Quality and Stability of Corn Germ Oil Obtained by Supercritical Fluid Extraction

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INTRODUCTION

Traditionally, the extraction of corn germ oil has been done by physical and chemical methods. In these conventional methods, the oil is first removed from the wet milled germ using a conditioning (heating) process, followed by mechanical expelling (prepress) ending up with hexane extraction. Also extrusion has been employed to prepare the germ for solvent extraction, leading a crude corn oil of high quality and high yield [1]. After oil extraction, the bagasse obtained as raffinate is normally used for animal nutrition.

Supercritical carbon dioxide (SC-CO_2) has been used as solvent to remove lipids and obtain defatted corn germ flour with a low level of peroxidase activity and high quality and stability during storage [2]. The functional properties of corn germ proteins isolated by alkaline extraction from meals defatted using a supercritical mixture of carbon dioxide and ethyl alcohol have been also investigated [3]. However, the optimization of the supercritical extraction process has been scarcely studied [4].

The aim of this work is to obtain corn germ oil and defatted corn germ flour using SC-CO_2 as solvent and study the influence of the main extraction parameters (pressure, temperature and solvent flow rate) on both oil extraction rate and tocopherols content in oil. Furthermore, supercritical fluid extraction followed by a fractionation in two separators has been explored in order to improve the quality of the corn oil.

MATERIALS AND METHODS

1. Raw material

Corn germ containing 33-40 % oil, 4-6 % moisture and 54-63 % proteins has been used as raw material.

2. SFE of corn germ oil extraction with SC-CO_2

The equipment used in corn oil extraction with SC-CO_2 is a homemade semi-pilot plant (extractor volume 2 L) designed and built to operate at a maximum specifications of T = 373 K, P = 65 MPa and solvent flow rate, F = 20 kg / h. The main features of this plant have been already described in the literature [5], although now it includes some modifications according to our requirements. The current P&I diagram is presented in Figure 1.

In a SFE experiment, approximately 350 g of corn germ, previously milled to a particle size between 0.5 and 1 mm, was mixed with 1400 g of raschig rings and placed into the extractor that was later pressurized up to the extraction pressure, *P*, with carbon dioxide (Carburos Metálicos, liquid $CO_2 \geq 99.9$ %). Then, the solvent was continuously circulated at the desired extraction temperature, *T*, and pressure, *p*, with a certain solvent flow rate, *F*, and during a specific time, *t*.

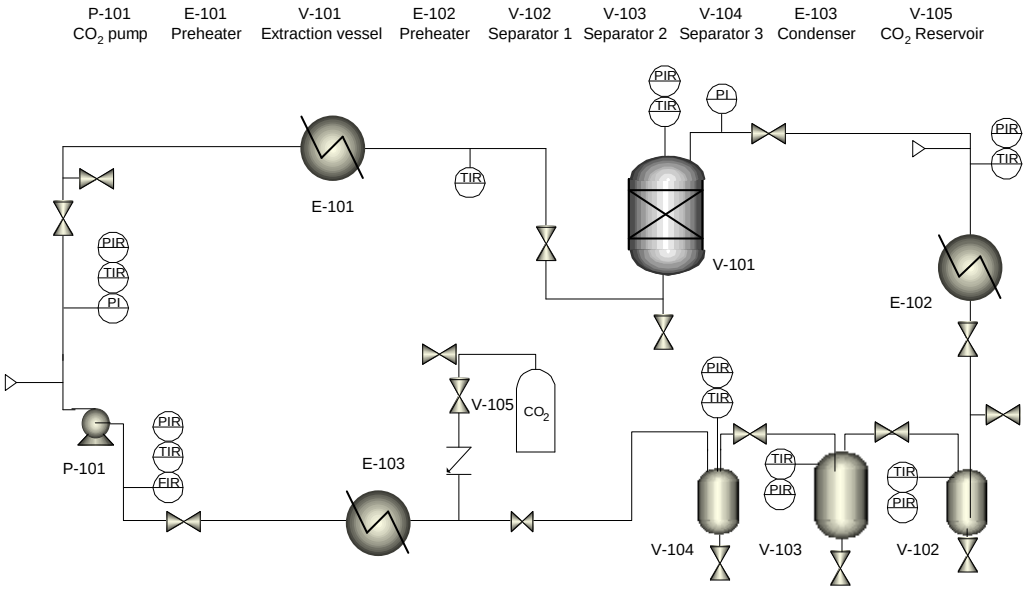

Figure 1. Flow-sheet of the SFE pilot plant

A total of ten experiments were carried out, which extraction conditions are reported in

Table 1. Runs 1-7 were performed without fractionation and the whole oil was recovered in a separator which was maintained at a pressure of 40 bar and a temperature lower than 40 ºC. Runs 8-10 were carried out with a subsequent fractionation in two separators installed in series, the first one was maintained at 100 bar and 40 ºC, in order to recover the less soluble compounds (triacylglycerides and tocopherols), and the second one maintained at a pressure of 40 bar and a temperature lower than 40 ºC, in order to recover the more soluble compounds (water and free fatty acids).

