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Supercritical CO₂ extraction of Moroccan argan (*Argania spinosa* L.) oil: Extraction kinetics and solubility determination

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ABSTRACT

Experimental and modelling investigations of supercritical CO₂ extraction of oil from *Argania spinosa* L. kernels were conducted at pressure range from 200 to 400 bar, temperature range of 313–333 K at a CO₂ flow rate of 0.14 kg/h. Regardless of the pressure and the temperature, the highest achievable yield was estimated at 0.63 kg_{oil} / kg_{biomass}. The extraction kinetics were modeled with Sovová's broken and intact cells model. The extraction of type B was found to be the most suited extraction type. Argan oil solubility in supercritical CO₂ was determined and modelled with the Chrastil equation. A retrograde solubility behaviour was observed at 200 bar and the faster extraction kinetics were found at 400 bar and 333 K. The total tocopherols concentration was found between 389.7 and 1688.6 mg/kg_{extract}. Experiments were performed on unroasted and roasted kernels.

1. Introduction

Argan tree (*Argania spinosa* L.) is an endemic tree from southern Morocco and Algeria. The oil extracted from argan seeds is mainly composed of monounsaturated and polyunsaturated fatty acids, carotenoids, sterols, tocopherols and squalene [1–4]. Argan oil is very well known for its antioxidant properties; it is a product of high added value mainly used in food, cosmetic and pharmaceutical industries in Maghreb and Europe [5–12]. When argan ripe fruits are collected they are sun dried then the peel is manually removed resulting in argan seeds. The seeds are then broken to collect the white argan kernel. The production of edible oil is performed by mechanical cold-pressing or by traditional hand pressing from roasted argan kernels by using water. The oil extracted from ground unroasted argan kernels using classical solvent extraction process is used as ingredient in cosmetic applications. For industrial cosmetic applications argan oil is extracted from ground kernels using a lipophilic or halogenated solvent such as cyclohexane, petroleum ether, chloroform or dichloromethane [13]. After solvent extraction process, the extraction yield is about 45–50 %. It is well-known that extraction processes using organic solvents like cyclohexane or dichloromethane, which are toxic and non-selective, lead inevitably to a separation steps which is time consuming and increase the production costs. A well-known alternative to organic solvent

extraction is the supercritical CO₂ (SC-CO₂) extraction. SC-CO₂ is a GRAS (Generally Recognized As Safe) solvent, and thanks to its low critical temperature (304.21 K) it can be used to extract heat-sensitive components. Its solvent power and selectivity towards neutral lipids can be improved by tuning temperature and pressure. Moreover, no separation step is needed since CO₂ is gaseous at ambient conditions of pressure and temperature. Lastly, CO₂ is recycled at industrial scale enabling a clean and compact process.

To our knowledge, only two studies dealing with the SC-CO₂ extraction of oil from unroasted argan kernels were reported in the literature [3,4]. These studies focused on the effects of pressure and temperature on both the extraction yield and the quality of the extracted oil. Through these studies SC-CO₂ extraction process appears to be a promising method for the extraction of oil from argan kernels. Taribak et al. [3] have extracted argan oil from 100 to 400 bar at temperatures from 308 to 328 K with a CO₂ flow rate of 1.2 kg/h. A mass of 15 g of ground argan kernels (mean particle diameter of 800 µm) from southern Morocco was considered for all experiments. The extractions lasted for 3 h.

Comparisons were made with 8 h Soxhlet extraction using *n*-hexane and semi industrial mechanical cold-pressing without water. The SC-CO₂ extraction yields varied between a few percent (100 bar at 318 and 328 K) to 48 % (400 bar and 318 K) while the extraction yields obtained by Soxhlet and mechanical-pressed were 52 % and 45 %, respectively.

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Nomenclature	
a_g	specific surface area of the microalgae powder (m^{-1})
a_s	specific area between the regions of intact and broken cells (m^{-1})
C_u	solute content in the untreated solid ($\text{kg}_{\text{oil}}/\text{kg}_{\text{biomass}}$)
D_{21}	Diffusion coefficient of oil (2) to CO_2 (1) (m^2/s)
d_p	mean particle diameter (m)
e	extraction yield of mathematical model ($\text{kg}_{\text{oil}}/\text{kg}_{\text{insoluble biomass}}$)
E	amount extracted (kg)
k_f	fluid-phase mass transfer coefficient (s^{-1})
k_s	solid-phase mass transfer coefficient (m/s)
K	partition coefficient
n	number of experimental points
N	solid charge in the extractor (kg)
N_m	charge of insoluble solid (kg)
P	pressure (bar)
q	relative amount of the passed solvent ($\text{kg}_{\text{CO}_2}/\text{kg}_{\text{insoluble biomass}}$)
q'	specific flow rate ($\text{kg}_{\text{solvent}}/\text{kg}_{\text{solid}}/\text{s}$)
\dot{Q}	solvent flow rate (kg/s)
r	grinding efficiency or fraction of broken cells
T	temperature (K)
t	extraction time (s)
t_f	extraction time to achieve the SC- CO_2 extraction (h)
V	CO_2 velocity in empty autoclave (m/s)
x_r	transition concentration ($\text{kg}_{\text{oil}}/\text{kg}_{\text{insoluble solid}}$)
x_u	concentration in the untreated solid ($\text{kg}_{\text{oil}}/\text{kg}_{\text{insoluble biomass}}$)
y_s	solute solubility ($\text{kg}_{\text{oil}}/\text{kg}_{\text{CO}_2}$)
<i>Greek letters</i>	
γ	solvent to matrix ratio in the bed ($\text{kg}_{\text{solvent}}/\text{kg}_{\text{insoluble solid}}$)
ϵ	bed void fraction
τ	Tortuosity

The authors reported that at a set temperature the yield increased with increasing pressure. A retrograde solubility zone was reported for pressures up to 200 bar, at 300 bar the extraction yield was reported to be independent of temperature. Concerning the quality of the oil extracted using SC- CO_2 : no significant differences were observed between the physicochemical parameters of the oils extracted at different conditions of pressure and temperature, the quality of the oil did not vary significantly compared to the oil extracted using press or *n*-hexane extraction. The extracted oils contained mainly oleic, linoleic, and palmitic acids. The oils extracted by SC- CO_2 and *n*-hexane Soxhlet had both the required physicochemical properties to be of edible grade according to the recommendations of the official argan oil guidelines (NM 08.5.090, Snima 2003) [14].

