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EXTRACTION/FRACTIONATION AND DEACIDIFICATION OF WHEAT GERM OIL USING SUPERCRITICAL CARBON DIOXIDE

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Abstract - Wheat germ oil was obtained by mechanical pressing using a small-scale screw press and by supercritical extraction in a pilot plant. With this last method, different pressures and temperatures were tested and the tocopherol concentration in the extract was monitored during extraction. Then supercritical extracted oil as well as commercial pressed oil were deacidified in a countercurrent column using supercritical carbon dioxide as solvent under different operating conditions. Samples of extract, refined oil and feed oil were analyzed for free fatty acids (FFA) and tocopherol contents. The results show that oil with a higher tocopherol content can be obtained by supercritical extraction-fractionation and that FFA can be effectively removed by countercurrent rectification while the tocopherol content is only slightly reduced.
Keywords: Free fatty acids; FFA; Wheat germ oil; Supercritical fluids; Tocopherols.

INTRODUCTION

Supercritical CO_2 extraction of vegetable oils from plant materials is an alternative process to solvent extraction. This technique has several well-known advantages: CO_2 is a nontoxic, nonflammable, nonexplosive and low-cost gas. It is also easily removed from the solute by reducing the pressure and has a relatively low critical pressure and temperature (King and Bott, 1993). This last property allows extraction of heat-sensitive material, such as flavor and aroma compounds. Another very important advantage of CO_2 is that its solvent power or selectivity can be modified by adjusting the temperature and pressure. This interesting feature has been used to extract volatile oils from solid matrices with minimum coextraction of triglycerides (Reverchon, 1997) and to concentrate important nutritional compounds, such as tocopherols and carotenoids (King et al. 1996; Ambrogi et al. 2002).

Tocopherols are a group of monophenolic antioxidants found in many plant materials. Antioxidants eliminate free radicals, providing in this way primary defense to our body. They accomplish the same task in vegetable oils, preventing the formation of hydroperoxides.

Wheat germ oil has the highest tocopherol content of all vegetable oils, up to about 2500 mg/kg (Shuler, 1990), and also the highest content of α-tocopherol, which represents around 60% of the total content. Also, wheat germ oil is highly valued due to its high content of unsaturated fatty acids: it has about 80%, mostly linoleic (18:2) and linolenic (18:3) (Wang and Johnson, 2001). These two fatty acids are of great importance in human metabolism and cannot be synthesized by the organism. They are precursors of a

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group of hormones called prostaglandins, which play an important role in muscle contractions and in the proper healing of inflammatory processes (Coultate, 1989). Furthermore, linoleic acid helps to eliminate cholesterol and is a precursor of cell membrane phospholipids (Salinas, 1993).

To increase stability and improve appearance, most oils are refined after extraction. One of the key objectives of this process is the removal of free fatty acids (FFA). FFA content in crude wheat germ is usually high (5-25 %) (Wang and Johnson, 2001). High FFA content affects stability and is responsible for bitter and soapy flavors (Mistry and Min, 1987). Also, during refining, together with the FFA and other unwanted substances, many important and valuable minor compounds, such as tocopherols, are either removed or destroyed.

In this work, several experiments regarding the processing of wheat germ oil with supercritical CO_2 are presented. Solid extraction kinetics was evaluated under different extraction conditions and tocopherol concentration in oil was monitored during extraction with the aim of obtaining tocopherol-enriched oil. Also, rectification experiments were performed with the objective of removing FFA while retaining the tocopherols.

MATERIALS AND METHODS

Supercritical CO_2 extraction experiments were carried out in two pilot plants. Pilot plant P1 is located at the Universidad Nacional de Río Cuarto (UNRC). It has a 2.3 liter extractor, single stage separation and solvent recycle capabilities. It can be operated at pressures up to 50 MPa and at flow rates up to 20 kg CO_2/h. A detailed description of this plant can be found in Ambrogi et al. (2002). The other plant, P2, located at the Technische Universität Hamburg-Harburg (TUHH), can be used for both extraction and rectification experiments. For extraction (1.3 l extractor), the plant can be operated up to 100 MPa and up to 20 kg/h with a piston pump. The rectification column has a height of 7.5 m and an inner diameter of 40 mm. The column can operate at up to 50 MPa, 100°C and at flow rates up to 20 kg CO_2/h at 50 MPa (one pump) or up to 45 kg CO_2/h at 30 MPa (2 pumps in parallel) (Jaeger, 2001).

