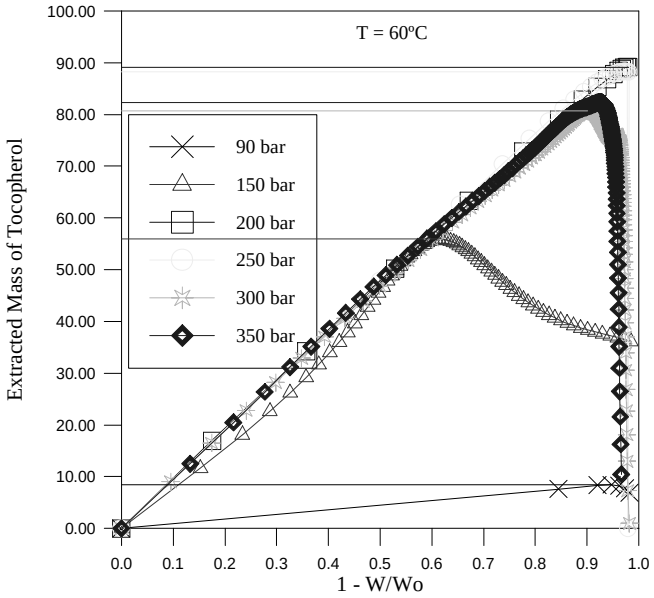


Figure 8: Variation of the mass of tocopherol extracted with the fraction of DDSO extracted (1-W/Wo) at 60°C and pressures of 90, 150, 200, 250, 300 and 350 bar for the CO_2-tocopherol-squalene system

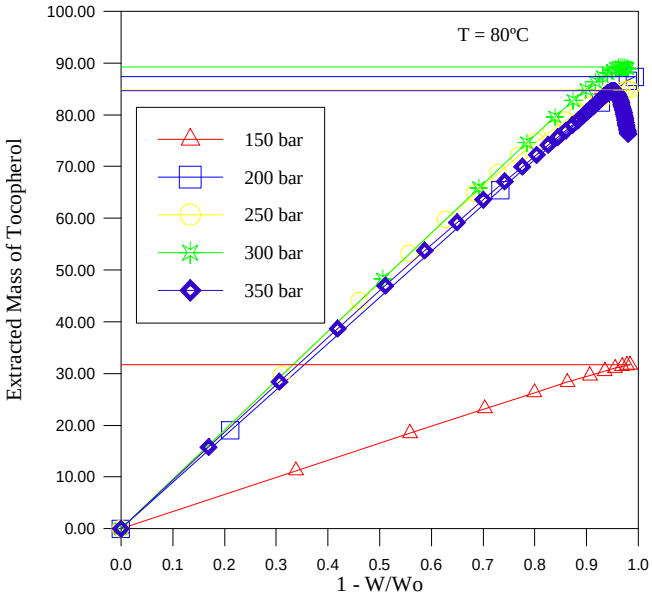


Figure 9: Variation of the mass of tocopherol extracted with the fraction of DDSO extracted (1-W/Wo) at 80^{0}C and pressures of 150, 200, 250, 300 and 350 bar for the CO_2-tocopherol-squalene system.