In all the experiments, the solvent was continuously recycled to the extractor after removing the solute in the last separator.

Table 1 Experimental conditions carried out in the SFE of corn germ oil with SC-CO_2

Run	p (bar)	T (ºC)	Solvent flow rate, F (kg CO_2/h)	Fractionation
R1	450 ± 31	40 ± 2	8 ± 2	No
R2	460 ± 30	63 ± 2	9 ± 2	No
R3	455 ± 49	77 ± 5	9 ± 3	No
R4	452 ± 22	86 ± 7	7 ± 2	No
R5	295 ± 19	81 ± 3	10 ± 3	No
R6	203 ± 8	39 ± 1	9 ± 1	No
R7	442 ± 33	78 ± 5	4 ± 2	No
R8	480 ± 53	86 ± 8	7 ± 3	Yes
R9	500 ± 48	35 ± 4	12 ± 2	Yes

R10	258 ± 28	85 ± 5	9 ± 3	Yes

3. Analytical methods

The quality of the oil fraction recovered in separator 1 in runs 8-10 was evaluated according to the rancimat test and tocopherols content.

The rancimat test was performed in a Metrohm rancimat 743 using a 1.5 g oil sample, a temperature of 110 ºC and an air flow rate of 9 L/h.

The tocopherols content was determined by HPLC-DAD (Agilent 1100) after Solid Phase Extraction (SPE). The silica cartridge (Waters®, 1000 mg / 6 mL) was conditioned with 5 mL of hexane before application of 1 mL of oil solution (0.1 mg/mL *n*-hexane). The examined compounds were obtained by elution using mixtures of *n*-hexane-diethyleter of different polarities: 5 mL of *n*-hexane, 5 mL of *n*-hexane:diethylether (98:2, v/v) and 50 mL of *n*-hexane:diethylether (99:1, v/v). The collected fraction was evaporated under reduced pressure at 45 ºC. The dry residue was dissolved in 1.5 mL *n*-hexane and 50 µL were injected in the HPLC. Tocopherols determination was carried out on a normal phase ACE 5 silica column (particle size 5 µm, 250 x 4.6 mm i.d.) maintained at 25 ºC. The mobile phase was *n*-hexane:2-propanol (99:1) and the flow rate was 1 mL/min. Detection was achieved with a UV-Vis detector at 296 nm. For quantification, external standard solutions of know concentrations of α-, β-, γ-, δ-tocopherol were used.

RESULTS AND DISCUSSION

Supercritical fluid extraction (SFE) of a solute from a solid raw material may involve three different stages: internal mass transfer, phase equilibrium and external mass transfer. Thus, oil extraction yield may be highly affected by operational parameters such as extraction pressure, temperature and solvent flow rate.

Figure 2 shows the influence of pressure extraction evaluated at two different temperatures. In both cases, the curves indicate that, at a constant temperature, the higher the pressure the higher the extraction rate, what may be attributed to the higher density of SC-CO_2 and therefore to its higher solvent power.

