

Analytical, Nutritional and Clinical Methods Section

High pressure extraction of vitamin E-rich oil from *Silybum marianum*

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Abstract

The efficiency of high pressure extraction in the production of oil with a high concentration of vitamin E, from seeds of *Silybum marianum*, was investigated. The solvents used in extraction were liquid or supercritical carbon dioxide and liquid propane. Operating parameters were 100, 200, 300 bar and 25, 40, 60 and 80°C for CO₂ and 60, 150, 200 bar and 40, 60 and 80°C for propane, respectively. The influence of process parameters on the total yield of extraction, vitamin E composition and acid value of the extracts was investigated. Results were compared with those obtained for conventional extraction with organic solvents (n-hexane, petroleum ether, dichloromethane, chloroform). The mathematical model based on the adsorption–desorption equilibrium of oil from solid tissue, the diffusion of oil to the surface and mass transfer through external film into the bulk, described the experimental extraction results well. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Silybum marianum (family: Compositae) is an annual or biennial plant, native to the Mediterranean area, which has now spread to other warm and dry regions. It attains a height of 60–150 cm and has large, white-veined leaves with toothed spiny edges. Purple flowers at the top of the stem and at the ramifications ripen into 6–7 mm long brownish fruits (achenes) with a white, silky pappus at their apex (Leng-Peschlow, 1996). *S. marianum* has been known since ancient times and recommended in traditional European and Asian medicine, mainly for treatment of liver disorders (Škottová & Krečman, 1998). A fruit of *S. marianum* contains a relatively high amount (approx. 20%) of oil, which makes one step extraction of silymarin from seeds impossible. Active component silymarin is a mixture of flavonolignans, of which silybin is the main constituent (Fig. 1). Oil has to be removed from seeds prior to the extraction of silymarin and is a by-product of silymarin production. This oil contains essential phospholipids

and a relatively high content of vitamin E. It is therefore of interest as a natural source of vitamin E.

Vitamin E functions primarily as an antioxidant, protecting the body tissues from damaging reactions (peroxidation) that arise from many normal metabolic processes and exogenous toxic agents (Ong & Choo, 1997).

Natural vitamin E is better absorbed in body tissues and has a higher activity than the synthetic one (Friedrich, 1987); therefore isolation and concentration of tocopherols from vegetable oils are of interest. Altogether there are at least eight naturally occurring forms of vitamin E, known as tocopherols and tocotrienols. Structural differences between the isomers have a marked effect on biological activity. α -Tocopherol (Fig. 2) is the most common form and also has the highest biological activity (Friedrich, 1987). The richest sources of vitamin E are seed oils. Nuts, seeds, whole grains, leafy green vegetables, eggs, and milk are also good sources. Tocopherols are stable to heat, acid, and alkali, but they are easily destroyed by ultraviolet light and oxidizing agents (Friedrich, 1987).

Extraction solvents, generally regarded as safe (GRAS) in compliance with good manufacturing practices (GMP) are: propane, butane, butyl acetate, ethyl acetate, ethanol, carbon dioxide, acetone, and nitrous

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Nomenclature

AARD	average absolute relative deviation, (%)
D_{AB}	binary diffusion coefficient, (m^2/s)
D_e	effective intraparticle diffusion coefficient, (m^2/s)
HPLC	high performance liquid chromatography
K	equilibrium adsorption coefficient, (–)
k_f	external mass-transfer coefficient, (m/s)
k_p	overall mass-transfer coefficient ($k_p = k'_p \times a_p$), (1/s)
k'_p	overall mass-transfer coefficient, (m/s)
k_a	adsorption rate constant, (1/s)
P	pressure, (bar)
T	temperature, ($^{\circ}C$)
Q_v	volumetric flow rate, (m^3/s)
Q_m	mass flow rate, (kg/s)
a_p	specific surface area, (1/m)
Bi	Biot number, (–)

c	solute concentration in the solvent, (g/ml)
c_o	initial concentration of a solute in solid, (g/ml)
c_i	concentration of essential oil in the pore of solid particle, (g/ml)
c_s	sorbed essential oil in the solid particle, (g/ml)
x	dimensionless solute concentration in effluent
y	dimensionless solute concentration in pores, (l)
t	time, (s)

Greek letters

α	bed void fraction, (–)
β	porosity of particle, (–)
ρ	density, (kg/m^3)
η	viscosity, (Pas)
Θ	dimensionless time, (l)
ϕ	dimensionless mass-transfer coefficient, (l)
τ	residence time, (s)

oxide (EEC, 1988). Four of the eight permitted solvents are gases (Knez & Rižner, 1997).

Conventional isolation and concentration of vitamin E from vegetable oils is based on the esterification of free fatty acids, partial glycerides and triacylglycerols into methyl esters, as well as separation of esters by distillation, crystallization and ion-exchange chromatography. Vitamin concentrate is then washed, dried and purified by molecular distillation. However, the industrial utilization of natural antioxidants is limited, mainly because of the low efficiency/cost ratio observed for the extraction of known natural antioxidants (Esquivel, Ribeiro, & Bernardo-Gil, 1999).

