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Kinetic study of pilot-scale supercritical CO_2 extraction of rosemary (*Rosmarinus officinalis)* leaves

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Abstract

Rosmarinus officinalis (rosemary) extracts were obtained in a supercritical pilot-scale plant. Based on experimental information available in the literature for analytical or low-scale processes, extraction temperature and pressure were selected to be 313 K and 30 MPa. At these extraction conditions, the kinetic behavior of the pilot-scale overall extraction curve were determined with respect to yield, antioxidant activity and carnosic acid content. The overall extraction curve was represented using Sovova's model; the average deviation between measured and calculated yields was lower than 2%. Mass transfer coefficients in the fluid and solid phases were determined and were compared with previous data reported in the literature for low-scale rosemary supercritical extraction.

A two-stage depressurization procedure was accomplished and the effect of both on-line fractionation and extraction time on the antioxidant activity of the samples collected was studied. The antioxidant activity of the different fractions could be straight correlated with the carnosic acid content with a regression coefficient of 0.92.

Keywords: Rosemary; Antioxidants; Supercritical Carbon Dioxide; Extraction; Modeling.

1. Introduction

The use of supercritical carbon dioxide ($SCCO_2$) to obtain extracts from plants is an attractive separation technique for the recovery of valued food ingredients. Particularly, the extraction of antioxidants from vegetable sources using organic solvents has the disadvantage of oxidative transformation during solvent removal [1]; it has been reported [2] that supercritical fluid extraction (SFE) can produce extracts with better antioxidant activity than those obtained using organic solvents.

Rosemary (*Rosmarinus officinalis*) has been recognized as one of the plants with large antioxidant activity. Main substances associated with the antioxidant activity are the phenolic diterpenes such as carnosol, rosmanol, carnosic acid, methyl carnosate, and phenolic acids such as the rosmarinic and caffeic acids [3].

Extraction temperature, pressure, type and amount of modifier determine the solubility of these substances in the supercritical solvent and thus have a direct effect on the extract composition and on the functional properties of the extract. Several authors [3-5] have compared supercritical rosemary extracts with the extracts obtained using liquid solvents (ethanol and hexane) and hydrodistillation, concluding the superior antioxidant activity of SFE extracts.

Carvalho et al. [4] studied rosemary SFE using pure carbon dioxide in low-scale extraction cells (up to 0.1 kg of vegetal material) of different size; different extraction conditions were studied, but no fractionation of the extract was accomplished. SFE extracts at 30 MPa and 313 K resulted to be the ones with the highest concentration of carnosic acid (up to 21.5 %wt) with an overall extraction yield around 5.0%. As well, Bensebia et al. [6] present a study about the effect of several process parameters (solvent flow rate, extraction pressure and temperature, fractionation of the extract) on

the SFE of rosemary leaves (0.01 kg) and calculated the corresponding mass transfer coefficients on the basis of Sovova model [7].

Celiktas et al. [8] demonstrated that even applying the same process conditions, extracts obtained from leaves collected in different locations and harvesting time have rather different composition: for the different sources of rosemary leaves extracted in their work (at 35 MPa, 100°C and with 5% of methanol as co-solvent), the carnosic acid content in the extracts obtained varied from 0.5 to 11.6 % wt.

Fractionation of the extract was first reported by Ibáñez et al. [9]: two successive extraction steps resulted in a low-antioxidant fraction in the first step (10 MPa and 313 K) and a high-antioxidant fraction in the second step (40 MPa and 333 K). In the same way, on-line fractionation of the extract in a depressurization system (comprised of two separators) to produce a selective separation of the antioxidant substances has been studied by these authors [10]; they confirmed a direct relationship between the carnosic acid content and the antioxidant activity of the 16 samples collected employing different extraction and fractionation conditions.

Besides the effect of the extraction conditions and separation schemes mentioned before it has to be considered that the composition of the extract varies during the extraction time. Reverchon et al. [11] reported that extraction time proved to be one of the main parameters that determine the composition of the fraction extracted. Decreasing percentages of lighter compounds (terpenes and oxygenated terpenes) were found as extraction time increase, while higher-molecular-weight compounds (sesquiterpenes and oxygenated sesquiterpenes) showed a continuous percentage increase at increasing extraction times.

The works reported by Bensebia et al. [6], Carvalho et al. [4], Reverchon and Sanatore [5], Celiktas et al. [8], Ibáñez et al. [3, 9] and Cavero et al. [10] are some examples of

the abundant studies reported in the literature about rosemary $SCCO_2$ extraction. All these works were carried out over analytical (less than 1-4 grams of sample) or low-scale apparatus (30-100 grams of sample). In this work a kinetic study of rosemary SFE was carried out using a pilot-scale extraction cell of 2 L capacity and processing 0.6 kg of rosemary sample. This study is our first step towards the large-scale SFE extraction of rosemary leaves.