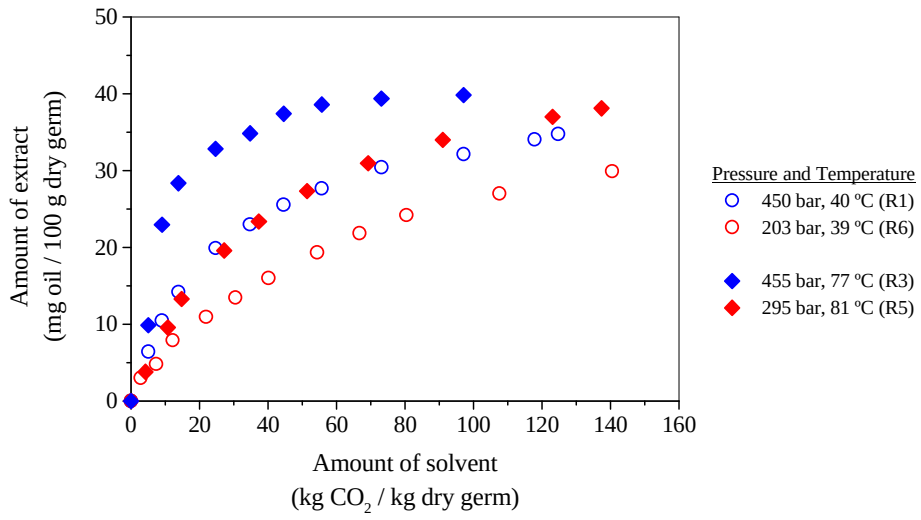

Figure 2. Influence of extraction pressure on corn germ oil extraction yield. Extraction curves obtained at a solvent flow rate of around 9 kg CO_2/h.

The influence of temperature at a constant pressure of 450 bar is shown in Figure 3. It is observed that the higher the temperature the higher the extraction rate, which may indicate that, at this pressure, the increase of oil vapor-pressure with temperature is more important than the depletion in SC-CO_2 density.

No significant effect on extraction rate has been observed when solvent flow rate was increased from 5 to 9 kg CO_2/h (see Figure 4), which may indicate that the external mass transfer resistance does not play an important role in the whole SFE process.

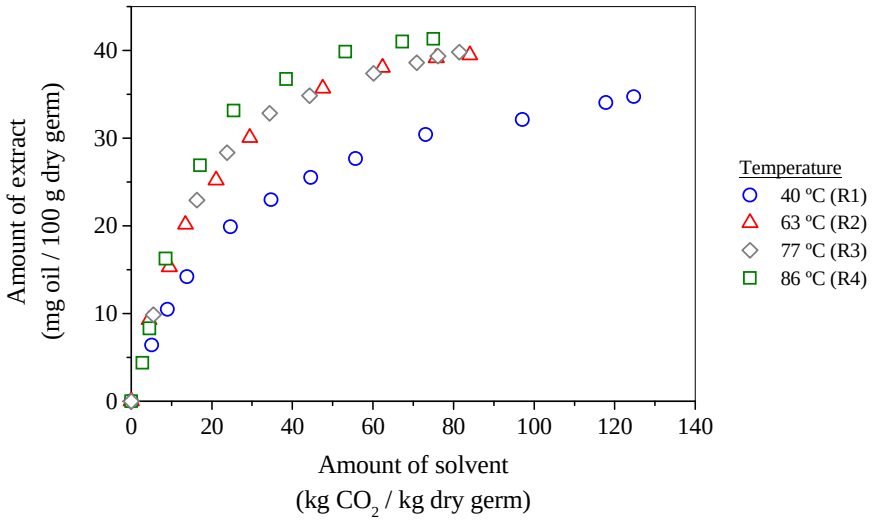

Figure 3. Influence of extraction temperature on corn germ oil extraction yield. Extraction curves were obtained at around 450 bar and 9 kg CO_2 / h

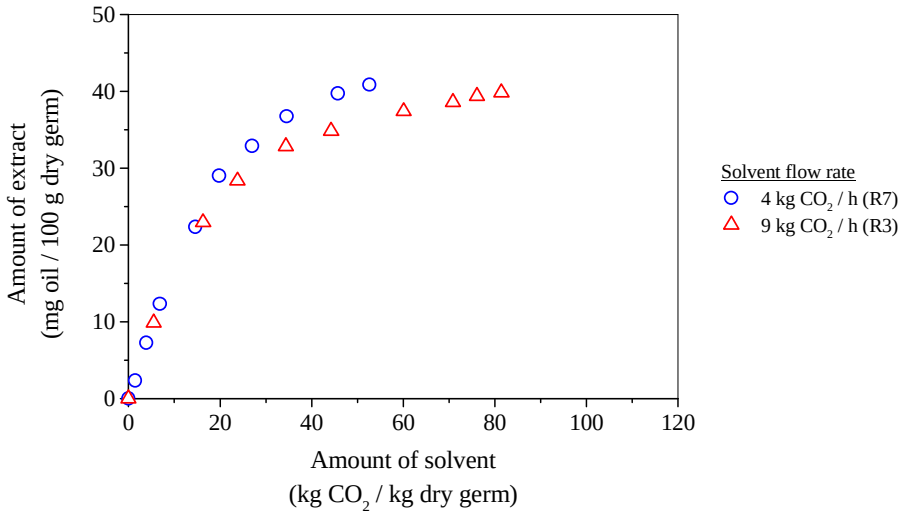

Figure 4. Influence of solvent flow rate on corn germ oil extraction yield. Extraction curves were obtained at around 70 ºC and 450 bar.