Lately, extended research work on the application of supercritical fluids in the vegetable oil industry has been carried out. The crude oils from plant materials (corn germs, soybean, cottonseed flakes) were extracted with supercritical CO_2 and properties were compared with a commercially extracted oil. Studies indicate that supercritical CO_2 extraction yields a product comparable with a hexane-extracted degummed oil, however; hexane-extracted oil exhibits better oxidative stability because natural antioxidants (phosphatides) are absent in supercritical CO_2 -extracted oils (List, Friedrich, &

Christianson, 1984; List & Freidrich, 1985; List, King, Johnson, Warner, & Mounts, 1993). The supercritical CO_2 degumming and physical refining of soybean oil was investigated by List et al. (1993) and results showed, that bleaching with absorbent clays may be eliminated by the supercritical CO_2 counter-current processing step.

Supercritical fluid extraction, has been investigated to obtain oil fractions with high concentrations of vitamins, especially β -carotene and tocopherols (Birtigh, Johannsen, & Brunner, 1995; Brunner, Malchow, Sterken, & Gottschau, 1991; De Franca, Reber, Meireles, Machado, & Brunner, 1999; Ohgaki, Tsukahara, Semba, & Katayama, 1989; Stoldt & Brunner, 1999).

The investigations of the applicability of supercritical fluid extraction to the deacidification of olive and husk oils were performed by Brunetti, Daghetta, Fedeli, Kirkic, and Zanderighi (1989) and Goncalves, Vasconcelos, de Azevedo, de Neves, and da Ponte (1991).

Fleck, Tiegs, and Brunner (1998) investigated fractionation of fatty acid ethyl esters by supercritical CO_2 according to the chain length. Ronyai, Simandi Tomoskozi, Deak, Vigh, and Weinbrenner, (1998) studied the composition of the oil from corn germ,

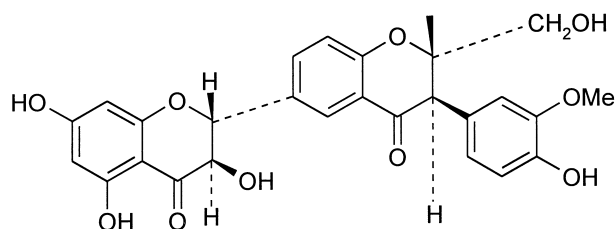


Fig. 1. Structural formula for Silybin.

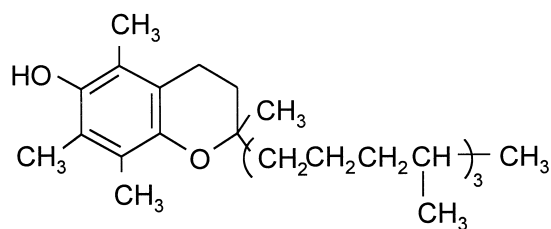


Fig. 2. Structural formula for α -tocopherol.

obtained with supercritical CO₂, the nutritive value and phospholipid content of defatted proteins. Selective extraction of phospholipids from Canola (Temelli, 1992) and soybeans (Montanari, King, List, & Rennick, 1996; Montanari, Fantozzi, Snyder, & King, 1999) with supercritical CO₂ and ethanol as cosolvent was studied.

In the present work, the efficiency of high pressure extraction in the production of oil with a high concentration of vitamin E, from seeds of *S. marianum*, was investigated. Seeds were extracted with liquid, supercritical carbon dioxide and liquid propane in the pressure range 60–300 bar and temperature range 25–80°C. The influences of process parameters on the total yield of extraction, vitamin E content and acid value of the extract were investigated.

2. Materials and methods

2.1. Materials

The *S. marianum* seeds originated from Arxfarm (Šentjernej, Slovenia). All chemicals used for analysis were purchased from Merck (Darmstadt, Germany). CO₂ (purity 99.97%) and propane (purity 99.95%) were obtained from Linde plin (Celje, Slovenia). Nitrogen was obtained from Messer-Griesheim Ruše, Slovenia, and was 99.999% pure.

2.2. Methods

2.2.1. Apparatus and experimental procedure

The extraction experiments with dense gases (CO₂ and propane) were performed on a semicontinuous apparatus, which is presented in Fig. 3. The apparatus was home built for a maximum pressure of 500 bar and

a temperature of 100°C. The system allows us to produce natural extracts with flammable gases.

The *S. marianum* seeds were ground and sieve analysis of ground material was carried out to determine the particle size distribution. Experiments were carried out on a laboratory scale, in small quantities and the heating due to grinding the raw material was minimal. The moisture content was determined by drying to constant weight at 105°C and the density of solid material was measured with a helium pycnometer (multi volume pycnometer 1305, Micrometrics, USA).

Approximately 30 g of ground material was charged into the extractor ($V=60$ ml). The temperature in the water bath was regulated and maintained at constant level ($\pm 0.5^\circ\text{C}$; LAUDA DR.R. WOBSEK GmbH & Co. KG, Lauda Königshofen, Germany). The apparatus was purged first with nitrogen and later with the gas used for extraction. In the next step, liquefied gas (CO₂ or propane) was continuously pumped with a high pressure pump (ISCO syringe pump, model 260D, Lincoln, Nebraska, $P_{\text{max}}=350$ bar) through the preheating coil and over the bed of sample in the extractor. The solvent flowrate was measured with a flow-meter (ELSTER HANDEL GmbH, Mainz, Germany). The product precipitated in the separator (glass trap), where the separation was performed at 1 bar and at a temperature of 25°C. The product collected in the glass trap was weighed (± 0.1 mg) and yield was calculated. Operating parameters are presented in Table 1.