Haloui et al. [4] have performed SC- CO_2 extractions of argan oil from southeast of Algeria (Tindouf). Extraction experiments ranged from 100 to 400 bar, temperatures from 308 to 328 K at a CO_2 flow rate of 0.252 kg/h. Extractions were performed on ground kernels with a mean particle size diameter of 1000 μm for 2 h. The biomass was introduced into an extraction autoclave of 5 cm^3 volume, the mass sample was not mentioned. The highest extraction yield was reported to be 83 % at 250 bar and 308 K on their biomass. At 100 bar, the yield was found to be lower than 7 %. The authors have reported a retrograde solubility behaviour at 250 bar. The extracted oils were mainly composed by fatty acids (palmitic, stearic, oleic, and linoleic acid) and squalene.

From these two studies, it appears that compared to classical extraction processes, similar compounds were recovered using SC- CO_2 extraction. A retrograde solubility behaviour was reported at pressures of 200–250 bar. Regardless of the temperature, the extraction yield at 100 bar was reported to be the lowest. Nevertheless, some gaps were identified: the highest extraction yield reported by Haloui et al. was 43.2 % and 38.3 % higher than the highest yield reported by Taribak et al. after SC- CO_2 (48 %) and *n*-hexane Soxhlet extraction (52–60 %), respectively. No extraction curves were reported in these studies. The extraction kinetics could have led to new insights in the comparison and the understanding of the differences in the reported results. It is worth noting that the extraction curves provide very important information such as the time needed to perform a complete extraction, the effects of process parameters on kinetics and extraction yield. Finally, when modelling studies are performed, a better understanding of the extraction phenomena is possible. Indeed, modelling gives access to very important parameters and data like oil solubility in SC- CO_2 and mass transfer coefficient. These data are of prime importance for theoretical knowledge and scale-up studies.

Argan oil is highly prized in cosmetic and food industry and the

investigation of green extraction process for its recovery is a subject of prime importance. Hence, the aim of this work is to complement the studies dealing with the extraction of oil using SC- CO_2 from unroasted and roasted argan kernels by providing useful information about extraction kinetics, argan oil solubility in SC- CO_2 , oil analysis and kinetics modelling. Based on previous studies [3,4], SC- CO_2 extractions from Moroccan argan kernel ranged from 200 to 400 bar, 313–323 K at a constant CO_2 flow rate of 0.14 kg/h. The effect of mean particle size diameter and roasting on extraction kinetics were also investigated at the experimental condition leading to the highest extraction kinetics from unroasted kernels. Soxhlet extractions using *n*-hexane were performed to compare the extracted oil yields and oils compositions. As tocopherols are products of high interest, it was chosen to focus on the concentration of tocopherol in the extracted oils. Extracted oils were analyzed by High Performance Liquid Chromatography (HPLC). Sovová's broken and intact cell (BIC) mathematical model [15] was applied to model the extraction curves.

2. Materials and methods

2.1. Raw material and chemicals

Argan fruits were collected in September 2019 from southwest Morocco (Essaouira region). The fruits were sun-dried for few days. The dried nuts were manually shelled to get the kernels.

Unroasted argan kernels were grinded and sieved into three granulometries. The mean particle diameters " d_p " considered in this study were 400, 750 and higher than 1000 μm . The highest mass fraction after grinding and sieving was obtained for mean particle size diameter of 750 μm . The mass fraction of the lowest mean particle size diameter considered in this study ($d_p = 400 \mu\text{m}$) was lower than 5 % due to a highly fatty biomass. Consequently, SC- CO_2 extraction kinetics were established considering mainly samples of $d_p = 750 \mu\text{m}$.

A sample of fresh argan kernels was roasted by conduction at about 423 K for 20–30 min. This sample was then grinded and sieved at $d_p = 750 \mu\text{m}$.

Samples were stored at 277 K prior to SC- CO_2 extraction experiments to avoid degradation of oil. The water content of the ground biomass was measured at 3.7 wt % through the mass loss of 5 g of sample after oven drying (Memmert, Schwabach, Germany) at 378 K for 24 h. Hence, no drying was applied on the samples. CO_2 was provided by Air Liquide (France) with a purity of 99.7 %, and *n*-hexane (VWR, HPLC grade, France) was used to perform Soxhlet extraction.

2.2. Extraction methods

2.2.1. SC-CO₂ extraction

SC-CO₂ extraction experiments were performed on a laboratory scale extractor supplied by Separex (Champigneulle, France). The process flow diagram of the facility is given in Fig. 1. The extraction autoclave is a 20 cm³ stainless-steel vessel placed in a heater. The CO₂ high pressure pump (3) was a SFC-24 high-pressure liquid CO₂ pump (Interchim France). A high-pressure solvent pump (10), GILSON 307 Pump with standard head pump of 5SC type (Gilson Inc., USA), was used to clean the pipes and the micrometric valve (V3) with ethanol at the end of each experiment. The pipes and the micrometric valve were dried with a flow of gaseous CO₂ for few minutes (Valves V2, V3 and V5 open, valve V4 closed). Extraction experiments with pure CO₂ were conducted with valves V4 and V5 closed. The CO₂ flow and pressure were controlled with micrometric valve (V3). A flowmeter located at the end of the extraction line (8) was used to measure the CO₂ flowrate.

For each experiment, the mass introduced in the extraction autoclave lies between 6 and 7 g. Regarding the small charges used for SC-CO₂ extraction experiments, the mass of extracted oil was estimated relative to the mass losses of the sample in the extraction autoclave. The yield was calculated considering Eq. 1.

$$\text{Yield (kg/kg)} = \frac{\text{mass of extracted oil (kg)}}{\text{biomass introduced in the extractor (kg)}} \quad (1)$$

Experiments were conducted at pressures of 200, 300 and 400 bar, temperatures of 313, 323 and 333 K at a CO₂ flowrate of 0.14 kg/h. The extraction curves were plotted as the variation of the yield as function of the CO₂/biomass mass ratio.