Oil extraction yield can be also highly affected by the water content in the raw material, especially when this content is higher than 18 % [6-8]. In the case of corn germ oil, the effect of moisture content (3.5 – 8 % wt.) in the oil extraction yield has been observed to be negligible [9]. However, because water is partially soluble in pressurized CO_2 [10], a certain amount of water can be co-extracted together with the oil, which may affect the oil quality and stability.

In order to remove the co-extracted water from the oil and improve the oil features, an extraction-fractionation process in two separators installed in series is proposed. It was observed that the fraction collected in the first separator was mostly oil whereas the fraction recovered in the second one was mostly an aqueous emulsion. Furthermore, it was observed that the induction time determined by the rancimat test in the oil fraction recovered in separator 1 (1.90 ± 0.3 h) was significantly higher than the induction time determined in the fraction recovered in separator 2 (0.5 ± 0.3 h). The higher stability found in the oil fraction recovered in separator 1 may be explained assuming that, due to the higher solubility in SC-CO_2, both water and free fatty acids, with a high tendency to oxidation, are mostly removed to the separator 2, whereas the less soluble compounds, such as triacylglicerides and tocopherols, with a protective effect against oxidation, are mostly recovered in separator 1.

Figure 5 shows the tocopherol content found in the oil fraction recovered in separator 1 at different extraction conditions. It can be observed that, at a constant pressure of around 490 bar, when temperature increased from 35 ºC to 86 ºC the total amount of tocopherols in the oil fraction recovered in separator 1 is almost double. However, at a constant temperature of around 85 ºC, when the extraction pressure is increased from 258 bar to 486 bar, the total amount of tocopherols found in the oil fraction recovered in separator 1 was slightly increased. Although further experiments are required, these preliminary results may indicate that, in the range studied, the solubility of tocopherols in SC-CO_2 is more sensitive to the vapor-pressure than to the solvent density.

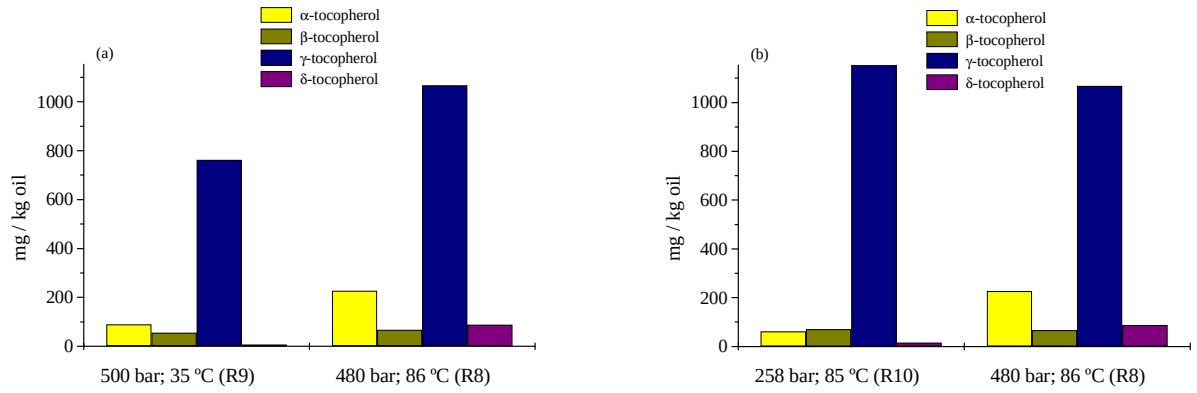

Figure 5. Tocopherol content of oils extracted at different pressures (a) and temperatures (b)

CONCLUSION

Supercritical carbon dioxide extraction has been studied as a procedure to obtain oil from milled corn germ. Extraction experiments have been performed by changing extraction pressure (250 - 500 bar), temperature (35 – 86 ºC) and solvent flow rate (5 – 9 kg CO_2/h). Preliminary results indicate that the whole extraction process may be controlled by the solubility of the oil in SC-CO_2 in the first stages of the extraction. The external mass transfer resistance has been found not to be important even at low solvent flow rates. On line fractionation in two separators installed in series allows separating the co-extracted water and improves the oil stability against oxidation. Moreover, it was found that the triglycerides rich fraction also had a significant tocopherol content, especially when high extraction pressures and temperatures were used. Nevertheless, further experiments are required in order to confirm the influence of extraction - separation conditions on the oil yield, quality and stability and to establish the optimal operational parameters.

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