Conventional extraction was performed in a Soxhlet apparatus. Approximately 50 g of ground material was extracted for 10 h with different organic solvents (n-hexane, petroleum ether, dichloromethane, chloroform). The extraction solvents were evaporated and the extract was analysed. Yield of extraction was calculated by the formula:

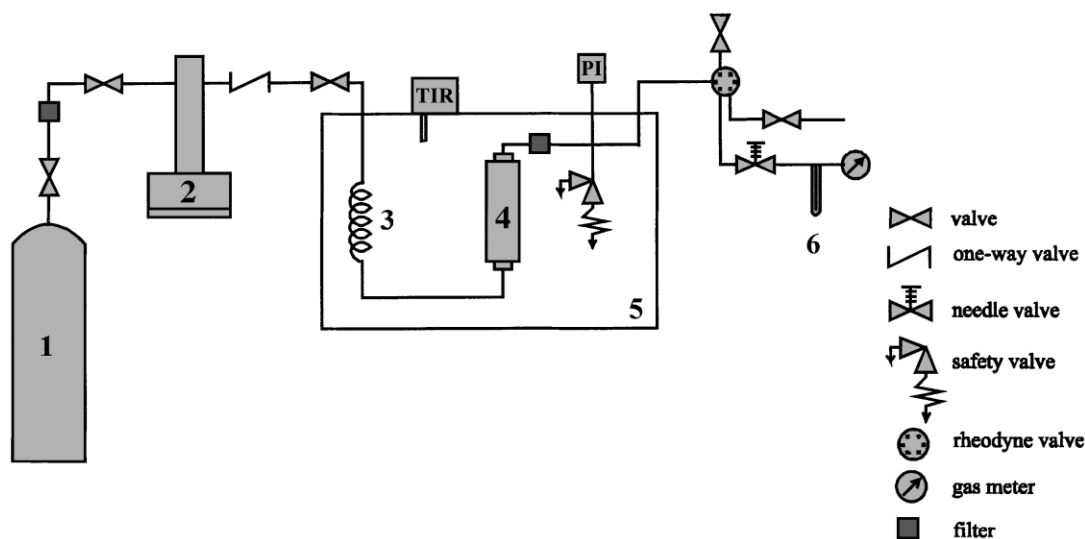


Fig. 3. Apparatus for high pressure extraction. 1, liquid CO₂ cylinder; 2, Isco syringe pump; 3, preheat coil; 4, extractor; 5, water bath; 6, trap.

$$\text{Yield}(\%) = \frac{m_{\text{extract}}}{m_{\text{raw material}}} \times 100\% \quad (1)$$

where m_{extract} is mass of the extract and $m_{\text{raw material}}$ is mass of the raw material (seeds of *S. marianum*) extracted.

Yield in respect to α -tocopherol content (Yield $_{\alpha\text{-tocopherol}}$) was calculated as:

$$\text{Yield}_{\alpha\text{-tocopherol}}(\%) = \text{Yield}(\%) \times \frac{\text{fraction } \alpha\text{-tocopherol in oil (\%w/w)}}{100} \quad (2)$$

where fraction α -tocopherol in oil (%w/w) is α -tocopherol content in the extracts determined by HPLC.

2.2.2. Analysis

HPLC (Chrom-Circle, 1998) was used for the quantitative determination of the α -tocopherol content of the extracts. The HPLC system consisted of a pump (VARIAN 9012 HPLC pump, Walnutcreek, California) and a diode array detector (VARIAN 9065, Walnutcreek, California). A LICHROSORB RP-18 250×4.0 mm column (Merck KGaA, Darmstadt, Germany) with 7- μm particle size was used. The mobile phase consisted of methanol/water = 95:5 (v/v). The flow rate was 1 ml/min and the detection was performed at 278 nm. The quantification was made with an external standard. Soxhlet and high pressure extractions were repeated twice and, for each extraction, an HPLC analysis of the product was made.

The HPLC method was validated and, on the 95% confidence range, results show no statistical differences;

Table 1
Operating parameters for the extraction of *Sylibum marianum*

T (°C)	P (bar)	ρ (kg/m ³)	$\mu \times 10^4$ (kg/ms)	Qv^a (ml/min)	τ (min)
<i>CO₂</i>					
25	200	914.8	0.963	7.58	7.91
25	300	967.0	1.109	6.40	9.38
40	100	629.7	0.482	15.17	3.96
40	200	840.6	0.796	6.97	8.61
40	300	910.6	0.951	6.10	9.84
60	200	724.4	0.606	8.55	7.02
60	300	830.4	0.779	6.78	8.85
80	200	594.8	0.459	8.98	6.68
80	300	746.1	0.643	5.85	10.26
<i>Propane</i>					
40	60	483.0	0.927	13.72	4.38
40	150	506.0	1.080	5.62	10.68
40	200	517.24	1.158	4.25	14.12
60	60	449.4	0.751	11.10	5.41
60	150	481.0	0.912	6.90	8.70
60	200	494.7	0.987	5.53	10.84
80	60	407.4	0.592	18.50	3.24
80	150	454.1	0.770	7.88	7.61
80	200	471.1	0.846	6.03	9.95

^a Volume flowrate at operating parameters.

that means that the accuracy is suitable. Each sample was analyzed three times and relative standard deviation between measurements was 2.4%. Acid value was determined for each sample, using the AOAC official method (AOAC, 1997).

Moisture content of lipid extracts was determined by the Karl–Fisher method.

