[Food Science and Technology (Campinas)]

On-line version **ISSN 1678-457X**

Ciênc. Tecnol. Aliment. vol. 17 n. 4 Campinas Dec. 1997

http://dx.doi.org/10.1590/S0101-20611997000400008

EXTRACTION OF OIL FROM PRESSED PALM OIL (*Elaes guineensis*) FIBERS USING SUPERCRITICAL CO_2[1]

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SUMMARY

Residual fibers from palm oil production are a good source of carotene, since they contain more than 5% of the original oil, with about 5000 ppm of carotenoids. As carotenoids are thermosensitive molecules, supercritical CO_2 can be used for oil recovery, because this technique employs low temperatures. In this work results of oil extraction experiments from pressed palm oil fibers are shown. Fibers were from AGROPALMA, an industry which is located in Tailândia (Pará, Brazil). Extractions were carried out at 200, 250 and 300 bar and at temperatures of 45 and 55°C. Oil was analyzed by UV/vis spectrophotometry for total carotene determination. Results showed a large increase in extraction rate from 200 to 250 bar and a small variation from 250 to 300 bar. The total amount of carotenes did not increase in the course of extraction at 300 bar, but it showed a large increase at 200 and at 250 bar. Free fatty acids are present in amounts larger than those found in commercial oils.

Keywords: Supercritical extraction, vegetable oil, palm oil, extraction kinetics, carotene

RESUMO

EXTRAÇÃO DE ÓLEO DAS FIBRAS PRENSADAS DO DENDÊ (*Elaes guineensis*) USANDO CO_2 SUPERCRÍTICO. As fibras residuais do processo de produção de óleo de palma (óleo de dendê), podem ser uma boa fonte de carotenos, pois contém, ainda, mais de 5% do óleo original, com cerca de 5.000 ppm de carotenóides. Como os carotenóides são moléculas termodegradáveis, é importante um estudo do emprego de CO_2 supercrítico na extração deste óleo, visto que esta é uma técnica que emprega baixas temperaturas. Neste trabalho são mostrados os resultados de experimentos de extração do óleo das fibras prensadas de dendê, feitas a 200, 250 e 300 bar e temperaturas de 45 e 55°C. As fibras prensadas foram obtidas da produção industrial da indústria AGROPALMA, localizada em Tailândia (Pará, Brasil). O óleo obtido foi analisado por espectrofotometria UV/vis para a determinação do teor de carotenos totais. Os resultados mostram um aumento na taxa de extração entre 200 e 250 bar, mas esta variação foi pequena entre 250 e 300 bar. O teor de carotenos totais não aumenta durante a extração a 300 bar, mas tem variações importantes a 200 e a 250 bar. Os ácidos graxos livres estão presentes em quantidades superiores àquelas encontradas em óleos comerciais.

Palavras Chave: Extração supercrítica, óleo vegetal, óleo de dendê, cinética de extração, caroteno

1 □ INTRODUCTION

The extraction of natural products from solid matters with supercritical fluids, mainly using CO_2 as the solvent, has been investigated as an alternative to conventional processes that use liquid organic solvents. This is motivated by the high energy costs required for solvent / solute mixture separation and product quality loss, in particular for food and pharmaceutical products, due to the retention of undesirable chemical products and the degradation of thermosensitive components such as vitamins.

Compared to conventional extraction with organic solvents such as hexane, extraction with supercritical fluids presents advantages and disadvantages. The advantages are: a) the ease with which product and solvent are separated, since this is accomplished with reduction of pressure or increase of temperature; b) the pressure and temperature control properties of solvent; c) the extraction can be realized at relatively low temperatures (important for temperature-sensitive products), and d) lower operational costs. The disadvantages are: a) the difficulty or impossibility of continuous processing of solid material and b) higher capital costs, which increase time of investment return [1].

This balance of advantages and disadvantages has not stimulated the substitution of the industrial utilization of supercritical fluids for conventional processes for products of relatively low commercial value, such as vegetable oils, although they are already used for decaffeination of coffee and tea and in hops and condiment extracts production. Thus, supercritical fluid extraction advantages prevail, for example, in the production of high value products such as carotene concentrate from a natural source.