Pure $SCCO_2$ was used bearing in mind the economic advantage that signifies avoiding the use of cosolvents from an industrial point of view. The extractions were carried out at 30 MPa and 313 K, taking into consideration the high yields and carnosic acid content reported by Carvahlo et al. [4] at these conditions and when no modifier is employed. On-line fractionation was accomplished using a depressurization system comprised of two separator vessels; fractions were collected at different intervals of time in each of the two separators. The kinetic behavior of the different samples extracted was studied with respect to yield, antioxidant activity and carnosic acid content.

2. Materials and methods

2.1 Chemicals

2, 2- Diphenil-1-pycril hydrazyl hydrate (DPPH, 95% purity) were purchased from Sigma-Aldrich (Madrid, Spain) and carnosic acid (≥96%) and carnosol (≥96%) were purchased from Alexis Biochemical (Madrid, Spain). Ethanol, acetonitrile and phosphoric acid were all HPLC grade from Lab Scan (Dublin, Ireland).

2.2 Rosemary leaves preparation

The rosemary sample (Rosmarinus officinalis L.) consisted of dried rosemary leaves obtained from an herbalist's producer (Murcia, Spain). Rosemary leaves were collected during September and dried using a traditional method previously described [9]. Cryogenic grinding of the sample was performed under carbon dioxide and the ground plant material was sieving to sizes between 500 and 1000 μm. The whole sample was stored at -20ºC until use.

2.3 Supercritical extraction method

Extractions were carried out in a pilot-plant-scale supercritical fluid extractor (Thar Technology, Pittsburgh, PA, USA, model SF2000) comprising a 2 L cylinder extraction cell and two different separators (S1 and S2), each of 0.5 L capacity, with independent control of temperature and pressure. The extraction vessel has a height/diameter ratio of 5.5 (0.42 m height, 0.076 m internal diameter). For each experiment, the cell was filled with 0.6 kg of rosemary.

Extraction and fractionation were performed under the experimental conditions shown in Table 1. Temperature was set to 313 K in the extraction vessel and in both separators. Extraction E1 was carried out for 8 h without fractionation of the extract and collecting samples at intervals of 2 h. For E2 assay the cascade decompression system produced two different extracts which were collected in S1 and S2 at intervals of 1.5 h (see Table 1). CO_2 flow rate was 2.4 kg/h in both E1 and E2 experiments. All extracts were kept under N_2, at -20°C in the dark until analysis.

2.4 HPLC analysis

The analysis of the samples was carried out in an HPLC (Varian Pro-star) equipped with a Nova Pack C_{18} column (Waters) of 15 mm × 4.6 mm and 3.5 μm particle size. The mobile phase consisted of acetonitrile (solvent A) and 0.1% of phosphoric acid in water (solvent B) applying the following gradient: 0–8 min, 23% A and 8-20 min, 75% A. This last composition was kept until the end of the chromatogram and initial conditions were gained in 5 min. The flow rate was constant at 0.7 mL/min. Injection volume was 20 μL and the detection was accomplished by using a diode array detection system Varian storing the signal at a wavelength of 230, 280 and 350 nm. The analysis is based on Almela et al. [12].

2.5 Antioxidant activity by the DPPH test

The effect of each extract on DPPH radical was estimated according to the procedure described by Brand-Williams et al. [13]. An aliquot (50 μl) of ethanol solution prepared from the extract concentrations (from 20 to 1 μg/ml) was added to 1.950 μl of DPPH in ethanol (23.5 μg/L) prepared daily. Reaction was completed after 3 h at room temperature and absorbance was measured at 516 nm in a Shimazdu UV-120-01 spectrophotometer (Shimazdu, Kyoto, Japan). The DPPH concentration in the reaction medium was calculated from a calibration curve determined by linear regression (y = 0.0247x-0.0029, R^2 = 0.9999). Ethanol was used to adjust zero and DPPH-ethanol solution as a reference sample.

This method consists in the neutralization of free radicals of DPPH by the antioxidant extracts. The percentage of remaining DPPH against the extract concentration was then

plotted to obtain the amount of antioxidant necessary to decrease the initial DPPH concentration by 50% or EC_{50}. The lower the EC_{50}, the higher the antioxidant power.

3. Mathematical modeling

The mathematical model of Sovova [7] was applied to represent the experimental overall extraction curve (OEC) obtained in the pilot-scale SFE of rosemary leaves.

The model is based on the assumption that X_p of solute is easy accessible to the solvent (due to cell wall disruption) while the rest (X_k) remains inside cell walls. Thus, the SFE process is divided in three steps:

- The constant extraction rate period, where only the easily accessible solute is removed and thus, is controlled by convection in the fluid phase;
- The falling extraction rate period, where both convection and diffusion are important;
- And the diffusion controlled extraction rate period, where the remaining solute is only inside the cell walls.