The extraction experiments were carried out at 40 and 60 °C at 20 MPa and 40 MPa. About 450 g and 220 g of solids were used at P1 and P2, respectively. The flow rates used were 8 kg CO_2/h for P1 and 6 kg CO_2/h for P2 and the separation conditions were 6 MPa and 50 °C. For some extractions, five different samples of oil were taken at different times. These samples were later analyzed for tocopherol content.

The wheat germs used at the UNRC and at the TUHH had been processed using the same milling procedures. This product was in the form of small flakes and had a 10.9% moisture content and a 10.3% oil content (dry basis) for the material used at the UNRC and a 11.9% moisture content and a 10.6% oil content for the one used at the TUHH. Oil content was determined using “Soxhlet” extraction equipment with petrol ether as extracting solvent.

To decrease the moisture content of the samples that were to be SCO_2 extracted, the wheat germs were placed in a thermostatic oven at 85°C until levels between 1.9 and 2.3 % were attained.

With the objective of comparing the characteristics of oils obtained by different methods, wheat germs were pressed using a laboratory screw press (Komet S 87G, IBG Monforts, Germany). The oil obtained by pressing, commercial pressed wheat germ oil, solvent extracted and supercritical CO_2 extracted oil were analyzed for free fatty acids, phosphorous and tocopherol contents.

For the deacidification experiments two different methods were tested. With the first method, called countercurrent supercritical spray extraction, the packing was removed and the oil sprayed in at the top of the column by forcing it through a capillar tube (0.25 mm id). With the second method, the column was filled with Sulzer BX packing and the oil was also fed in at the top. These experiments were performed with both supercritical extracted oil (40 MPa – 40 °C) and commercial pressed wheat germ oil. For each experiment between 1.7 and 2 kg of oil were used. Samples of the extract, raffinate and feed material were also analyzed for free fatty acids and tocopherol contents. The separation conditions were 6 MPa and 50 °C.

Tocopherol content analyses were carried out by HPLC. The apparatus is equipped with a Merck Superspher 4 Si 60, 125 × 4 mm column and a Shimadzu RF 530 fluorescent detector. The mobile phase used was isooctane:ethyl acetate (90%:6%), the flow rate was 0.8 ml/min and the detector was set at 294 nm/ 330 nm (excitation/emission wavelengths).

FFA and phosphorous contents were determined using the AOCS Ca 5a-40 and the Ca 12-55 methods, respectively (AOCS, 1993).

RESULTS AND DISCUSSION

The difference in extraction rates at different temperatures and pressures is shown in Figure 1. As

expected, at higher pressures, faster extraction rates were achieved. At 40 MPa, the initial slope of the curves is similar, indicating that the so-called crossover point (equal solubilities at different temperatures) should be situated nearby (Eggers et al. 1985). In this figure, an extraction curve obtained using pilot plant 2 (P2) is also shown. As can be seen, the results agree with those obtained in P1, indicating that experiments can be reproduced using different plants and feed materials.

Figures 2 and 3 show the experimental results of the tocopherol fractionation study for the solid extraction experiments. From both graphs it can be seen that there is a variation in concentration of both α and β-tocopherol in the extracted oil during extraction. At the lower pressure higher concentrations of both components were achieved, indicating that this condition is more favorable for tocopherol fractionation.