The most important carotenoids found in nature are b and a-carotene because they exhibit provitamin-A activity [9]. Moreover studies have confirmed that b-carotene impedes or delays the growth of tumors induced in the laboratory by chemical agents and viruses. However, as b -carotene is always associated with other natural carotenoids, its action has also been investigated, and there is already evidence that a -carotene is active in preventing the development of cancer [6].

An oil rich in carotenoids can be obtained from pressed palm oil fibers. These fibers are usually burned as fuel in the palm oil industry. They contain more than 5% of the residual oil. This oil contains between 4000 and 6000 ppm of carotenoids, a concentration six times higher than that found in crushed palm oil, which is composed primarily of a-and b-carotene [3]. This oil has a high concentration of free fatty acid, a characteristic that facilitates carotenoid purification if supercritical extraction is employed [4].

In this work the results of experiments of extraction of oil from pressed palm oil fiber produced by AGROPALMA, an industry which is located in Tailândia (Pará, Brazil), are presented. Experiments were conducted at pressures of 200, 250 and 300 bar and at temperatures of 45 and 55^{o}C. Total amount of carotene was determined by UV/vis spectrophotometry.

2 □ MATERIALS AND METHODS

2.1 – Raw material

Fibers were taken from the production line just after leaving the presses. They were packed in plastic bags and sent to Belém (Pará, Brazil). The time elapsing between sample collection and its receipt was not more than three days. Material with a humidity of about 30% was placed in a oven with air circulation (Model 179, FABBE, Brazil) during 24 hours at 60^{o}C, and afterwards seeds were separated from fibers. Resulting material was put in plastic bags and stored in a domestic freezer (CONSUL, Brazil) at approximately -5^{o}C. The amount of solid material (100 g) required for one experimental run was left in the oven at 60^{o}C during one hour to guarantee uniformity of humidity for the raw material (about 5%). As lipid content in palm oil fibers decreases during storage as a result of decomposition, raw material was used within 60 days.

Fiber density was determined with the technique described by Buczek and Geldart [2]. Kaolin of a size between 0.053 and 0.074 mm was used as the picnometric fluid. Humidity was measured by drying the material at 105^{o}C up to constant weight. Total amount of lipids was determined by exhaustive extraction with petroleum ether (CHEMCO) in a Soxhlet apparatus; Total amount of proteins was determined by the Kjeldahl method and a 6.25 factor was used. Total amount of ashes was obtained by burning material, initially at a temperature of 180^{o}C for 30 minutes and after that at a temperature of 500^{o}C.

2.2 – Extraction equipment

Extractions were conducted using the equipment illustrated in *Figure 1*, which is a modification of a pilot scale extraction plant, located in the Laboratory of Chemical Engineering of UFPA (Pará, Brazil). The equipment has a membrane compressor (HOFER, Germany) (C) with the capacity to elevate pressure from 100 to 350 bar; a stainless steel recipient with an inside diameter of 6 cm and a length of 35 cm, heated by a thermostatic bath, was used as an extractor (E1); a removable recipient made of stainless steel (5 cm diameter and 20 cm length) used as a separator (R1); and a gas flow rate meter (MV). Pressure indicators (PI) are Bordon-type manometers (0 - 400 bar, ± 10 bar; model DIN.S, Wika, Germany) and the extractor□s temperature indicator (TI) is made of a NiCr/Ni thermocouple connected to a microprocessor that decodes, enlarges and stabilizes a signal which is graphically recorded (± 5^{o}C). Temperature was measured with a mercury thermometer close to the gas flow meter.