Additionally, it is considered that the supercritical solvent flows axially through a cylindrical extraction bed, the solvent is solute-free at the bed inlet and particle size distribution is homogeneous throughout the extraction cell.

Based on these assumptions Sovová [7] solved the mass balance equations for both fluid and solid phases, leading to the following equations to calculate the mass extracted (m) as a function of extraction time (t):

Constant extraction rate period: $m = Q\,Y^{*}\left[1-\exp(-Z)\right]t$ (1)

Falling extraction rate period: $m = Q\,Y^{*}\left[t - t_{CER}\exp(Z_w - Z)\right]$ (2)

Diffusion controlled extraction rate period:

$$m = m_{SI}\left\{X_o - \frac{Y^{*}}{W}\ln\left[1+\left[\exp\left(\frac{WX_o}{Y^{*}}\right)-1\right]\exp\left[\frac{WQ(t_{CER}-t)}{m_{SI}}\right]\left(\frac{X_k}{X_o}\right)\right]\right\} \quad (3)$$

Where:

$$Z = \frac{m_{SI} k_{YA} \rho}{Q\ (1-\varepsilon)\rho_s} \tag{4}$$

$$W = \frac{m_{SI} k_{XA}}{Q\ (1-\varepsilon)} \tag{5}$$

$$Z_W = \frac{ZY^*}{WX_o} \ln\left\{ \frac{X_o \exp\left[WQ\ (t - t_{CER}) / m_{SI}\right] - X_k}{X_o - X_k} \right\} \tag{6}$$

$$t_{CER} = \frac{m_{SI}(X_o - X_k)}{Y^* ZQ} \tag{7}$$

$$m_{SI} = X_o F \tag{8}$$

Process parameters needed to apply the model are: bed porosity (ε), CO_2 mass flow rate (Q), mass of feed (F) and solid density (ρ_s). Additionally, extraction temperature and pressure define CO_2 density (ρ), solubility of the extract in the extraction solvent (Y^*) and global extraction yield (X_o).

Model parameters which are optimized according to the experimental OEC are the intra-particle solute ratio (X_k) and the fluid phase and solid phase mass transfer coefficients (k_{YA} and k_{XA}).

4. Results and discussion

Considering the extractor volume (2 liters) and the mass of rosemary leaves load (0.6 kg) the apparent bed density is ρ_{app} = 300 kg/m^3.

As mentioned before, extractions were carried out at 30 MPa and 313 K, since high extraction yields are reported in the literature at these process conditions and when no modifier is employed. The CO_2 flow (Q) was selected according to the correlation proposed by Carvalho et al. [4] to maintain the same kinetic behavior in two different SFE units:

$$\frac{Q_2}{Q_1} = \left(\frac{F_2}{F_1}\right)^2 \times \frac{H_1}{H_2} \times \left(\frac{D_1}{D_2}\right)^3 \quad (9)$$

where H and D are, respectively, the extraction cell height and diameter and F is the mass of vegetal material placed into the extraction cell.

Carvalho et al. [4] reported high extraction yield (ca. 4.0%) in the $SCCO_2$ extraction of 0.0307 kg (F_1) of rosemary leaves after 4 hours of extraction at 30 MPa and 313 K, and using: (a) 2.8 H/D extraction cell (H_1=0.095m; D_1=0.0339m) and Q_1 = 0.3 kg/h; (b) 0.67 H/D extraction cell (H_1=0.0367m; d_1=0.0548m) and Q_1 = 0.189 kg/h. In both cases, and considering the dimensions of the extraction cell employed in this work (H_2=0.42m; D_2=0.076m) and the mass of rosemary placed into the extraction cell (F_2 = 0.6 kg), the CO_2 flow resulted from Eq. (9) is $Q_2 \approx 2.4$ kg/h. This CO_2 flow should provide for our large-scale SFE unit a kinetic behavior similar to that observed for Carvalho et al [4]. in the low-scale SFE units.

Tables 2 and 3 report the mass collected, respectively, in extractions E1 and E2 on Table 1. Also given in the corresponding tables are the EC_{50} values and the carnosic acid content of the different fractions obtained in the separators at the different intervals of time.

The OEC obtained by merging the results obtained for E1 and E2 assays are shown in Figure 1, together with some of the data reported by Carvalho et al. [4]. As can be observed in the figure the kinetic behavior of the low-scale SFE units with 0.67 and 2.8 H/D ratios is reasonably reproduced in our pilot-scale extraction experiment, although is somewhat delayed. On possible reason of this retarded kinetic behavior could be the larger particle size employed in our assays (500-1000 μm) in comparison to the particle size utilized by Carvalho et al. (660 μm).

4.1 Mathematical modeling of the large-scale OEC

The model of Sovova [7] was applied to reproduce that large-scale OEC and estimate the corresponding mass transfer coefficients. Table 4 shows all model parameters employed.