3. Results and discussion

3.1. Extraction

Dry material was ground and sieve analysis was performed. The median particle size was determined from the integral distribution curve and the average particle diameter was estimated from the differential distribution curve. Characteristics of extraction material are presented in Table 2. Seeds of *S. marianum* were first extracted with several organic solvents (n-hexane, petroleum ether, dichloromethane, chloroform) in the Soxhlet apparatus for comparison of the results, which are summarized in Table 3. The best results were obtained with petroleum ether, where the yield of extraction was 22.5%; acid value was 2.95 and α -tocopherol content was 0.043% (w/w). Moisture content of the light yellow lipophilic extracts was from 0.09 to 0.12% (w/w).

Experiments on semicontinuous extraction of seeds of *S. marianum* with dense CO₂ and propane under different operating conditions are presented in Figs. 4–6. In the case of CO₂ (Figs. 4a, b and 6a) it can be observed that, at 200 bar, the maximum yield obtained decreases with an increase of temperature (25–80°C) from 19.9 to 5.2%. However, at 300 bar, the yield increases with increase of temperature (25–80°C) from 15.3 to 20.5%.

Table 2
Characteristics of ground material

Property	Value
Median particle size	910×10 ⁻⁶ m
Average particle diameter	900×10 ⁻⁶ m
Moisture content	5.63%(w/w)
Solid density	1330 kg/m ³
Apparent density	485 kg/m ³

Table 3
Extraction of oil from *Sylibum marianum* with different organic solvents

Solvent	Yield (%)	Acid value	Tocopherol content (%w/w)
Petroleum ether	22.50	2.95	0.043
Hexane	20.90	4.49	0.030
Dichloromethane	21.90	5.44	Not detected
Chloroform	21.70	5.72	Not detected

A similar cross-over effect is well known for equilibrium solubility (solubility decrease with increase of temperature). This is a consequence of the endothermicity or exothermicity of the adsorption of the solute on solid tissue.

In the case of propane (Figs. 5a, b, c and 6b) at 40°C, the yield is independent of pressure and is approximately 21–23%. At 60°C, the yield decreases with increasing pressure (60–200 bar) from 23 to 15%. At 80°C, the yield is generally lower and increases with the increasing pressure from 14 to 18%. Generally, at lower pressures (under 100 bar), the yield is independent of pressure and temperature in the range 25–60°C and is the highest obtained: 22–23%. With an increase of the temperature to 80°C, the yield decreases.

3.2. Analysis of experimental extraction curve by the model

The extraction runs were modelled with the method used by Peker, Srinivasan, Smith, and McCoy (1992) and Goto, Sato, and Hirose (1993), which is based on the following assumptions:

1. adsorption–desorption equilibrium of extractable component from solid tissue;
2. the diffusion of extractable component dissolved in supercritical fluid to the surface; and
3. mass transfer through the external film into the bulk.

With this model, the governing differential equation for the time-dependent solute concentration in the solvent is:

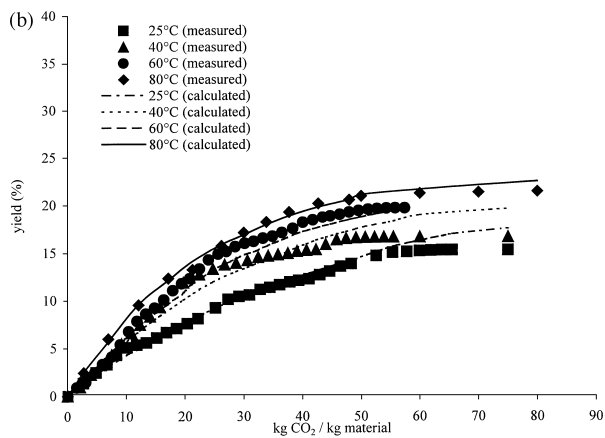
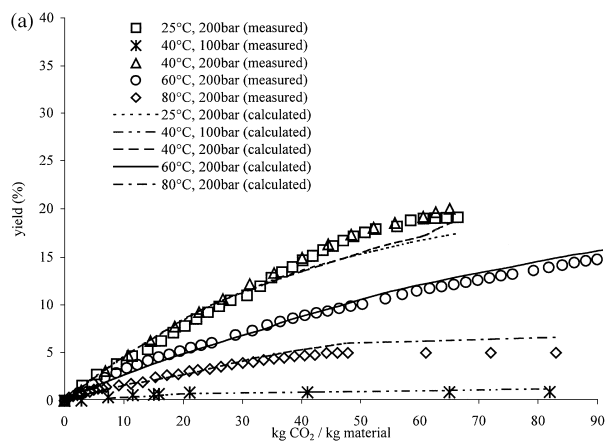


Fig. 4. Kinetics of semicontinuous extraction of seeds of *Silybum marianum* with dense CO₂: (a) 100 and 200 bar; and (b) 300 bar.