2.2.2. Soxhlet extraction

Soxhlet extractions, using *n*-hexane, were performed for 5 and 8 h in two different capacities apparatus. The mass samples were about 7.34 and 14.77 g when extraction was performed at 8 and 5 h, respectively. At the end of extraction, *n*-hexane was evaporated under vacuum in a

rotary evaporator (Heidolph Laborota 4000) at 313 K. The extraction yield was estimated relative to the mass of extracted oil (Eq. 2).

$$\text{Soxhlet extraction yield (kg/kg)} = \frac{\text{mass of extracted oil (kg)}}{\text{biomass introduced in the Soxhlet apparatus (kg)}} \quad (2)$$

2.3. Tocopherol analysis

Tocopherol analysis was carried out using an Agilent 1290 Infinity HPLC system equipped with a Quaternary Pump, an automatic liquid sample and a fluorimetric detector (FLD 1260). The detection was set at 295 nm for excitation wavelength and at 330 nm for emission wavelength. The separation column was a LiChrosorb® SI60 column (250 mm × 4.6 mm i.d., 5 μm, Merck KGaA Darmstadt, Germany). Elution was performed with HPLC grade solvents *n*-hexane/isopropanol (99/1, v/v) in isocratic mode at a flow rate of 1 mL/min, during 20 min. Column compartment was set at 25 °C. Oil samples were dissolved in 1 mL of mobile phase before injection (1 μL). The identification of tocopherol isomers was confirmed by co-injection of a sample with authentic standards α-, β-, γ- and δ-tocopherols (Sigma Aldrich) then by comparison of retention time. Quantification of the 4 tocopherols was achieved according to the external standard method.

2.4. Scanning electron microscopy (SEM)

Grinded and sieved unroasted argan kernels were observed with a scanning electron microscopy (Hitachi TM3000 Tabletop microscope) before and after extraction experiments. The samples were deposited on an adhesive pastille and metallized with a thin layer of Au-Pd to allow a better visualization. The metallization time did not exceed 30 s, the visualizations were done at 15 kV.

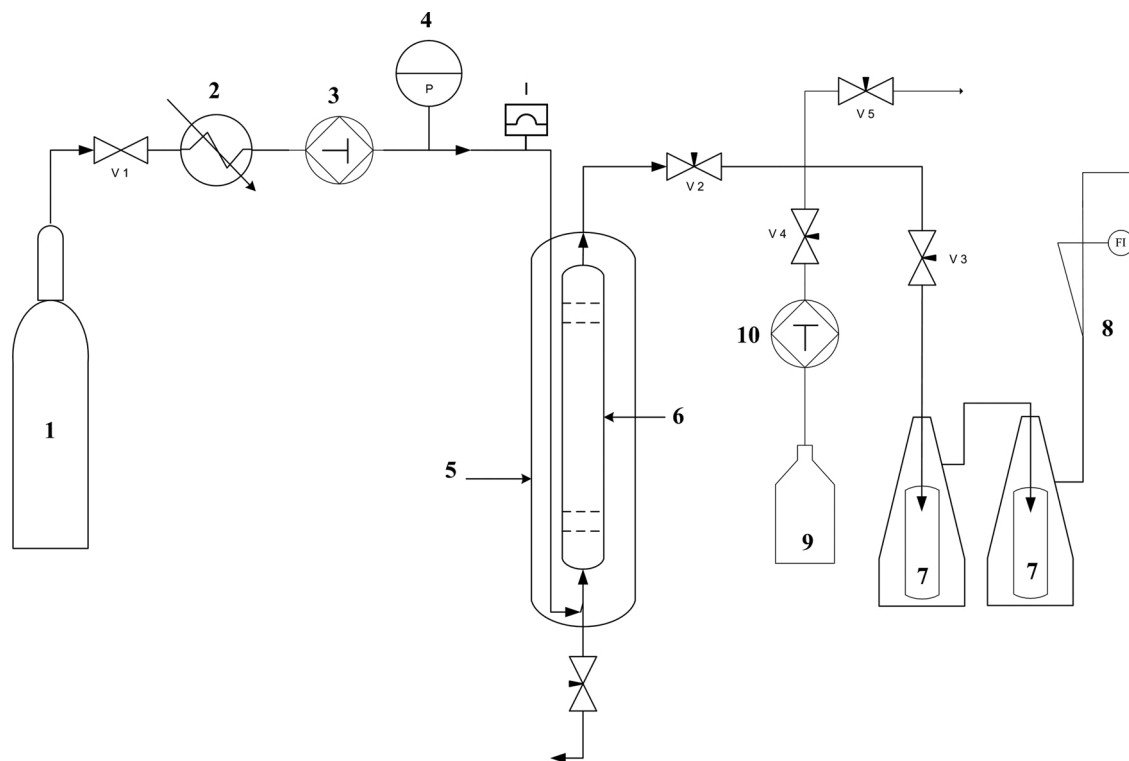


Fig. 1. Process diagram of the extraction setup: (1) CO₂ tank, (2) cooler, (3) CO₂ high pressure liquid pump, (4) pressure gauge, (5) extraction apparatus heater, (6) extraction vessel, (7) glass vessel, (8) flowmeter, (9) ethanol tank, (10) Gilson high pressure solvent pump.

3. Modelling

3.1. SC-CO₂ extraction curves

The extraction curves were modelled using Sovová's BIC mathematical model [15–17]. This model considers the structure of the biomass and accounts for the sudden reduction in extraction rate after the first extraction period that is observed during SC-CO₂ extractions from samples. The extraction can be of type A, B, C or D. In the decision on extraction type, it is possible to refer to the aspect of the extraction curves (Fig. 2).

If the first part of the extraction curve consists of one straight section, the type is A or D. If it consists of two straight sections, it is of type B or C. The shape of the extraction curves reported in this study exhibits a first part consisting in two straight sections. The extraction type is then B or C. For type C, the second straight line starts very early, at a relative amount of the passed solvent $q = q_1$ not far from 1. In the results reported in this study, the second straight line starts at $q = q_1 \gg 1$ for all extraction curves indicating that extraction of type B is the most suitable extraction type. The choice of model equations depends on the flow pattern in the extraction autoclave.

In order to optimize the contact between the argan biomass and CO₂, it is required to have a CO₂ plug flow in the extraction vessel. A CO₂ plug flow means that the CO₂ velocity is uniform throughout the extractor section without any axial dispersion. These flow conditions can be checked using the pore Reynolds number (Re_p) or the modified pore Reynolds number (Re'_p) [18,19] in Eqs. 3–6.

$$Re_p = \frac{\rho_{CO_2} U_p CO_2 d_p}{\mu_{CO_2}} \quad (3)$$

and

$$Re'_p = \frac{\rho_{CO_2} V}{(1 - \epsilon) a_g \mu_{CO_2}} \quad (4)$$

$$\text{with } U_p CO_2 = \frac{V}{\epsilon} \tau \quad (5)$$

and

$$a_g = \frac{6}{d_g} \quad (6)$$

To avoid axial dispersion, the CO₂ flow regime has to be a linear laminar. The threshold between a linear laminar regime to a transitory regime is 6 for the pore Reynolds number and 1 for the modified pore Reynolds number [19]. The threshold for both pore Reynolds numbers between the transitory regime and a non-linear laminar regime for which axial dispersion may occur is 75.