The solubility of the extract in $SCCO_2$ (Y*) at 30 MPa and 313 K was estimated as the slope of the first part of the extraction curve. Global yield (X_o) was fixed as the asymptotic value for large extraction times ($t \rightarrow \infty$). X_o together with the mass transfer coefficients (k_{YA} and k_{XA}) and the intra-particle solute ratio (X_k) were simultaneously optimized in order to minimize the absolute average deviation (*AAD*) between the experimental and calculate yield:

$$AAD\% = \frac{100}{N} \times \sum \left| \frac{y^{\exp} - y^{cal}}{y^{\exp}} \right| \tag{10}$$

The optimal parameters obtained are given in Table 4 and the *AAD%* resulted to be 1.96%. Also given in Table 4 are some significant parameters, such as the constant extraction rate period (t_{CER}) and the falling extraction rate period. The OEC obtained is depicted in Figure 1, indicating the three different extraction rate periods. As can be observed in Table 4, the resulted value for X_o is 0.053, which is in accordance with the 5% of global extraction yield reported by Carvalho et al. [4] at 30 MPa and 313 K. Additionally, the extract solubility estimated in this work (Y^* = 0.00330 kg/kg) is very similar to the value calculated by Carvalho et al. (0.00335 kg/kg).

Table 5 presents a comparison between the parameters (X_k, k_{YA} and k_{XA}) regressed using Sovova's model in low-scale OEC [4, 6] and in the pilot-scale OEC measured in this work. Figure 2 shows the variation of (a) k_{YA} with solvent velocity and (b) k_{XA} with extraction pressure. The k_{YA} value obtained in this work is quite in accordance with the values reported by Bensebia et al. [6], asserting a k_{YA} increase with a solvent velocity increase. However, the k_{XA} value obtained is around one order of magnitude lower than

those reported by Bensebia et al [6]. This low k_{XA} value is a result of the high particle size employed in our experimental assays (500-1000 μm). Consequently, large amounts of solute remained inside the cell walls (ca. 64% of the extractable solute, according to the X_k value), the constant extraction rate period is quite short (t_{CER} = 547.4 s) and the OEC is mainly governed by mass transfer diffusion in the solid phase.

4.2 Analysis of carnosic acid content and antioxidant activity of extracts

Figure 3 shows the carnosic acid (CA) content (%wt) determined for all fractions collected. The amount of CA in these fractions increases linearly with increasing extraction time. As expected, the fractionation accomplished in E2 produced a selective accumulation of CA in S1 separator. The estimated slope for S2 fractions is clearly higher than those of S1 fractions and the no-fractionated samples. This effect could be explained due to the decreasing amounts of lighter compounds (terpenes and oxygenated terpenes) that are obtained as extraction time increase [11], since these substances are mainly precipitated in S2 separator.

The antioxidant activities of the different fractions obtained increase with increasing CA content (see Tables 2 and 3). The EC_{50} values obtained can be correlated with the amount of CA contained in the sample (Figure 4). The type of correlation obtained is similar to that reported by Cavero et al. [10], although in our experiments much higher CA concentrations were obtained. The correlation depicted in Figure 4 is $EC_{50} = -12.575 \ln(\%wtCA) + 47.872$ with R^2 = 0.92. Indeed, other compounds with antioxidant activity, such as carnosol or methyl carnosate, could be present in the extracted fractions. Yet, the correlation depicted in Figure 4 indicates that carnosic acid is one of the main compounds that set the antioxidant activity of rosemary extracts.

Conclusions

SFE rosemary extracts were obtained in a pilot-scale plant of 2 L capacity at 30 MPa, 313 K and processing 0.6 kg of grinded rosemary leaves. Pure $SCCO_2$ was employed as solvent, and its flow (2.4 kg/h) was set according to the extraction cell dimensions and following a scaling correlation from the literature. Global extraction yield achieved proved to be as high as the ones obtained in analytical or low-scale equipments, although higher extraction time was necessary. This slower kinetic behavior in comparison with low-scale extractions [4, 6] could be attributed to the higher size of solid particles employed, which make the process to be controlled mainly by the solute diffusion in the solid phase.

The antioxidant activity of the fractions extracted shown to be directly related with the carnosic acid content and revealed a significant increase with extraction time.

Acknowledges

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Figure captions

Figure 1. Rosemary extract yield as a function of extraction time obtained at 30 MPa and 313 K. Pilot-scale SFE unit H/D = 5.5 (this work): (■) E1 and (□) E2. Low-scale SFE units [4]: (○) H/D = 2.8 and (△) H/D = 0.67. Lines represent the mathematical model: (····) constant extraction rate period; (—) falling extraction rate period; (– –) diffusion controlled extraction rate period.