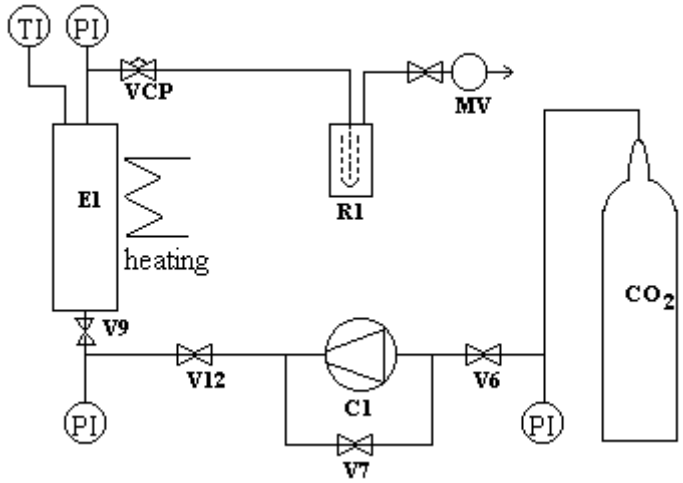

FIGURE 1. Flow sheet of apparatus employed for organic solvent extractions

Oil was collected in recipients used as a separator (R1) that were previously weighed. Extract samples were obtained every 10 or 15 minutes for the first 45 minutes and every 20 or 30 minutes afterwards up to the end of experimental run. Once removed from the circuit, each recipient with the sample was placed in an oven (Model 179, FABBE, Brazil) at 65^{o}C for about 20 minutes. This procedure was adopted to evaporate external wall humidity and to melt oil. After that the sample was weighed (GEHAKA, Model BG4400, ± 0.01 g) and transferred to a 25 ml dark glass flask and stored in a refrigerator (CONSUL, Brazil).

2.3 –Methods

2.3.1 - Product Analysis

The free fatty acid content expressed as oleic acid, saponification number, and unsaponifiable residue were determined by AOAC Official Method 28.029 (a), 28.026 and 28.068, respectively [7].

2.3.2 - Spectrophotometric analysis

About 20mg of extracts were diluted with petroleum ether (CHEMCO, Brazil, 30 - 65^{o}C). The mixture was weighed (Model J.L. 200, CHYO, Germany) and absorbance was read at 450nm (CELM, E225D, Brazil). The amount of carotene was calculated in terms of b-carotene, using a standard curve. The standard curve was prepared with 0.1 g of b-carotene (Merk, 99% purity) diluted up to 100 mL with petroleum ether. Aliquots were taken from this solution and diluted to five different concentrations and absorbance was read at 450nm.

3 □ RESULTS AND DISCUSSION

Experiments were conducted using a fixed bed formed with 100 g of material whose characteristics are given in *Table 1*. The fixed bed (20.0 cm L x 6.0 cm ID) had a porosity of 0.758.

TABLE 1. Pressed Palm Oil Fiber Characteristics

density	0.730 g/cm^3
humidity	5.0 % w/w
amount of lipids	7.15 % w/w
total protein	7.21 % w/w
ash	5.23 % w/w

A factorial experiment with replication for temperatures of 45 and 55^{o}C and pressures of 200, 250, and 300 bar was performed to study the effect of pressure and temperature on extraction yield. Due to limitations of the experimental apparatus, solvent flow rate could not be set at a preselected value, but as this variable influences extraction it was monitored during the whole run.

TABLE 2. Experimental Conditions and Results

Press. (bar)*	Temp. (^{o}C)*	(gCO_2 /min)	t_{CER} (min)[§]	M_{CER} (g/min)[a]	t_{TOTAL} (min)	Yield (%)
300 ± 5	55 ± 2.5	19.0 ± 1.0	38 ± 2	0.120	112	7.01[¨]
300 ± 5	55 ± 2.5	18.4 ± 1.0	38 ± 2	0.120	130	7.03
250 ± 5	55 ± 2.5	19.8 ± 1.0	39 ± 8	0.092	130	6.89[¨]
250 ± 5	55 ± 2.5	18.0 ± 1.0	39 ± 8	0.092	130	6.67
200 ± 5	55 ± 2.5	17.9 ± 1.0	70 ± 5	0.045	140	5.18[¨]
200 ± 5	55 ± 2.5	18.8 ± 2.0	70 ± 5	0.045	140	5.17
300 ± 5	45 ± 2.5	18.5 ± 0.7	24 ± 2	0.113	90	6.11[¨]
300 ± 5	45 ± 2.5	19.1 ± 0.8	24 ± 2	0.113	90	6.05
250 ± 5	45 ± 2.5	19.6 ± 0.8	31[©]	0.114	110	6.59[¨]
250 ± 5	45 ± 2.5	19.7 ± 1.0	31[©]	0.114	110	6.45
200 ± 5	45 ± 2.5	19.3 ± 1.0	45 ± 1	0.068	120	5.44