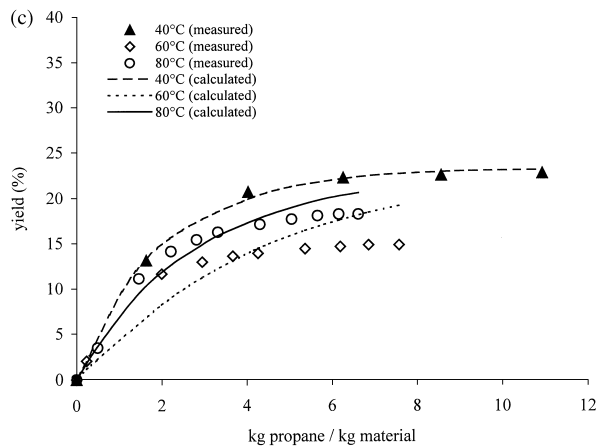
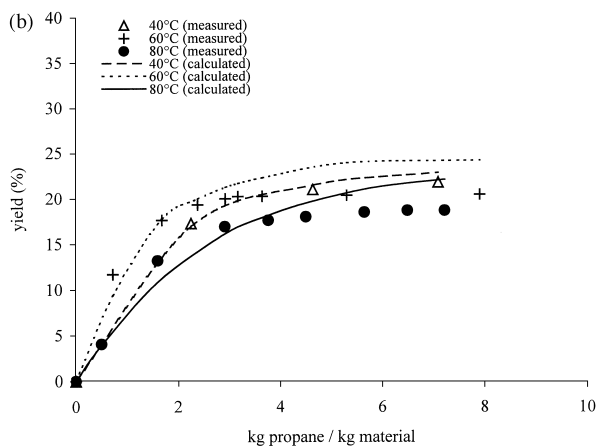
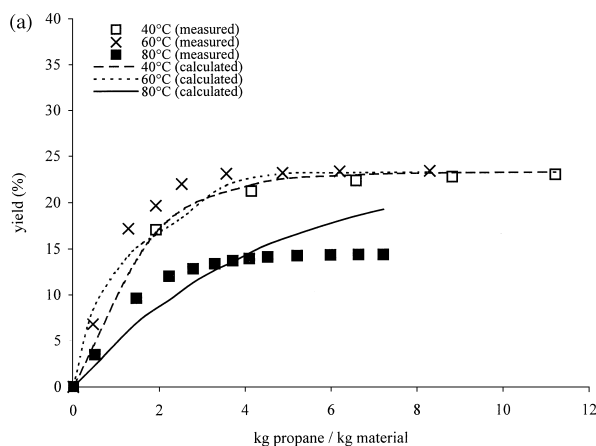


Fig. 5. Kinetics of semicontinuous extraction of seeds of *Silybum marianum* with dense propane: (a) 60 bar; (b) 150 bar; and (c) 200 bar.

$$\alpha \frac{dc}{dt} + \frac{c}{\tau} = -(1 - \alpha)k'_p a_p [c - c_i] \quad (3)$$

where the residence time τ is given as the total bed volume divided by the volumetric flow rate of supercritical fluid at the conditions of the extractor column. k'_p is the overall mass-transfer coefficient and $k_p = k'_p \times a_p$. α is the bed void fraction and a_p is the specific surface area given for the sphere by $a_p = 3/R \cdot c_i$ is the concentration of essential oil in the pore of solid particle.

It is assumed that the combined internal and external mass transfer processes are described by a linear driving-force approximation, which is based on the parabolic concentration profile within the particle. The overall mass-transfer coefficient k_p is given for the sphere by equation (Peker et al., 1992):

$$k_p = \frac{15 \times k_f / R}{5 + \text{Bi}} \quad (4)$$

The Biot number Bi is expressed in terms of the effective intraparticle diffusion coefficient D_e :

$$\text{Bi} = \frac{k_f \times R}{D_e} \quad (5)$$

$$D_e = D_{AB} \times \beta^2 \quad (6)$$

where D_{AB} is the binary diffusion coefficient for essential oil in supercritical fluid and β is the porosity of the particle. When $\text{Bi} \gg 5$, intraparticle diffusion resistance would dominate over the external mass-transfer resistance (Peker et al., 1992).

The mass balance for the intraparticle solute concentration is:

$$\beta \frac{dc_i}{dt} = k'_p a_p (c - c_i) - (1 - \beta) \frac{dc_s}{dt} \quad (7)$$

The rate of adsorption is given by:

$$\frac{dc_s}{dt} = k_a (c_i - \frac{c_s}{K}) \quad (8)$$

It is supposed, that equilibrium in the pores is established instantaneously for a relatively fast adsorption-desorption rate:

$$c_s = K \times c_i \quad (9)$$

where: c_s is sorbed essential oil in the solid particle and c_i is the concentration of essential oil in the pore of solid particle. For $K \ll 1$, the essential oil would be totally desorbed from the bean tissue into the pore volume (Peker et al., 1992). Dimensionless quantities are defined as:

$$x = \frac{c}{c_0} \quad (10)$$

$$y = \frac{c_i}{c_0} \quad (11)$$

$$\Theta = \frac{t}{\tau} \quad (12)$$

$$\phi = k'_p a_p \tau \quad (13)$$

where c is the concentration of a solute in a solvent, and c_0 is the initial concentration of a solute in material.