Figure 2. Mass transfer coefficients for the SFE of rosemary leaves at 313 K and different extraction pressures (10-30 MPa). (a) k_{YA} as a function of solvent velocity; (b) k_{XA} as a function of extraction pressure. (▲) Carvalho et al. [4]; (●) Bensebia et al. [6]; (■) this work.

Figure 3. Carnosic acid content (%wt) as a function of extraction time. (■) Fractions obtained in E1; (□) fractions obtained in (S1+S2) separators of E2; (▲) S1 fractions of E2; (△) S2 fractions of E2.

Figure 4. Antioxidant activity (EC_{50} values) of the different fractions obtained at 30 MPa and 313 K as a function of carnosic acid content. (■) E1; (▲) S1 separator of E2; (△) S2 separator of E2.

Table 1. Experimental extraction and fractionation conditions employed in the CO_2-SFE of rosemary leaves. Extraction and fractionation temperature: 313 K. S2 separator pressure: 0.1 MPa. CO_2 flow rate: 2.4 kg/h.

Extraction	Pressure (MPa)		Extraction time (h)
	extraction vessel	S1 separator	
E1[a]	30	-	8
E2[b]	30	10	4.5

[a] Samples were collected at intervals of 2.0 h with no fractionation of the extract.

[b] Samples were collected at intervals of 1.5 h with two-step fractionation of the extract.

Table 2. Mass extracted, E_{C50} value and carnosic acid content of the different samples collected in extraction E1.

time (h)	mass extracted (g)	accumulated yield [a]	E_{C50} ($\mu g \cdot ml^{-1}$)	carnosic acid content (%wt)
2	16.14	2.69	21.8	7.8
4	5.24	3.56	9.9	14.7
6	4.72	4.35	7.2	18.0
8	2.40	4.75	6.0	28.0

[a] overall mass extracted / mass load x 100

Table 3. Mass extracted, E_{C50} value and carnosic acid content of the different samples collected in S1 and S2 separators of extraction E2.

time (h)	mass extracted (g)		accumulated yield [a]	E_{C50} ($\mu g \cdot ml^{-1}$)		carnosic acid content (%wt)	
	S1	S2	S1+ S2	S1	S2	S1	S2
1.5	6.29	5.60	1.98	22.3	39.8	12.0	1.8
3.0	3.00	3.75	3.11	14.2	22.1	15.5	7.5
4.5	2.22	2.14	3.83	12.6	18.0	19.0	12.3

[a] overall mass extracted / mass load x 100

Table 4. Process and model parameters obtained for the pilot-scale SFE of rosemary leaves at 30 MPa and 313 K.

Process parameters:	
CO_2 density, ρ (kg/m^3)	910.8
Solid particle density, ρ_s (kg/m^3)	1046.0
Bed porosity, ε	0.71
Extractor height, H (m)	0.42
Extractor diameter, D (m)	0.076
Rosemary leaves load, F (kg)	0.60
CO2 flow, Q_{CO2} (kg/s)	$6.7 \cdot 10^{-4}$
Sovova's model parameters:	
Extract solubility, Y^* (kg/kg)	0.00330
Global yield, X_o (kg/kg)	0.053
Intra-particle solute ratio, X_k (kg/kg)	0.034
Mass transfer coefficient in the fluid phase, k_{YA} (s^{-1})	$3.5 \cdot 10^{-3}$
Mass transfer coefficient in the solid phase, k_{XA} (s^{-1})	$3.0 \cdot 10^{-5}$
Constant extraction rate period, t_{CER} (s)	547.4
Falling extraction rate period (s)	7796.8

Table 5. Mass transfer coefficients obtained using Sovova's model in low-scale rosemary $SCCO_2$ extraction (4,6); and in the pilot-scale OEC measured in this work. For all experiments the extraction temperature was 313 K.

P (MPa)	D (m)	particle size (μm)	F (kg)	Q_{CO2} 10^5 (kg/s)	CO_2 density ρ (kg/m^3)	CO_2 velocity[a] 10^4 (m/s)	X_k (kg/kg)	k_{YA} 10^2 (s^{-1})	k_{XA} 10^4 (s^{-1})	t_{CER} (s)	Reference
10	0.0230	436.4	0.010	8.33	629.9	3.18	0.009	0.91	0.84	4012.9	[6]
12	0.0230	436.4	0.010	8.33	718.4	2.79	0.011	0.71	0.91	3681.9	[6]
15	0.0230	436.4	0.010	8.33	780.9	2.57	0.017	0.67	0.98	3232.9	[6]
18	0.0230	436.4	0.010	8.33	820.3	2.44	0.019	0.64	1.17	2327.9	[6]
30	0.0548	660	0.0307	5.25	910.8	0.24	n. r.	3.90	n. r.	1815.6	[4]
30	0.0339	660	0.0307	8.33	910.8	1.01	n. r.	3.00	n. r.	3127.2	[4]
30	0.0760	500-1000	0.600	66.7	910.8	1.61	0.034	0.35	0.30	574.4	this work

[a] CO_2 velocity = $(Q_{CO2}/\rho)/(\pi D^2/4)$

n. r. = data no reported.