200 ± 5	45 ± 2.5	20.2 ± 0.8	45 ± 1	0.068	105	5.53¨

*measurement accuracy; § standard error; © standard error smaller than 3%; [a] standard error smaller than 10%; ¨ sample analyzed for carotene content.

In general, the extraction curves (extract mass against extraction time or CO_2 mass) show three periods: a) the constant extraction rate period (CER), when particle surfaces are entirely covered with a solute thin layer; b) the falling extraction rate period, when patches without solute appear on the particle surfaces; and c) the diffusion period, which is characterized by the diffusion of the solute-solvent mixture inside particles and through the bulk of the fluid [5]. *Figure 2* shows a typical extraction curve where the three extraction periods can be observed. Using experimental data, mass transfer rate or extraction rate for the CER period (M_{CER}) and duration of constant extraction rate period (t_{CER}) were calculated. The method explained by Rodrigues [8] was employed for the calculations. *Table 2* shows results along with experimental conditions. Figures 3 and 4 show extraction curves along with M_{CER}.

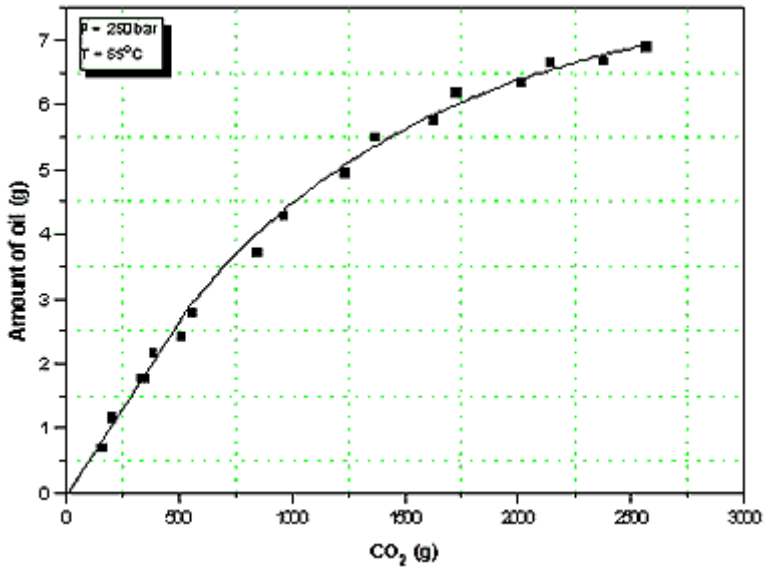

FIGURE 2. Typical extraction curve for oil from pressed palm oil fiber. Data refers to duplicated experimental run (*Table 2*).

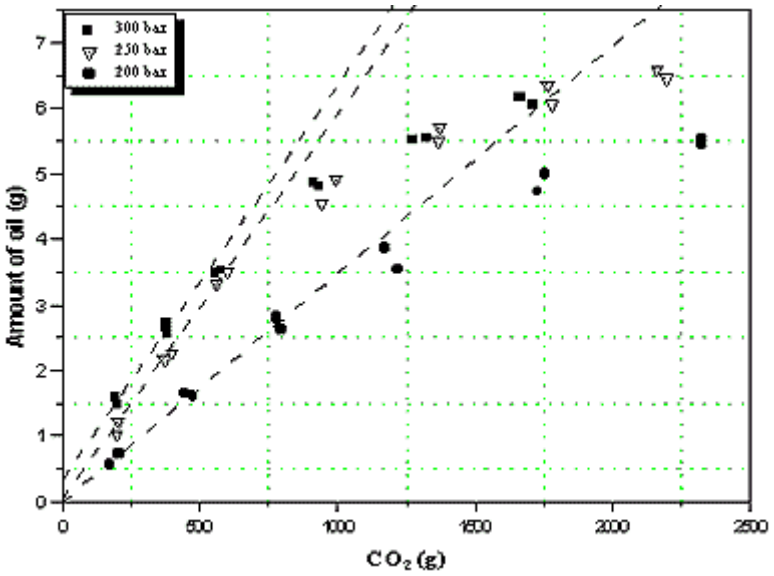

FIGURE 3. Extraction curve for 45°C. Dashed line is the linear regression by SAS program [8].