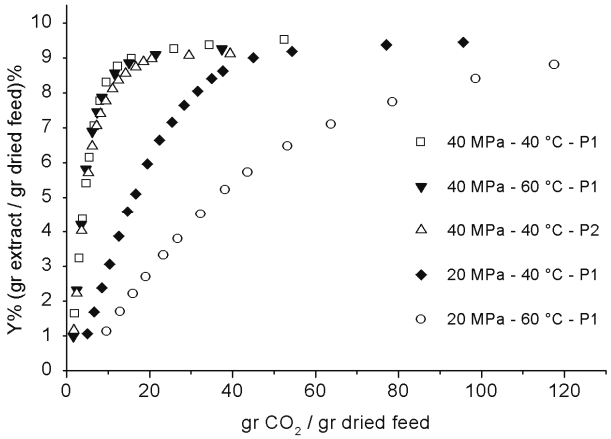

Figure 1: Effect of extraction conditions on extraction kinetics

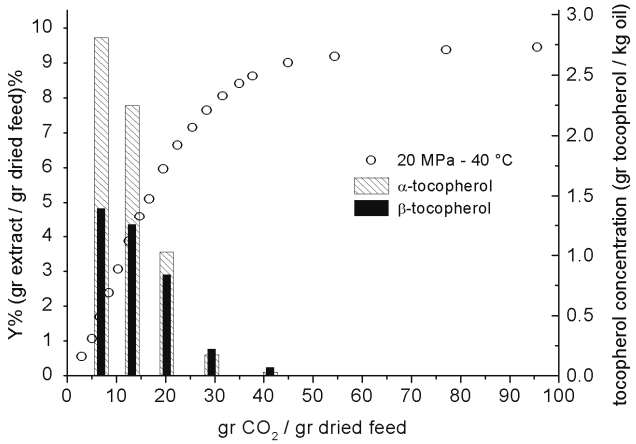

Figure 2: Tocopherol fractionation 20 MPa and 40 °C

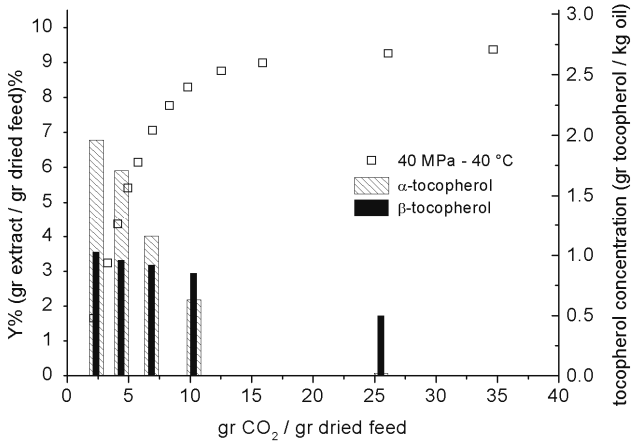

Figure 3: Tocopherol fractionation 40 MPa and 40 °C

In Table 1 an analysis of the samples obtained by solvent extraction, supercritical extraction and pressing as well as an analysis of a sample of commercial wheat germ oil are presented. The parameters evaluated were free fatty acids, phosphorous and tocopherol contents. As expected, the phosphorous content in supercritical extracted oil was below the detection limit because phosphatides are practically insoluble in carbon dioxide under the experimental conditions evaluated (Eggers and Sievers, 1989). In the case of FFA content, all the results obtained are in the same range, with the pressed oil showing a higher value. These values are high but similar to values found in the literature (Wang and Johnson, 2001). Tocopherol contents showed the highest values for solvent-extracted oil and the lowest for pressed oil. Similar results are also available in the literature (Shuler, 1990; Wang and Johnson, 2001; Formo et al. 1979).

Table 1: FAA, phosphorous and tocopherol contents of oil samples

Type	FFA	Phosphorous	α-Tocopherol	β-Tocopherol	γ-Tocopherol
	%	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Solvent	8.8	1100	1970	548	88
SCO_2 (40 MPa, 40 °C)	6.4	<16	1500	559	72
Pressed	10.2	719	1070	570	84
Commercial (Pressed)	7.0	1671	1660	779	142

The experimental parameters used for the deacidification experiments are shown in Table 2. Figures 4 and 5 show the extract/feed and raffinate/feed ratio for each experiment and the amount of FFA in each stream, respectively. In these graphs it can be observed that, although the higher pressure condition yielded a lower FFA content in the refined oil, the extract/feed ratio is too high. This ratio should be as close as possible to the amount of FFA in the feed oil to minimize refining losses. Bondioli et al. (1992) and Dunford and King (2000) reported similar results for the deacidification of other vegetable oils. Relevant work in the field has been carried out by Ziegler and Liaw (1993) and Simoes et al. (1994) among others.

For the operating conditions and the column length tested, the results for the two methods show no significant difference, with the spray results slightly better than those obtained with packing. In Figure 6 the level of α-tocopherol of each stream for the three spray experiments can be observed. Here, lower pressure seems to be more favorable due to the lower levels of these important antioxidants removed from the feed oil.