Writing Eqs. (3) and (7) in dimensionless form yields:

$$\frac{dx}{d\Theta} + \frac{x}{\alpha} = -\frac{\phi(1 - \alpha)}{\alpha} (x - y) \quad (14)$$

$$\frac{dy}{d\Theta} = \frac{\phi(x - y)}{[\beta + (1 - \beta)K]} \quad (15)$$

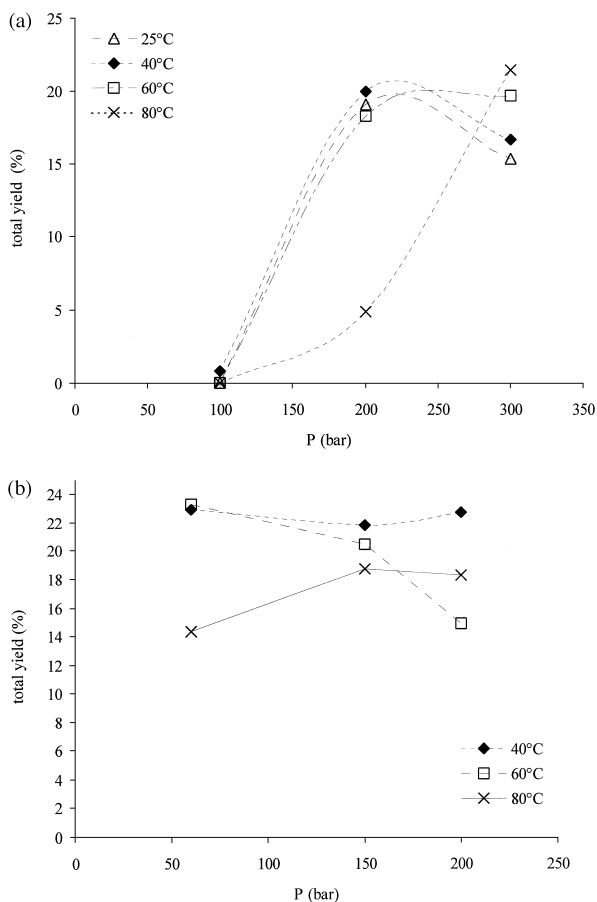


Fig. 6. Yield of semicontinuous extraction of seeds of *Silybum marianum* with dense gases as function of pressure at constant temperatures: (a) liquid and supercritical CO₂; and (b) liquid propane.

Initial conditions are:

$$x(\Theta = 0) = 0 \quad (16)$$

$$y(\Theta = 0) = \frac{1}{[\beta + (1 - \beta)K]} \quad (17)$$

The solution to Eqs. (14)–(17) is the expression for dimensionless solute concentration in effluent:

$$x(\Theta) = A[\exp(a_1 \times \Theta) - \exp(a_2 \times \Theta)] \quad (18)$$

where:

$$a_1 = \frac{1}{2}(-b + \sqrt{b^2 - 4 \times c}) \quad (19)$$

$$a_2 = \frac{1}{2}(-b - \sqrt{b^2 - 4 \times c}) \quad (20)$$

$$A = \frac{(1 - \alpha) \times \Phi}{[\beta + (1 - \beta) \times K] \times \alpha \times (a_1 - a_2)} \quad (21)$$

$$b = \frac{\Phi}{\beta + (1 - \beta) \times K} + \frac{1}{\alpha} + \frac{\Phi(1 - \alpha)}{\alpha} \quad (22)$$

$$c = \frac{\Phi}{[\beta + (1 - \beta) \times K] \times \alpha} \quad (23)$$

The expression for the commulative fraction of a solute extracted up to dimensionless time Θ as defined as:

$$F(\Theta) = \frac{1}{1 - \alpha} \int_0^\Theta x \times d\Theta \\ = \frac{A}{1 - \alpha} \\ \times \left[\frac{\exp(a_1 \times \Theta) - 1}{a_1} - \frac{\exp(a_2 \times \Theta) - 1}{a_2} \right] \quad (24)$$

F approaches unity at large values of time. α is the void fraction in bed and β the porosity of particle.

3.2.1. Estimation of properties for theoretical analysis

The bed void fraction, α , was estimated to be 0.26 as it is in dense layers of spheres with face-centered cubic structure of unit cell (Van Vlack, 1974) and the porosity of the particle, β , was calculated from solid and apparent density (Table 2) to be: $\beta' = 1 - \rho_p/\rho_s = 0.635$ and $\beta = \beta' - \alpha = 0.375$.

The estimation for the initial concentration of extractable substance in the ground seeds was obtained experimentally where the extraction was continued until all extractable substance was removed and was found to be 23%.

The binary diffusion coefficients, D_{AB} , were estimated by the Takahashi method (Reid, Prausnitz, & Polins,

Table 4
Extraction conditions and estimated parameters

T (°C)	P (bar)	$k_f \times 10^5$ (m/s)	k_p (s ⁻¹)	$D_{AB} \times 10^9$ (m ² /s)	$D_c \times 10^{11}$ (m ² /s)	K (-)	AARD ^a (%)
<i>CO₂</i>							
25	200	0.356	0.017	1.814	73.2	175.49	8.36
25	300	0.189	0.009	1.046	42.2	113.34	4.93
40	100	2.030	0.083	7.116	286.9	6003.62	23.1
40	200	0.521	0.024	2.639	106.4	176.56	8.11
40	300	0.258	0.012	1.403	56.6	89.34	6.87
60	200	1.006	0.045	4.550	183.5	375.92	5.85
60	300	0.577	0.027	2.937	118.4	88.76	7.41
80	200	1.433	0.063	6.184	249.4	849.52	17.7
80	300	0.772	0.036	4.009	161.6	66.63	2.29
<i>Propane</i>							
40	60	0.570	0.026	2.751	110.9	16.41	2.08
40	150	0.436	0.022	2.751	110.9	6.98	3.04
40	200	0.407	0.020	2.751	110.9	5.77	1.84
60	60	0.447	0.021	2.183	88.0	15.87	9.86
60	150	0.050	0.002	0.285	11.5	2.73	10.41
60	200	0.020	0.001	0.119	4.8	5.19	20.23
80	60	1.486	0.063	5.692	229.5	60.42	18.25
80	150	0.303	0.014	1.576	63.6	11.50	10.72
80	200	0.163	0.008	0.920	37.1	10.26	8.26

^a AARD(%) = $\frac{100}{N} \times \sum_{i=1}^n \frac{|\text{yield}_{\text{calc}} - \text{yield}_{\text{exp}}|}{\text{yield}_{\text{exp}}}$.