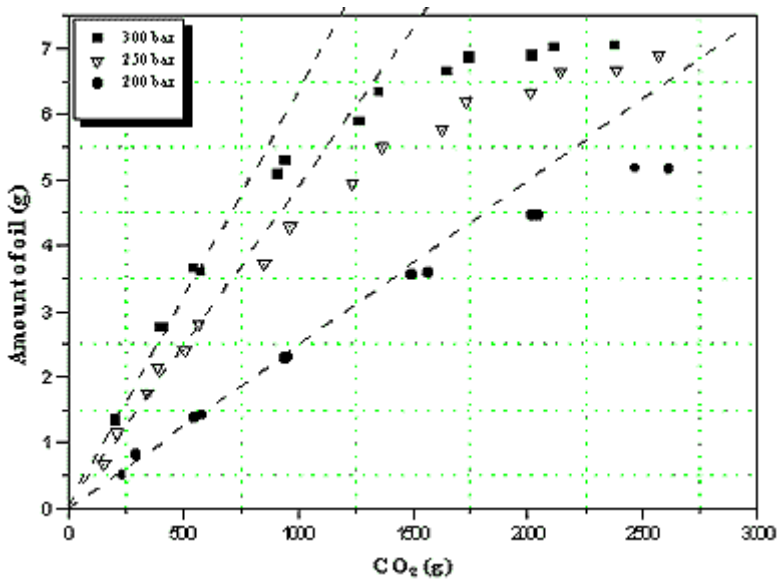

FIGURE 4. Extraction curves for 55°C. Dashed line is the linear regression by SAS program [8].

A large increase in mass transfer or extraction rate (M_{CER}) is noticed between 200 and 250 bar; however, the increase is small for a pressure variation from 250 to 300 bar, and is imperceptible at 45°C. Extract solubility in CO_2 increases for this pressure interval [4]. Thus, the small increase of mass transfer rate above 250 bar can be justified by the decrease in diffusivity [11]. This can be also due to an increase in solvent viscosity that reduces its penetration power in solid matrix.

Crushed palm oil is composed of 88.7% triglycerides, 3.5% free fatty acid, and about 700 ppm of carotenoids. Main free fatty acids are palmitic, oleic and linoleic acids [10]. On the other hand, oil extracted from pressed palm oil fibers has a larger content of free fatty acid, as shown in *Table 3*, although the composition remains the same [4]. High free fatty acid content makes raw material more convenient for carotene concentrate production, since carotenes are more easily separated from free fatty acids than from triglycerides [4].

TABLE 3. Characteristics of Oil from Pressed Palm Oil Fibers

	CO_2	hexane
Acidity (g oleic acid/100 g oil)	58.7 ± 0.2	62.9 ± 0.1
Saponification value (mg_{KOH}/g_{oil})	240 ± 10	--
Unsaponified matter (mg/ g_{oil})	2.4 ± 0.2	--

Carotene concentrations are shown in Figures 5 and 6. As can be observed, extract carotene concentration is high from the beginning for the process at 300 bar while at 200 and 250 bar concentration gradually increases. The increase in carotene concentration at 250 bar is sharper than at 200 bar for a temperature of 55°C. At 250 or 300 bar about 50% of total oil was extracted in the first 40 minutes, while for the same period only 20% was extracted at 200 bar and 55°C. Based on the results, a good strategy to obtain an extract with a high carotene content would be to use a pressure of 200 bar for the first 30 minutes and afterwards increase it to 250 bar; temperature should be held constant at 55°C.