The tortuosity τ has been considered equal to $\pi/2$, corresponding to a CO₂ flow around spherical particles. Under the operating conditions studied in this work, the Re_p lies between 3 and 13, while Re'_p ranges from 1 to 2. Hence, it can be considered that there is no axial dispersion. The CO₂ flow corresponds to a linear laminar regime or to a transitory regime depending on the operating conditions.

The bed void fraction of argan kernels ϵ was estimated by immersing a known amount of biomass powder residue in a test tube with ethanol. The mass of introduced ethanol led to the value of bed void fraction of $\epsilon = 0.63$ which is similar to the one reported by Taribak et al. [3] for a close granulometry. Helium pycnometer (Quantachrome Instruments, Stereopycnometer) was used to measure the biomass solid density, six measurements were performed. The mean argan kernel density was measured at 1228 kg/m³.

Equations for plug flow configuration were chosen. In type B extraction, the first part of the extraction curve is composed of two straight lines (Fig. 2) given by Eqs. 8–10. The first straight line (Eq. 8) is controlled by solute solubility in SC-CO₂. The second straight line (Eq. 10) indicates that the solute concentration in the biomass is considerably reduced and the equilibrium is controlled by solute-matrix interactions. This implies that the solute concentration is much lower than its solubility. The transition between the two straight lines occurs at the transition concentration x_t : the solid-phase concentration became lower than " x_t " and all the solute interacted with the matrix. Hence, the transfer no longer depends on solubility but on the partition coefficient K which represents the constant of proportionality of the linear relationship between solid and fluid-phase concentrations. The transition concentration x_t is equal to the matrix capacity for interaction with the solute, if $x_t = 0$ there is no solute-matrix interaction. Solute-matrix interactions can be related to the desorption of the solute from the biomass. The last part of the extraction curve, described by Eq. 11, is controlled by solute diffusion from intact cells to broken cells.

• First part of the extraction curve

$$e = qy_s \text{ for } 0 \leq q \leq q_1 \quad (8)$$

with e , the extraction yield (kg_{oil}/kg_{insoluble biomass})

$$q_1 = \frac{r(x_u - x_t) - \gamma K x_t}{y_s - K x_t} \quad (9)$$

$$e = q_1 y_s + (q - q_1) K x_t \text{ for } q_1 \leq q \leq q_c \quad (10)$$

• Second part of the extraction curve

$$e = x_u [1 - C_1 \exp(-C_2 q)] \text{ for } q > q_c \quad (11)$$

A straight line of slope y_s , which represents the solubility of the

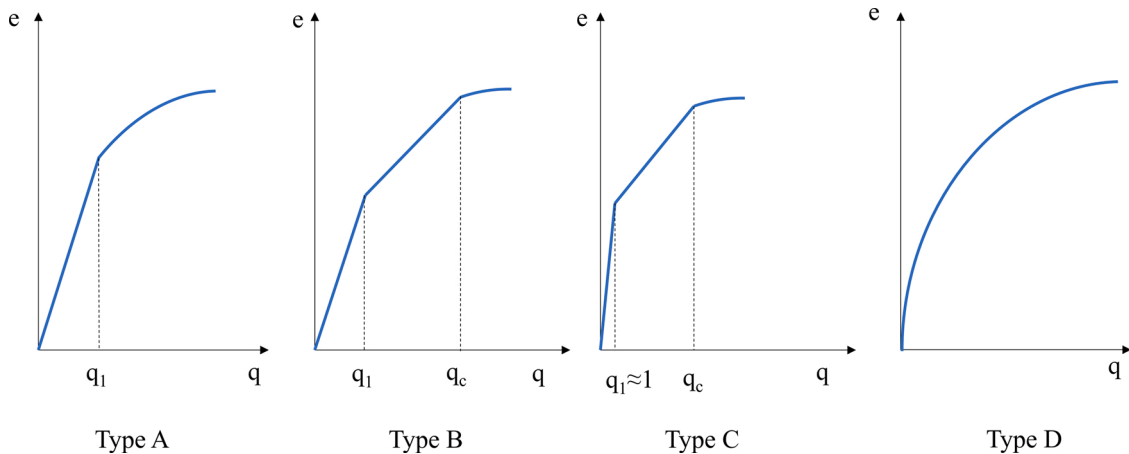


Fig. 2. Type of extraction in Sovová's BIC model.

extracted oil in SC-CO₂ is fitted to the first part of the extraction curve (Eq. 8).

The values of q_c and q_1 were determined by considering that:

- q_c is the value of q at the crossing point with the estimate for the second part of the extraction curve and
- q_1 is the value of q at the crossing point with the first linear part and the second straight part considering the expression of q_1 in Eq. 9.

The second part of the extraction curve ($q > q_c$) is described by adjusting constant parameters C_1 and C_2 . Estimations of parameters $k_s a_s$, the mass transfer coefficient, and r , the fraction of the broken cells, can be obtained by considering Eq. 12 to 17:

$$r = 1 - C_1 \exp(-C_2 q_c) \quad (12)$$

$$k_s a_s = \frac{(1-r)(1-\varepsilon)\dot{Q}C_2}{N_m[1 - ((1-r)C_2/K)]} \text{ for } xt > 0 \quad (13)$$

With:

$$e = \frac{E}{N_m} \quad (14)$$

$$q = \frac{\dot{Q}t}{N_m} \quad (15)$$

$$N_m = (1 - C_u)N \quad (16)$$

$$C_u = \frac{x_u}{1 + x_u} \quad (17)$$

Where “ E ” is the amount of extract (kg), “ \dot{Q} ” is the solvent flowrate (kg/s) and “ C_u ” is the solute content in the untreated solid. The solute concentration in the untreated solid “ x_u ” (with insoluble solid as reference) was supposed equal to the asymptotic extraction yield at infinite time. The adjustable parameters “ C_1 ” and “ C_2 ” were calculated by minimizing the sum of least squares between the experimental and calculated values of “ e ”. The absolute average relative deviation (AARD) given in Eq. 18, was used to evaluate the efficiency of the model.

$$AARD \left(\% \right) = \frac{100}{n} \sum \left| \frac{\text{Experimentalyield} - \text{Calculatedyield}}{\text{Experimentalyield}} \right| \quad (18)$$

In this work, the modelled extraction curves were expressed as the variation of the yield (Eq. 1) as a function of the CO₂/biomass mass ratio.