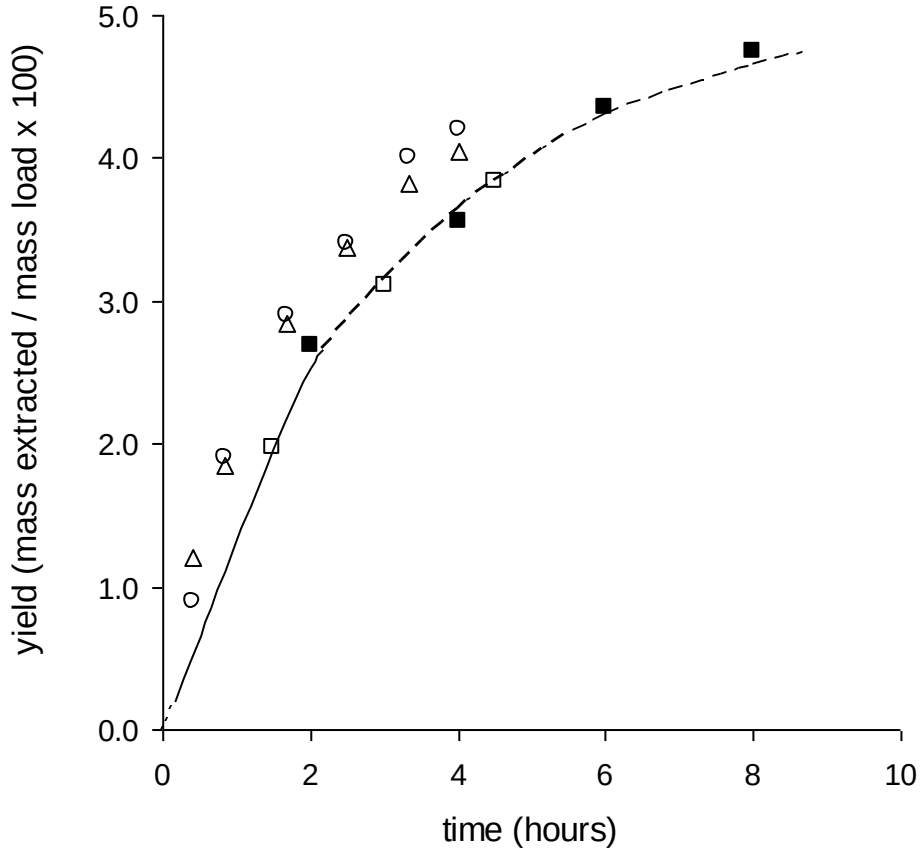
yield (mass extracted / mass load x 100)
5.0
4.0
3.0
2.0
1.0
0.0
0
2
4
6
8
10
time (hours)

Figure 1

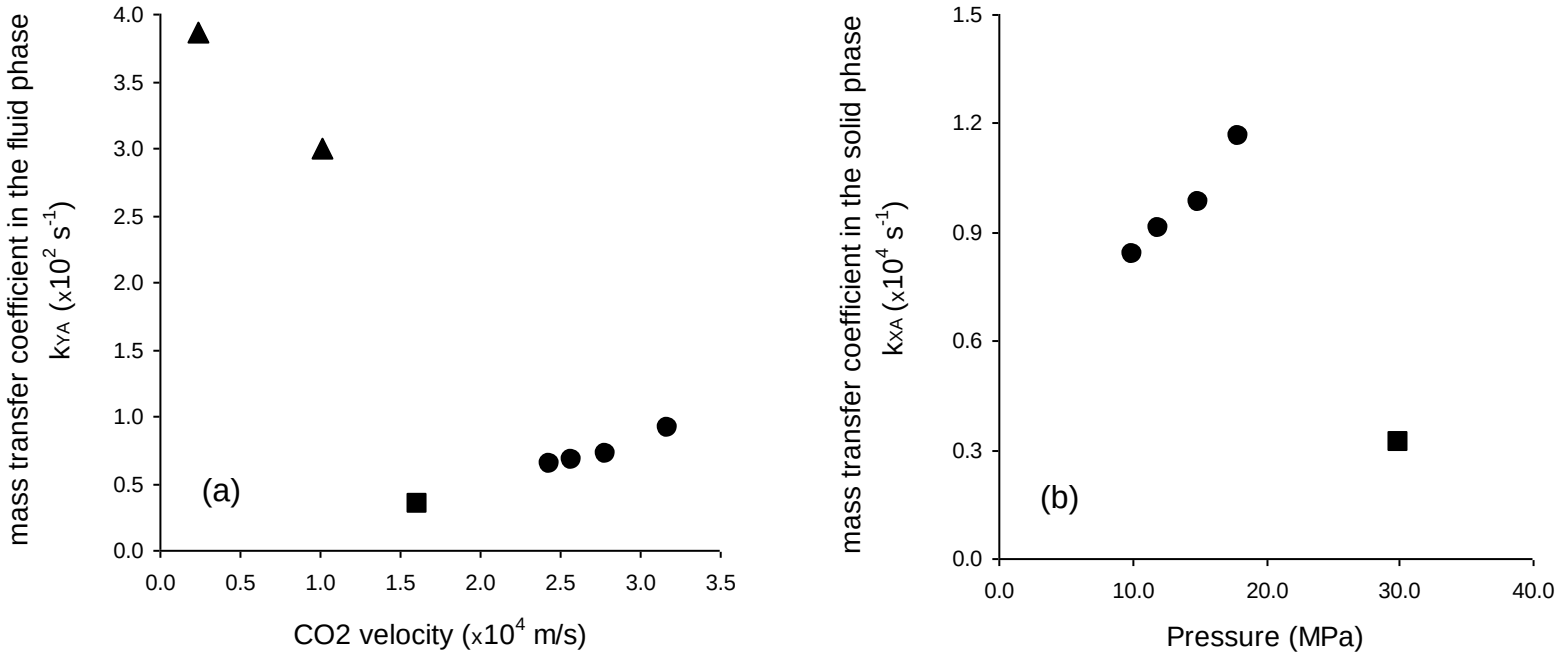
mass transfer coefficient in the fluid phase
k_{YA} (x10^2 s^{-1})
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(a)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
CO2 velocity (x10^4 m/s)
mass transfer coefficient in the solid phase
k_{XA} (x10^4 s^{-1})
1.5
1.2
0.9
0.6
0.3
0.0
(b)
0.0
10.0
20.0
30.0
40.0
Pressure (MPa)