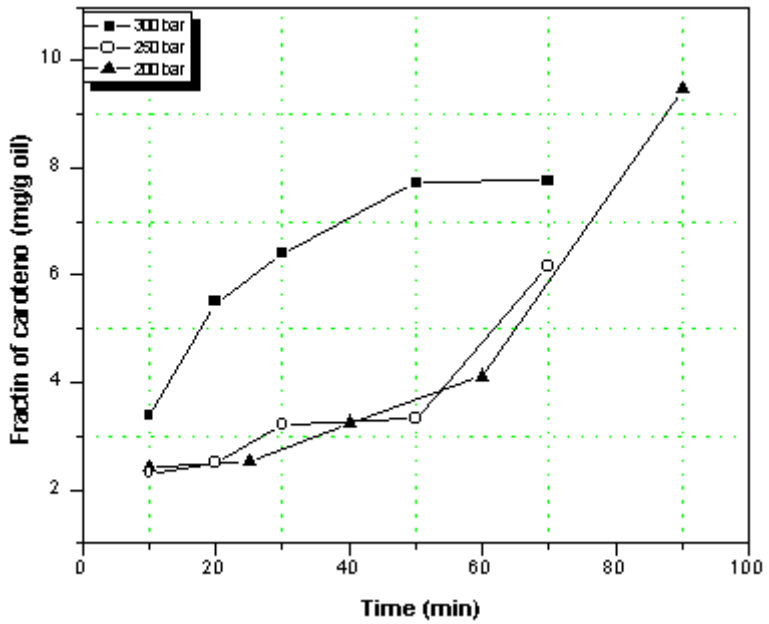

FIGURE 5. Total carotene concentration in oil fractions at 45°C.

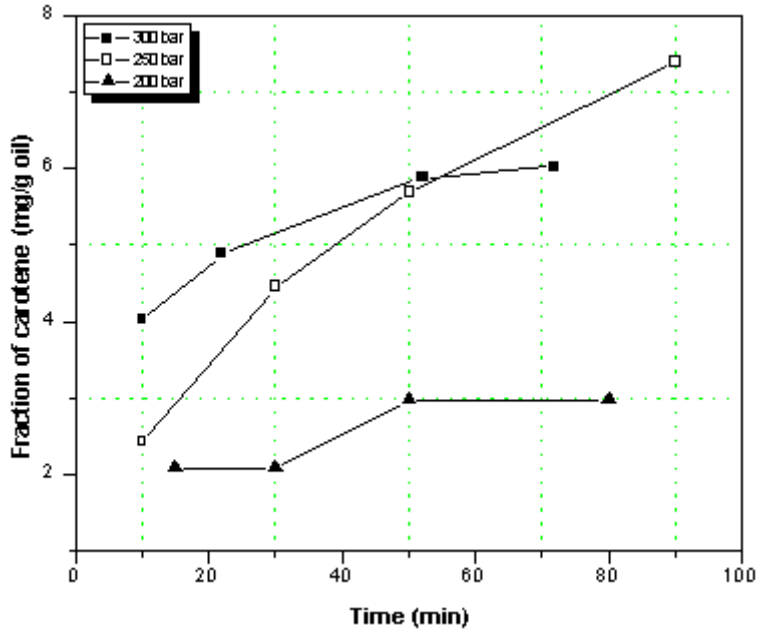

FIGURE 6. Total carotene concentration in oil fractions at 55°C.

4 □ CONCLUSIONS

Results demonstrated that oil extraction from palm pressed fibers using supercritical CO_2 is a promising technology and must be further investigated as an alternative process to obtain carotene concentrate.

Low carotene content in oil fractions was obtained for the first 30 minutes of extraction at 200 bar and 55°C. An accentuated increase after 20 minutes at 250 bar and 55°C, suggests the usefulness of a combined extraction technology.

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6 □ AKNOWLEDGEMENT

White Martins S.A. provided the CO_2 and AGROPALMA the pressed fibers from the palm tree. This work was partially financed by CAPES.

1 *Received for publication on 05/08/97. Accepted for publication on 3/12/97.*

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