1987) using the Fuller equation. The external mass-transfer coefficients, k_f , were calculated with the Wakao and Kaquei correlation (Brunner, 1984; Goto et al., 1993; Peker et al., 1992) and are presented in Table 4. The adsorption equilibrium constant, K , was calculated (Table 4) with the regression of experimental data and is dependent on temperature and pressure. For the calculation, FORTRAN was used and the Hooke-Yeeves numerical method was applied for the search of the function optimum in order to minimize the deviation between the calculated and experimental data. In the case of CO_2 , at constant pressure 200 bar, K increases with an increase in temperature. Such behaviour shows that, with increasing temperature, desorption decreases and lower yields are obtained with extraction runs. The opposite behaviour is observed at pressure 300 bar, where K decreases with an increase in temperature, which shows that desorption increases and higher yields are obtained at higher temperatures. At constant temperature, K decreases with an increase in pressure. The values of K are generally lower when propane is used as a solvent and vary from 2.7 at 60°C and 150 bar to 60.4 at 80°C and 60 bar.

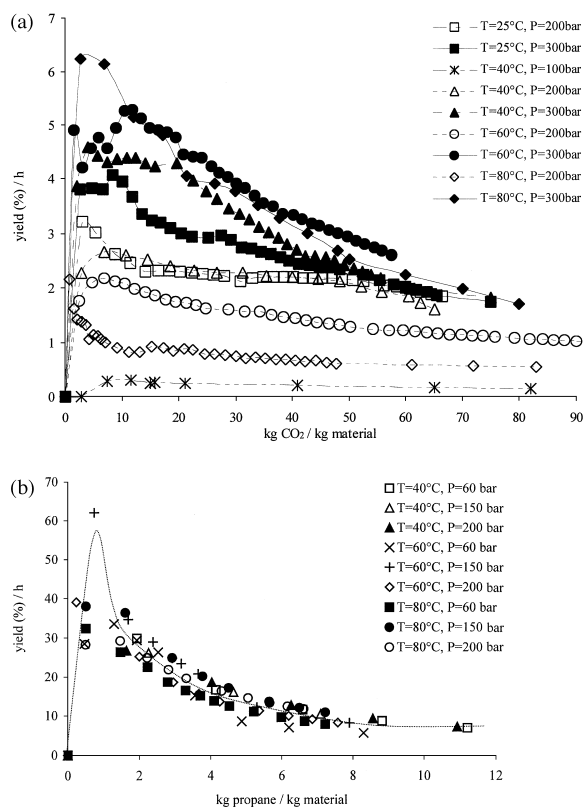


Fig. 7. Extraction rates of semicontinuous extraction of seeds of *Silybum marianum* with dense gases under different operating conditions: (a) liquid and supercritical CO_2 ; and (b) liquid propane.

Figs. 4a, b and 5a, b, c show the comparison of experimental and calculated extraction curves, and Table 4 presents average absolute relative deviation (AARD). When CO_2 is used, AARD is under 10% (from 2.29% to 8.36%) except at conditions 40°C, 100 bar and 80°C, 200 bar, where the adsorption constant K is high and AARD is 23.1 and 17.7%, respectively. In the case of propane, AARD varies between 1.84 and 20.23%.

Results show, that a simplified model which describes desorption process at equilibrium can successfully describe cumulative rate data and this is especially interesting for the observation of the cross-over effect for adsorption-desorption, i.e. how the desorption is changed with the increase of temperature at constant pressure.

For detailed description the concentration history data should be observed, which enables more accurate discriminating between models (Peker et al., 1992).

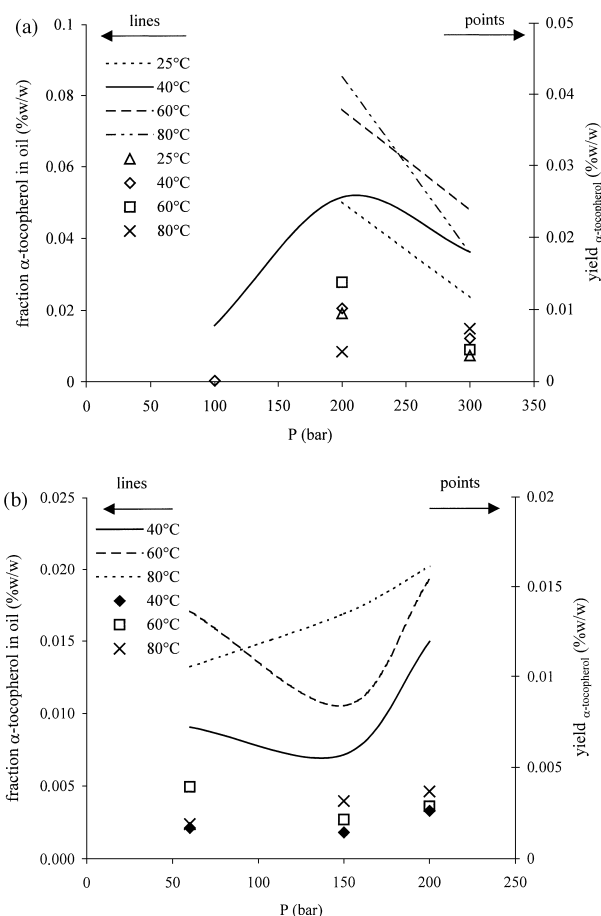


Fig. 8. Concentration of α -tocopherol in extracts obtained with semicontinuous extraction of seeds of *Silybum marianum* with dense gases: (a) liquid and supercritical CO_2 ; and (b) liquid propane.