3.2. Argan oil solubility in SC-CO₂

The solubility of argan oil in SC-CO₂ was calculated by considering the slope of the first linear part of the extraction curve (Eq. 8). The experimental data were modelled by the Chrastil model given in Eq. 19. This model considers that one molecule of solute can associate with k molecules of solvent forming a solvated complex molecule in equilibrium with the fluid.

$$\ln(y_s) = k \ln \rho_{CO_2} + \frac{a}{T} + b \quad (19)$$

With:

- k : the association number
- a : which depends on the heat of solvation and vaporization of solute
- b : a parameter which is dependent on the molecular weight of species

The parameters k , a and b were calculated by minimizing the sum of least squares between the experimental and calculated values of y_s .

4. Results and discussions

4.1. Soxhlet extraction

The yields of argan oil extracted from unroasted kernels by n -hexane Soxhlet were 0.57 and 0.59 kg_{oil}/kg_{biomass} after a period of 5 and 8 h, respectively. These results are in good agreement with the extraction yields reported in the literature: from 0.52 and 0.60 kg_{oil}/kg_{biomass} [3, 20–23] depending on the harvest location and storage conditions [20, 23,24]. Furthermore, an extraction time of 5 h seems appropriate for n -hexane Soxhlet extraction.

4.2. SC-CO₂ extraction kinetics

4.2.1. Repeatability test on unroasted kernels

A repeatability test (Fig. 3) was performed on two sets of measurements at 300 bar and 333 K prior to extraction experiments. The average deviation between the two sets of experiments is about 4.6 % which is satisfactory.

4.2.2. Effects of pressure and temperature on unroasted kernels

The experimental and modelled SC-CO₂ extraction curves are presented in Fig. 4. The effects of pressure are shown in Fig. 4(a)–(c) and the effects of temperature are shown in Fig. 4(d)–(f). One of the major results was observed above 200 bar. At extraction time ranging between 4 and 10 h (corresponding to a CO₂/biomass mass ratio of 86 and 236, respectively), it was possible to reach an experimental yield of 0.62 kg_{oil}/kg_{biomass} for all extraction experiments which is very close to the highest reachable extraction yield according to n -hexane Soxhlet extraction (0.59 kg_{oil} / kg_{biomass} for 8 h). The residue is dry and discoloured suggesting that almost all neutral lipids were extracted, a similar behaviour was reported for *Jatropha curcas* oil extraction [25]. According to the extraction kinetics reported in Fig. 4, the highest extraction yield reported by Taribak et al. [3] (0.48 kg_{oil} / kg_{biomass} at 400 bar and 318 K) should be considered as the extraction yield for a CO₂/biomass mass ratio of 240 kg/kg at their experimental extraction condition (CO₂ flow rate of 1.2 kg/h, a mass sample of 15 g, d_p =800 μm). At 200 bar, regardless of the temperature, the SC-CO₂ extraction curves exhibit very slow extraction kinetics. For a CO₂/biomass mass ratio ranging between 84 and 113 kg/kg (corresponding to an extraction time ranging between 4 and 5 h), the experimental data exhibits only the two first linear parts of type B extraction curve (Fig. 4(d)).

As the highest extraction yield (0.63 kg_{oil}/kg_{biomass}) was systematically reached at pressures above 200 bar, the assumption that a similar tendency may be obtained at 200 bar was made. A similar behaviour was reported on the SC-CO₂ oil extraction from *Jatropha curcas* kernels at 200 bar [25]. A linear extension of the second part of the extraction curves was considered to estimate the end of the second extraction period and the beginning of the third extraction period. The BIC model

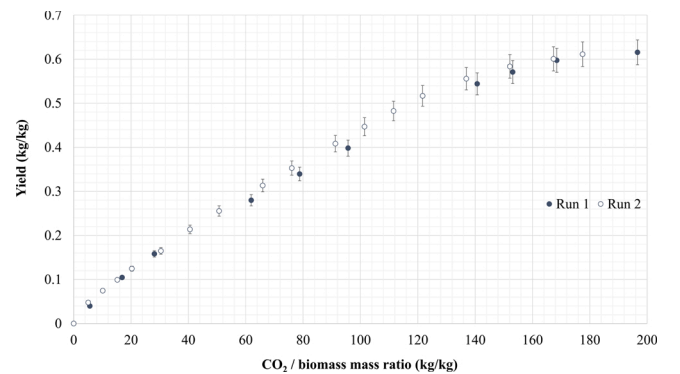


Fig. 3. Repeatability test performed on unroasted argan kernels (d_p =750 μm) at 300 bar and 333 K.