Figure 2

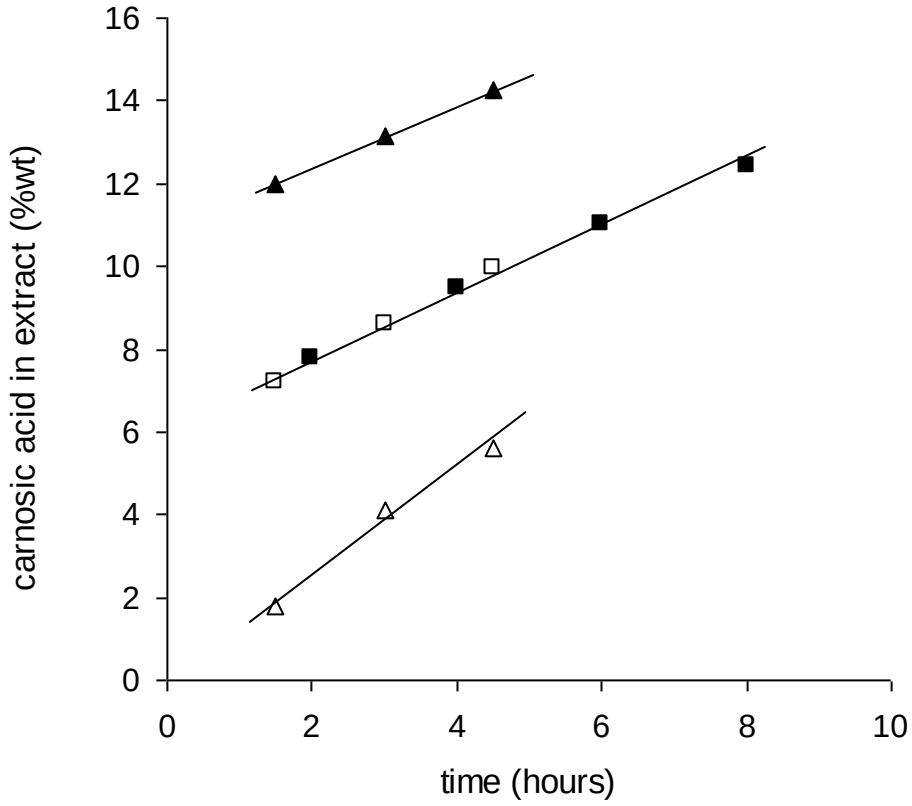

Figure 3

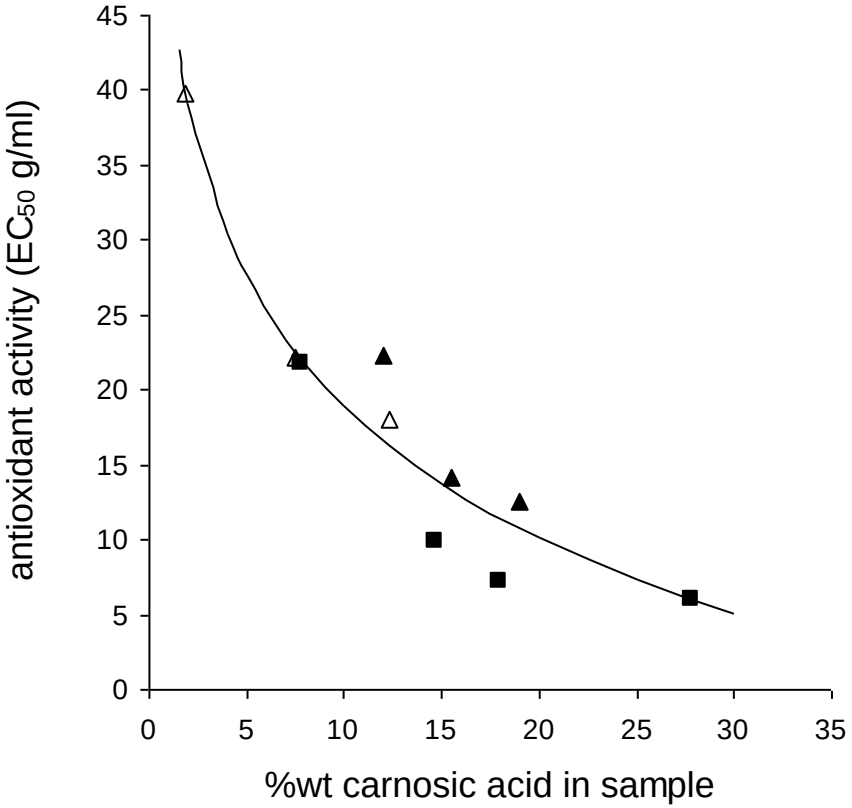
antioxidant activity (EC50 g/ml)
%wt carnosic acid in sample
0
5
10
15
20
25
30
35
40
45

Figure 4

Graphical Abstract

Kinetic study of pilot-scale supercritical CO_2 extraction of rosemary (*Rosmarinus officinalis)* leaves