3.3. Extraction rates

In Fig. 7a, b, the extraction rates at different operating conditions are presented. It can be observed that the extraction rates, in the case of propane, are considerably higher than in the case of CO₂. Furthermore, the course of extraction rate does not depend on operating conditions (pressure and temperature) when propane is used as a solvent. On the other hand, extraction rates obtained with CO₂ depend on pressure and temperature. The extraction rate increases with increasing pressure and at 300 bar it increases with increasing temperature. At 200 bar, the extraction rate decreases with an increase in temperature.

Another important fact, which can also be seen from the extraction results, is that the amount of propane needed for the extraction of oil from *S. marianum* is generally much lower (approx. 10 times lower) than that of CO₂.

3.4. α -Tocopherol content of extracts

Fig. 8a, b presents concentrations of α -tocopherol in the extracts. It can be seen that in case of CO₂ at con-

stant temperature, the content of α -tocopherol is the highest at 200 bar and decreases with a further increase of pressure. The most concentrated extract, which is obtained at 80°C and 200 bar, contains 0.085% of α -tocopherol. The maximal yield, in respect to α -tocopherol, is attained at 60°C and 200 bar (0.014%) and concentration of α -tocopherol in the obtained extract is 0.08%. In the case of propane at temperatures 40, 60 and 80°C, the fraction of α -tocopherol in the extract is relatively low, approximately 0.02% or even lower, and does not vary much with pressure and temperature. The maximal yield in respect to α -tocopherol is attained at 60°C and 60 bar and is 0.004%.

3.5. Acid value of extracts

Fig. 9a, b presents the acid value of extracts as a function of pressure at constant temperature. In the case of CO₂ (Fig. 9a) it can be observed that acid value increases with increasing temperature at constant pressure. At 40 and 60°C, acid value increases with increasing pressure.

In the case of propane (Fig. 9b) acid value decreases with the increasing pressure and increasing temperature. Acid value is in the range from 46 at 40°C and 60 bar to 5.5 at 60°C and 200 bar. At 300 bar, acid value decreases at 80°C.

Generally, opposite an influence of pressure and temperature on acid value, in the case of CO₂ and propane, can be observed. Pressure has a greater influence on acid value of obtained extracts in the case of propane compared to that obtained with CO₂. Furthermore, acid values of the obtained extracts can be much lower when propane is used as a solvent.

It can be concluded that optimal operating conditions for the extraction of vitamin E rich oil with CO₂ are at 60°C and 200 bar, where the yield of extraction is relatively high (19%); the content of vitamin E in the extract is 0.08% and acid value is 31.5.

The content of vitamin E in propane extracts is generally low, therefore propane is not an appropriate solvent for the extraction of vitamin E-rich oil.

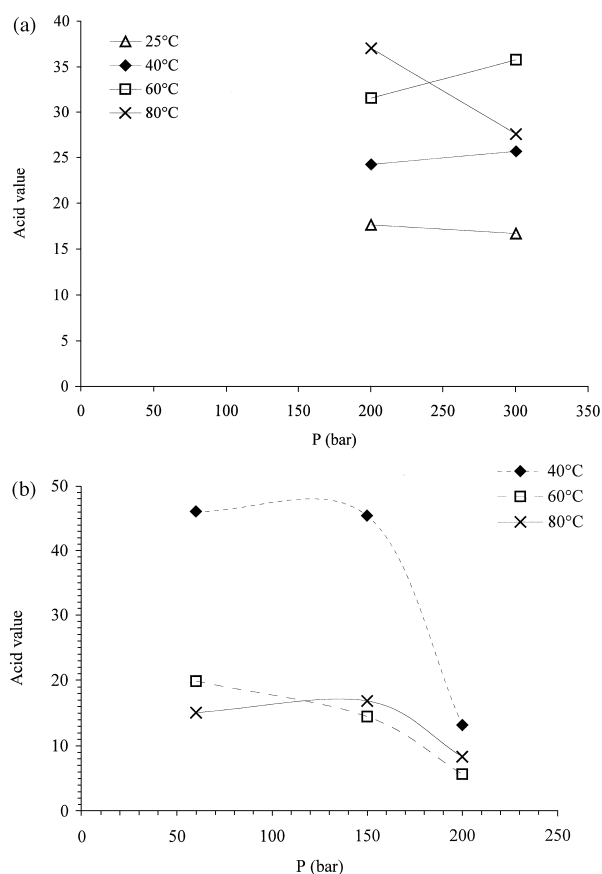


Fig. 9. Acid value of extracts obtained with semicontinuous extraction of seeds of *Silybum marianum* with dense gases: (a) liquid and supercritical CO₂; and (b) dense propane.

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