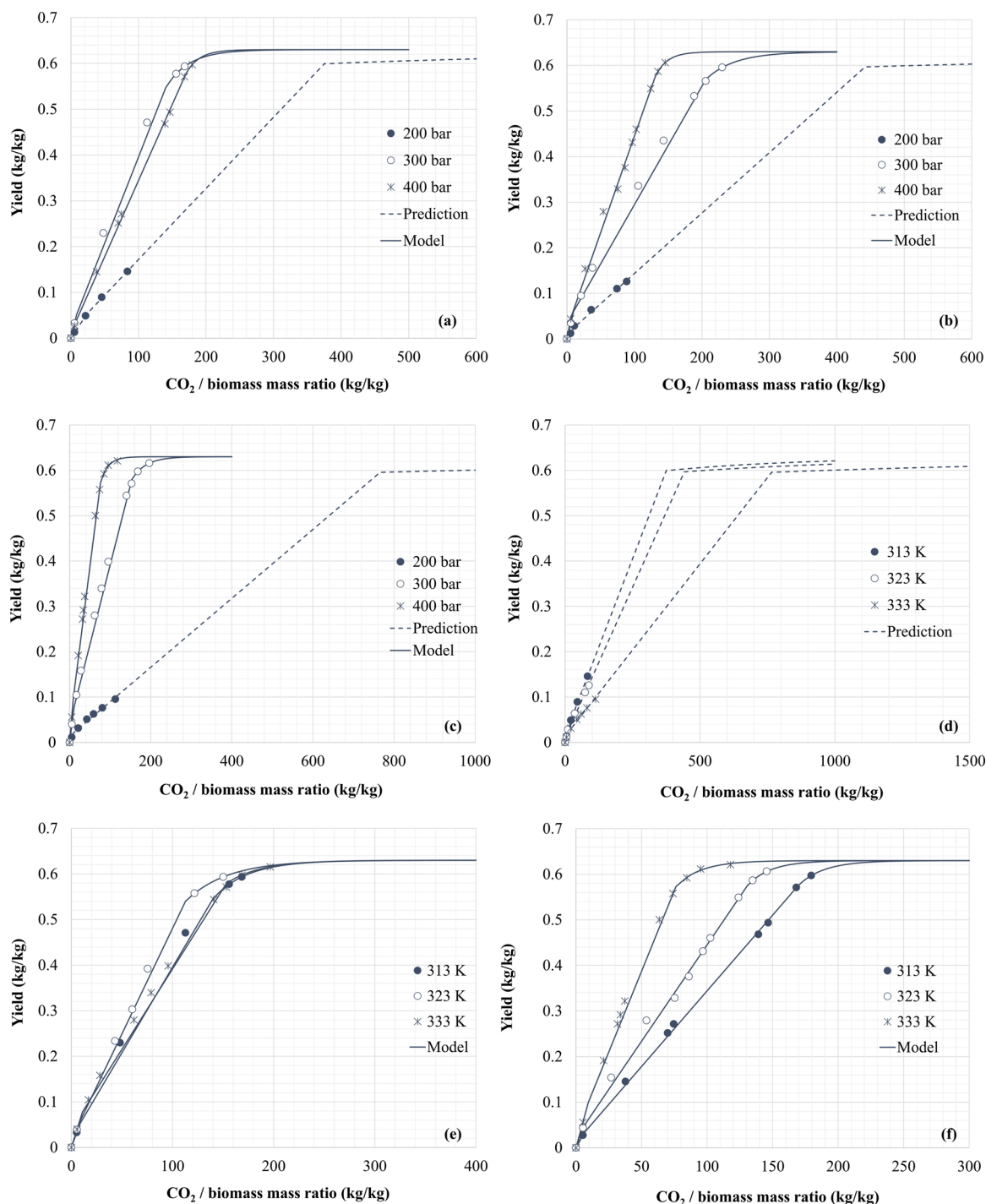


Fig. 4. Experimental and modelled SC-CO₂ extraction curves from unroasted argan kernels ($d_p = 750 \mu\text{m}$). Effects of pressure (a) 313 K, (b) 323 K, (c) 333 K; effects of temperature (d) 200 bar, (e) 300 bar, (f) 400 bar.

was then used as a predictive tool to obtain a possible shape of the overall extraction curves at 200 bar and an order of magnitude of the total extraction times. The predictive curves were given in dotted lines in Fig. 4, the calculated total extraction times were ranging from 17 to 44 h.

At a set temperature, increasing the pressure from 200 to 400 bar leads to an enhancement of the extraction kinetics (Fig. 4(a)–(c)). At 313 K some differences were found: increasing the pressure from 300 to 400 bar did not lead to a significant enhancement of the extraction kinetics. Furthermore, at 400 bar the second part of the extraction curve exhibits stronger solute-matrix interaction compared to the extraction curve at

300 bar due to a lower value of partition coefficient K (Table 1). The highest extraction kinetics were obtained at the highest studied pressure and temperature: 400 bar and 333 K.

A retrograde solubility behaviour was observed at 200 bar (Fig. 4 (d)), a similar observation was reported by Taribak et al. Above 200 bar, increasing the temperature leads to faster extraction kinetics. Nevertheless, at 323 and 333 K at 300 bar, the extraction kinetics were found to be very close (Fig. 4(e)). Considering these results, pressure of 200 bar should be avoided.

Table 1BIC model parameters for $d_p = 750 \mu\text{m}$ from unroasted kernels.

P (bar)	T (K)	N (g)	y_s (g _{oil} /kg _{CO2})	C_1	C_2	$K_s a_s$ (s ⁻¹) × 10 ⁵	r	$K \times 10^3$	x_t (kg _{oil} /kg insoluble solid)	q_1 (kg solvent/kg insoluble solid)	q_c (kg solvent/kg insoluble solid)	γ (kg _{CO2} /kg _{insoluble solid})	AARD (%)
200	313	6.44	2.250	–	–	0.030	0.93	0.940	1.654	63.497	1015.025	1.144	–
	323	6.479	2.229	–	–	0.020	0.93	0.794	1.670	33.088	1195.253	1.072	–
	333	6.221	2.114	–	–	0.010	0.93	0.457	1.662	27.386	2070.917	0.995	–
300	313	6.536	6.114	7.915	0.011	0.894	0.92	2.289	1.640	23.183	379.135	0.730	9.19
	323	6.152	6.857	2.181	0.009	0.036	0.88	2.821	1.641	22.198	304.364	1.203	5.42
	333	6.902	7.086	6.896	0.011	0.465	0.95	2.222	1.586	29.910	414.493	1.147	9.53
400	313	6.538	5.114	518.879	0.019	10.058	0.91	1.999	1.661	18.751	442.487	1.328	3.04
	323	6.503	8.114	130.601	0.021	1.944	0.93	2.591	1.632	15.580	353.554	1.282	3.43
	333	6.652	10.600	4.962	0.019	0.906	0.94	4.433	1.597	25.649	205.841	1.235	6.20

4.2.3. Modelling

The model parameters are reported in Table 1. The AARD ranges between 2.72 and 9.53 % suggesting that the extraction of type B from the BIC model is well suited for describing the SC-CO₂ extraction curves from argan kernels. It denotes the presence of solute-matrix interactions when oil is extracted by SC-CO₂ from unroasted argan kernels. Applying Sovová's mathematical model led to an accurate determination of the highest achievable yield of $C_U = 0.63 \text{ kg}_{\text{oil}} / \text{kg}_{\text{biomass}}$.

Regardless of the extraction conditions, the calculated transition concentrations x_t and grinding efficiency parameter r remained relatively constant around an average value of $1.633 \text{ kg}_{\text{oil}} / \text{kg}_{\text{insoluble solid}}$ and 0.93, respectively. The calculated values of r imply a high volumetric fraction of broken cells in the particles suggesting that the grinding pre-treatment was efficient.