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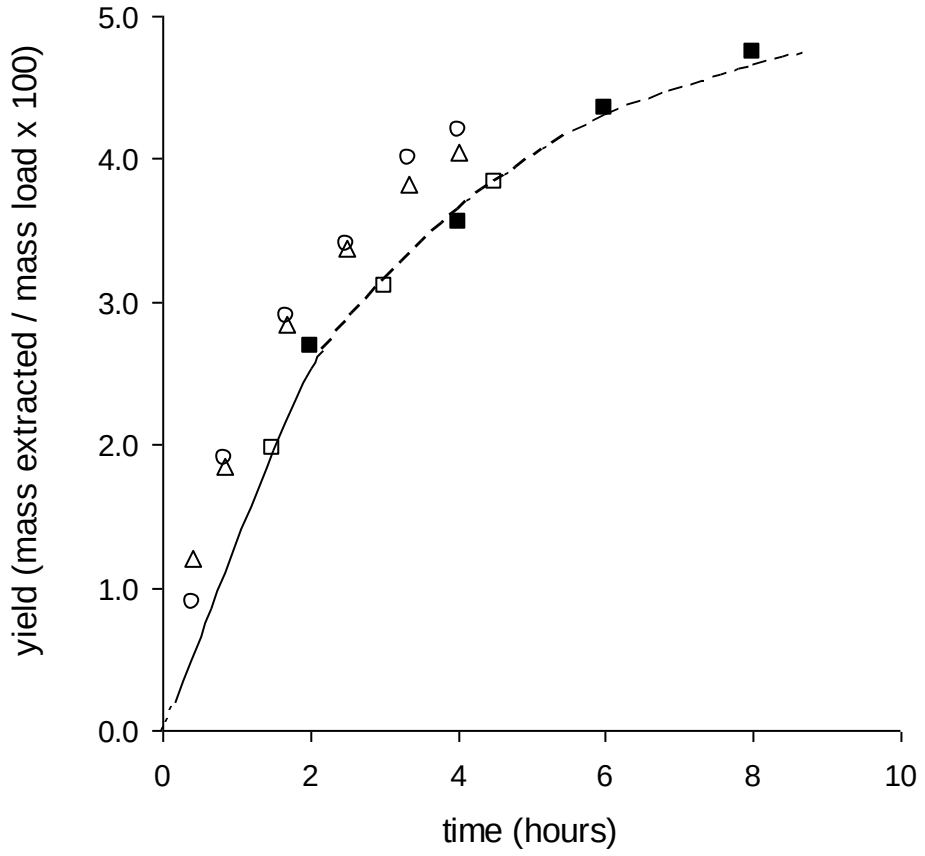

Rosemary supercritical extraction at 30 MPa and 313 K. Comparison between (■, □) large-scale overall extraction curve (this work) and (○, △) low-scale extraction data from the literature. Lines: Sovova's model.