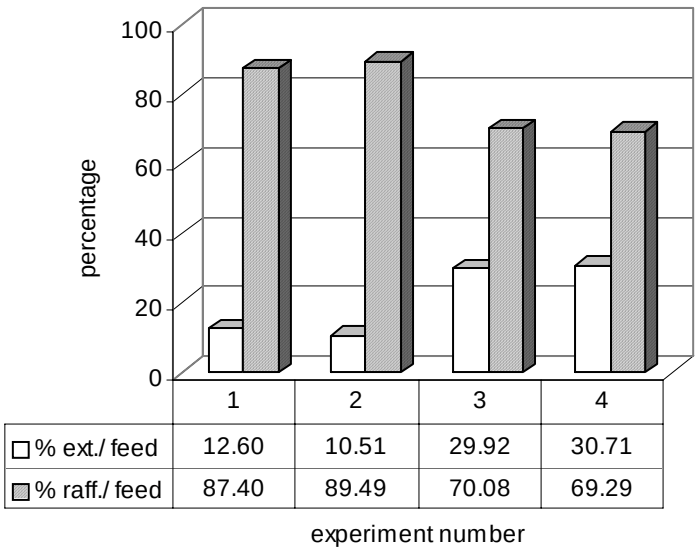

Figure 4: Extract/feed and raffinate/feed ratio for the different experimental conditions

Table 2: Parameters for the countercurrent deacidification experiments

Experiment number	Oil	Method	Pressure (MPa)	Temperature (°C)	CO_2 Flowrate (kg/hr)	Feed Flowrate (kg/hr)
1	SFE (40 MPa, 40 °C)	Spray	26.5	65	17.44	0.762
2	Commercial	Spray	26.5	68.5	16.8	0.742
3	Commercial	Spray	35	68	17.16	0.762
4	Commercial	Packing	35	65	19.2	0.762

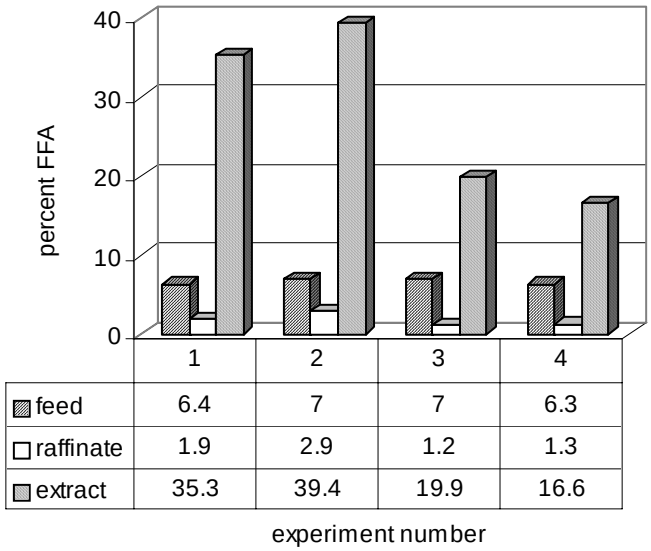

Figure 5: FFA levels for the different experimental conditions

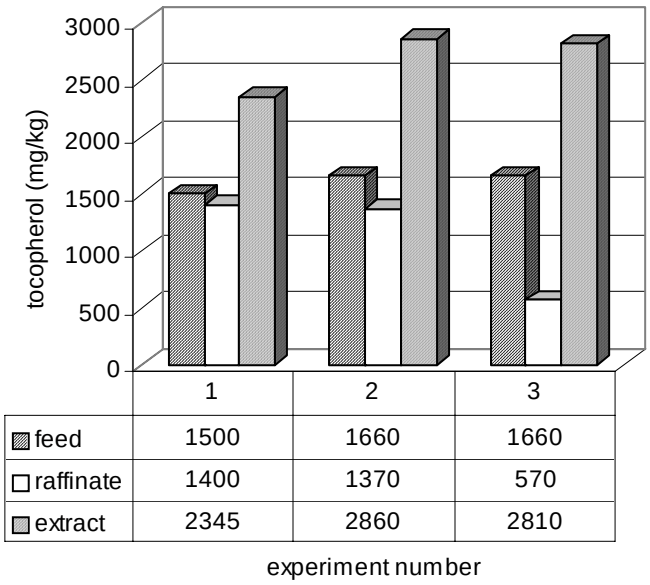

Figure 6: α-Tocopherol levels for the different experimental conditions

CONCLUSIONS

The extraction kinetics for wheat germ oil was studied at different temperatures and pressures. Experiments could be reproduced in two different pilot plants and with raw material from different sources. Also, enriched tocopherol fractions could be obtained by extraction-fractionation. Finally, wheat germ oil was deacidified using countercurrent supercritical rectification techniques. The results showed that the deacidification effect improved with an increase in operating pressure. But as this variable increases, the amount of coextracted oil also increases, causing the refining-loss levels to rise.

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