Operating conditions at 333 K, 300 and 400 bar seem to be the most interesting ones from kinetic point of view as they allow a longer extraction period related to solubility (q_1) associated to high solubility of oil in SC-CO₂ (y_s), a short solute-matrix interaction period (q_c) and an enhanced transfer of oil in SC-CO₂ (K). Indeed, by considering the association effect of all parameters (Table 1), it was found a relatively long solubility period (relative high value of q_1), a short solute-matrix interaction period (low value of q_c), high values of solubility and partition coefficients.

SEM images were performed on unroasted argan kernel samples before and after extraction (Fig. 5). After both SC-CO₂ and *n*-hexane Soxhlet extraction (Fig. 5(b) and (c)), the surface aspects were very similar. The residues exhibit a porosity confirming a high surface area favouring solute matrix interactions and the use of type B in the BIC model.

4.2.4. Solubility of argan oil from unroasted kernels in SC-CO₂

Chrastil equation was chosen to model the experimental data of argan oil solubility y_s in SC-CO₂ (Eq. 20). This equation is relatively simple and provides a very good fit between calculated and experimental data as the AARD is about 1.3 %.

$$\ln(y_s) = 7.715 \ln \rho_{CO_2} - \frac{5716.71}{T} - 39.72 \quad (20)$$

The evolution of argan oil solubility according to SC-CO₂ density ($\ln(y_s) = f(\ln(\rho_{CO_2}))$) is given in Fig. 6. Above 200 bar, increasing both pressure and temperature leads to an increase of argan oil solubility in SC-CO₂. The highest solubility, $y_s = 10.6 \text{ g}_{\text{oil}}/\text{kg}_{\text{solvent}}$ was found at 400 bar and 333 K which correspond to the faster extraction kinetics' experimental conditions.

Predictive correlations were developed by Del Valle et al. and Sovová et al. [26–28] for the determination of vegetable oil solubility in SC-CO₂. These correlations allow the solubility assessment of several vegetables' oil solubility in SC-CO₂ and hence can be used for predictive studies. It is interesting to check their ability to assess the solubility of argan oil in SC-CO₂. The calculated solubilities were compared to the experimental argan oil solubility in SC-CO₂ (Table 2).

The deviations between experimental and calculated values ranges between 0.4 and 59.8 %. The highest deviations (57.3 up to 59.8 %) were found at 400 bar and 313 K. These correlations gave an estimation

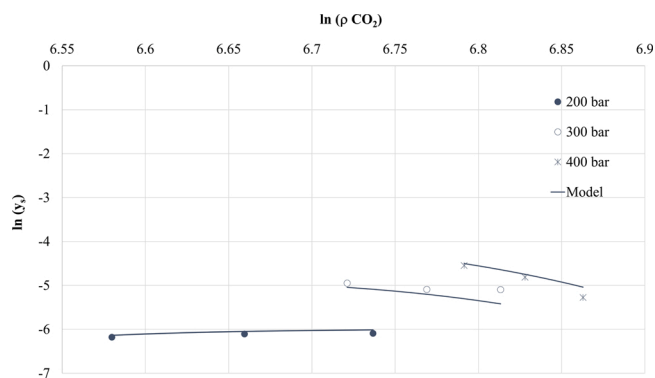


Fig. 6. Experimental and modelled solubility of argan oil from unroasted kernels in SC-CO₂ from 200 to 400 bar and 313 to 333 K.

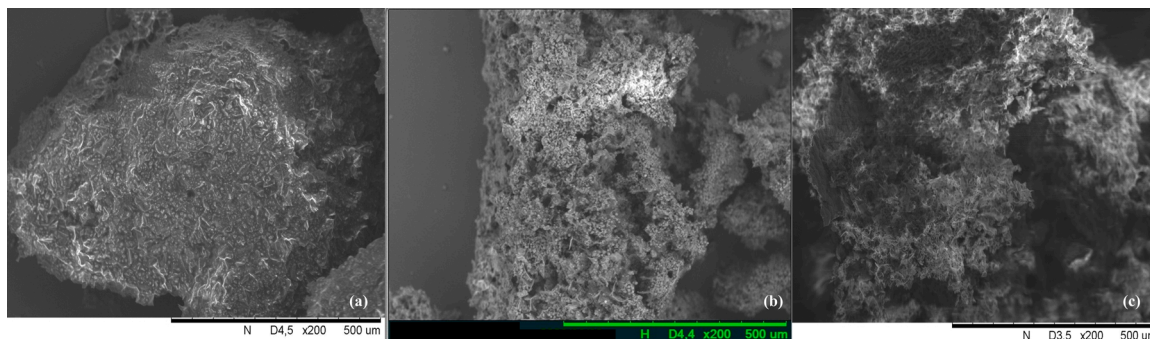


Fig. 5. SEM images of unroasted argan kernels: (a) before extraction, (b) after SC-CO₂ extraction at pressures above 200 bar, (c) after 8 h *n*-hexane Soxhlet extraction.

Table 2
Evaluation of argan oil solubility in SC-CO₂ using empirical correlations.

P (bar)	T(K)	Y _s (g oil /kg CO ₂)			Deviation from experimental values (%)			
		Experimental	Del Valle 1988 [26]	Sovová 2001 [27]	Del Valle 2012 [28]	Del Valle 1988 [26]	Sovová 2001 [27]	Del Valle 2012 [28]
200	313	2.250	3.514	3.248	3.745	35.7	30.4	39.6
	323	2.229	2.707	2.205	2.532	17.7	1.1	12
	333	2.114	2.056	1.370	1.680	0.7	33.8	18.8
	313	6.114	7.403	7.403	8.114	17.4	17.4	24.6
300	323	6.857	7.852	7.593	7.991	21.8	19.1	23.1
	333	7.086	8.125	7.117	7.385	12.8	0.4	4.0
	313	5.114	11.98	12.12	12.73	57.3	57.8	59.8
400	323	8.114	13.94	14.09	14.25	41.8	42.4	43.1
	333	10.6	16.09	15.36	15.21	34.1	31	30.3

with a correct order of magnitude when pressures are lower than 400 bar. The deviations between the experimental values and the calculated ones can be explained by several factors: the solubility was calculated considering the straight line of the first part of the extraction curve considering one experimental point, which can lead to some approximation, the extracted mixture from the other vegetable oils may have a different composition according the operating conditions of extraction finally, the correlation proposed by Del Valle 2012 [28] can predict solubility of vegetable oils within +/- 40 %. Nevertheless, it is recommended to use Chrastil model (Eq. 20) for accurate determinations of argan oil solubility in SC-CO₂ from 200 to 400 bar.