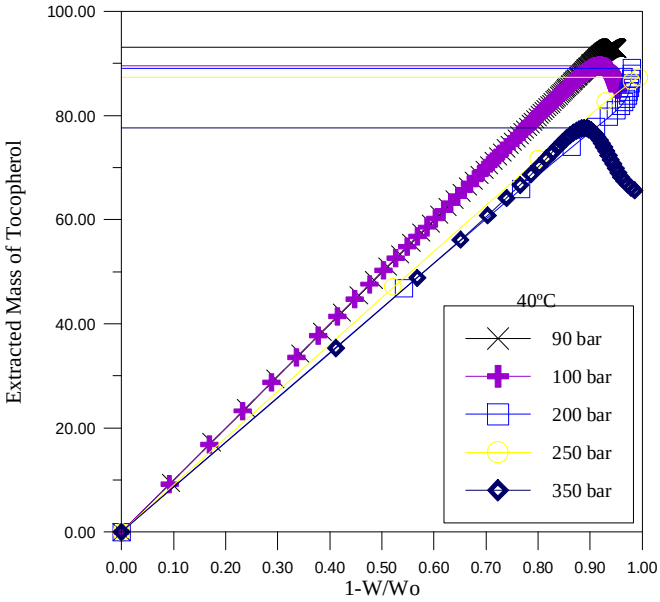


Figure 10: Variation of the mass of tocopherol extracted with the fraction of DDSO extracted (1-W/Wo) at 40^{0}C and pressures of 90, 100, 200, 250 and 350 bar for the CO_2-tocopherol-linoleic acid system

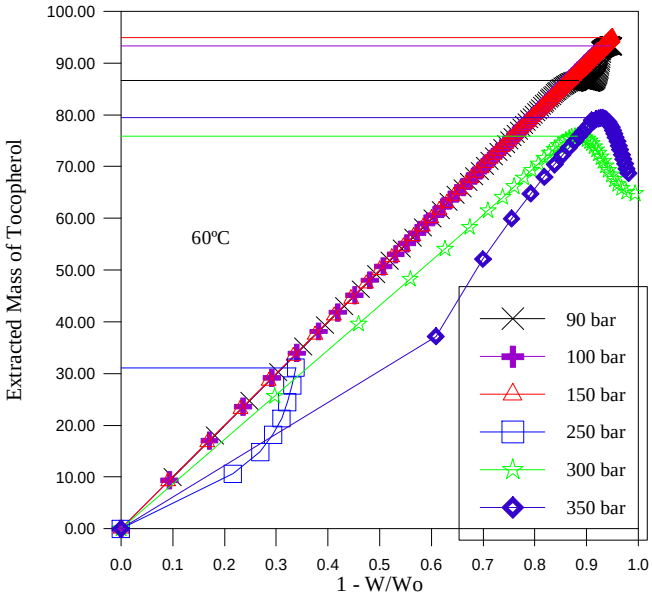


Figure 11: Variation of the mass of tocopherol extracted with the fraction of DDSO extracted (1-W/Wo) at 60^{0}C and pressures of 90, 150, 200, 250, 300 and 350 bar for the CO_2-tocopherol-linoleic acid system

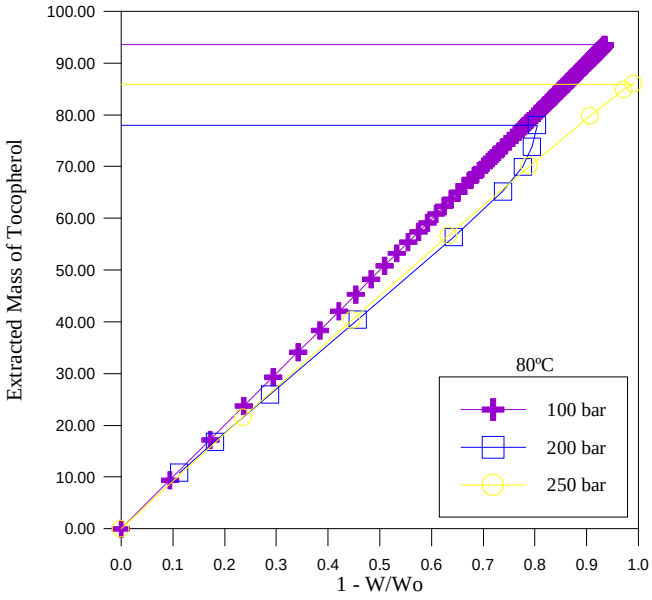


Figure 12: Variation of the mass of tocopherol extracted with the fraction of DDSO extracted (1-W/Wo) at 80^{0}C and pressures of 100, 200 and 250 bar for the CO_2-tocopherol-linoleic acid system

The simulation results show a behavior qualitatively similar to that of the experimental ones presented in Figures 5 and 6. Table 3 shows the efficiency and concentration factors for the two systems studied.

The concentration factors obtained for the separation of tocopherol and linoleic acid are higher than the factors obtained for the separation of tocopherol and squalene. This means that the separation of the vitamin E and fatty acids is easier than the other separation. This occurs because the volatility of tocopherol is similar to that of squalene making it difficult to separate them.

The concentration factors for the separation of linoleic acid and squalene decrease with the increase in pressure. The best results obtained in the semi-continuous process simulation were applied to the continuous process with the objective to simulate an industrial plant separating vitamin E from the other compounds of raw material. The success of the simulation of the continuous process stimulates interest in an economic analysis of the viability of an industrial supercritical process. In the continuous process, a ternary mixture with normalized compositions was studied. Table 4 shows the efficiencies and concentration factors obtained in the continuous process simulation. The simulation results indicate that the best operational conditions were at 40ºC and 150 bar, where the concentration factors show the same behavior and were higher for the separation of tocopherol and linoleic acid.

The objective of the work was achieved because the simulation and the experimental steps produced a product free of fatty acids at an efficiency of 40%.

Table 3: Comparison of the semi-continuous simulations

T(ºC) P(bar)	Tocopherol-Linoleic Acid		Tocopherol-Squalene	
40ºC	E (%)	FC	E (%)	FC
90	93.10	∞ *	77.52	1.76
100	89.58	60.95	86.04	1.01
150	89.01	7.08	78.65	4.68
200	89.13	2.81	89.07	7.90
250	87.34	1.03	88.27	19.51
300	85.77	1.05	91.28	35.37
350	77.59	2.24	91.03	55.44
60ºC				
90	92.74	∞ *	8.42	1.20
100	92.34	∞ *	43.29	2.16
150	94.99	∞ *	55.89	7.68
200	84.13	3.44	89.17	1.44
250	31.09	16.17	88.27	1.70
300	75.94	2.11	80.75	5.63
350	79.34	1.95	82.38	12.23
80ºC				
90	94.22	∞ *	6.46	1.12
100	93.55	∞ *	47.59	1.09
150	93.17	8.32	31.69	1.01
200	78.02	5.85	87.37	1.04
250	85.93	1.02	84.83	1.10
300	78.10	1.03	89.24	1.55
350	53.12	1.05	84.62	2.63

∞ means that the complete separation between tocopherol and linoleic acid occurs

Table 4: Efficiencies and concentration factors from the continuous process simulation

P (bar)	Efficiency (%)	Tocopherol-Linoleic acid	Tocopherol-Squalene
40ºC			
90	48.23	10.4241	0.7020
150	34.59	16.7415	0.5730
60ºC			
90	35.39	1.2227	0.5001
150	46.44	3.6100	1.0206
80ºC			
90	36.28	1.0309	0.5000
150	49.70	1.3350	1.0278

CONCLUSIONS

In this work, the concentration of vitamin E from DDSO using supercritical carbon dioxide as solvent was studied. The simulation and the experimental separation of tocopherols from squalene and linoleic acid were done by a semi-continuous and a continuous process. The experimental and simulation steps were studied and compared under the same operational conditions, temperatures of 40, 60 and 80ºC and pressures from 90 to 350 bar.

The experimental results were presented for 150 bar, where the best efficiency was at 40ºC. The simulation results represent well the experimental results, although in the simulation the raw material was a mixture of its mainly components, tocopherol, squalene and linoleic acid. They showed that the efficiency and concentration factor decrease with the increase in temperature. This behavior was characteristic at higher temperatures and pressures because the solubility of the tocopherols increased and they were extracted together with the fatty acids and the squalene. The results showed a better separation of tocopherols and fatty acids than of tocopherols and squalene.

The simulation of the ternary systems in a semi-continuous mode indicated a good representation of the behavior of the CO_2 – tocopherol - linoleic acid - squalene quaternary system. The results were promising for implementation of industrial supercritical extraction because of the high level of vitamin E (tocopherols) without fatty acids. Even though squalene was still present, no restrictions were mentioned in the literature on that component in the sale of tocopherol.

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