4.2.5. Effects of particle size and roasting on extraction kinetics

The effect of particle size distribution on extraction kinetics was investigated on unroasted kernels at 400 bar and 333 K at a CO₂ flow rate of 0.14 kg/h corresponding to the faster extraction kinetics. The extraction kinetics were reported in Fig. 7(a). Regardless of the granulometry, the slopes of the first part of the extraction curves have very close values (about 10 g_{oil} / kg_{CO₂}) confirming that it is linked to the solubility of argan oil in SC-CO₂ and that argan kernels contain a high amount of free solute on its surface.

Surprisingly, the extraction kinetics at $d_p = 400 \mu\text{m}$ were not found to be the highest ones. The highest and lowest extraction kinetics were obtained for $d_p = 750 \mu\text{m}$ and $d_p > 1000 \mu\text{m}$ respectively (Fig. 7(a)). The adjusted model parameters are given in Table 3. As expected, the fraction of broken cell r was lower when the mean particle diameter of the biomass was higher than 1000 μm (0.8 and about 0.93 for $d_p > 1000 \mu\text{m}$ and $400 < d_p < 750 \mu\text{m}$, respectively). Usually, the transition concentration x_t was slightly lower (average of 1.56 kg_{oil}/kg_{insoluble solid}) than the one obtained with a mean particle size diameter of 750 μm (1.597 kg_{oil}/kg_{insoluble solid}). The partition coefficient K was of the same order of magnitude than the one obtained with $d_p = 750 \mu\text{m}$ for pressures higher

than 200 bar (average of 2×10^3).

When the extraction was performed on a biomass with a mean particle size of 400 μm , the parameter $k_s a_s$ has a value of the same order of magnitude than the one obtained when extraction was performed at 200 bar (on the average of $0.05 \times 10^{-5} \text{ s}^{-1}$). This parameter is the product of the solid-phase mass transfer coefficient (k_s) and the specific area between the regions of intact and broken cells (a_s). Considering that the parameter a_s for $d_p = 400 \mu\text{m}$ should be higher than the one for $d_p = 750 \mu\text{m}$, the parameter k_s should also be higher. The low value obtained is probably due to the low extraction kinetics observed indicating that channelling of SC-CO₂ in the extraction autoclave may probably occur due to sticky kernels caused by the high amount of oil on the biomass surface (oil which should have been expelled from cells after grinding). It is then advised to perform SC-CO₂ extraction at particle size diameter close to 750 μm .

The effect of roasting on extraction kinetics at 400 bar and 333 K was reported on Fig. 7(b). It shows that the extraction kinetics are lower when SC-CO₂ extraction is performed on roasted kernels probably due to a different oil composition due to roasting. The highest extraction yield achieved was the same the one reported in section 4.2.1 (0.63 kg_{oil}/kg_{biomass}). It was achieved after an extraction duration of about 5.1 h. The solubility of the oil extracted from roasted samples in SC-CO₂ was found to be 8.4 g_{oil}/kg_{CO₂} which is about 21 % lower than the solubility reported from unroasted kernels. The extraction curve is also of type B and exhibits a short extraction period related to solubility of oil in SC-CO₂ and a long solute-matrix extraction period.

4.3. Tocopherols concentrations in the extracted oils

Tocopherols concentration in the extracts is reported in Table 4. The composition of the oil extracted from the roasted sample was compared to the composition of a Moroccan commercial food oil named "Argapur"

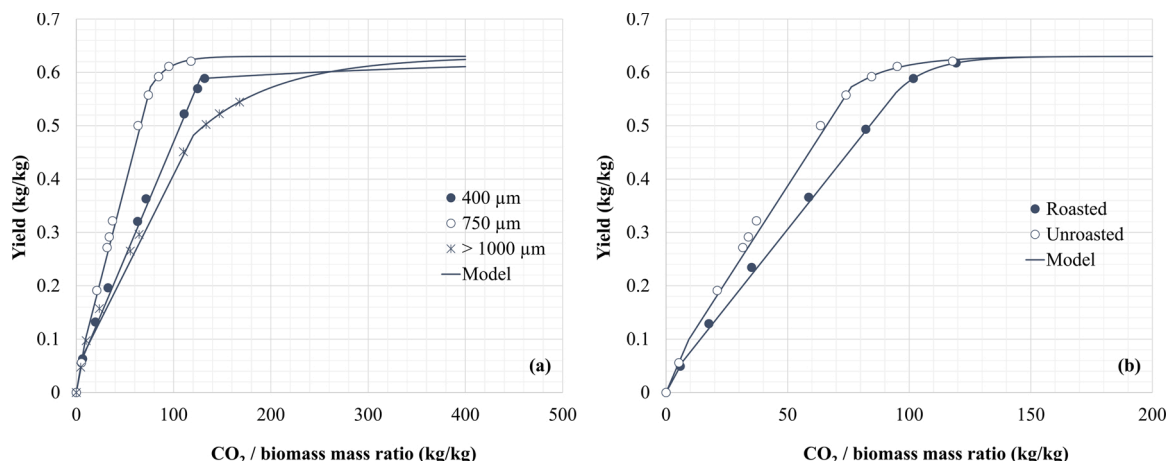


Fig. 7. Effects of (a) granulometry and roasting (b) on extraction kinetics at 400 bar, 333 K and 0.14 kg/h.

Table 3BIC model parameters for unroasted samples ($d_p = 400 \mu\text{m}$ and $d_p > 1000 \mu\text{m}$) and roasted samples ($d_p = 750 \mu\text{m}$) at 400 bar and 333 K.

Roasting	d_p (μm)	N (g)	C_1	C_2	$K_p a_s$ (s^{-1}) $\times 10^5$	r	$K \times 10^3$	x_t (kg _{oil} / kg insoluble solid)	q_1 (kg solvent / kg insoluble solid)	q_e (kg solvent / kg insoluble solid)	γ (kg _{CO2} / kg _{insoluble solid})	AARD (%)
no	400	5.369	0.095	0.001	0.051	0.93	2.721	1.59	18.385	344.302	1.235	4.24
	>1000	7.721	0.952	0.004	0.696	0.80	2.352	1.54	20.259	325.143	1.235	9.09
yes	750	5.965	75.418	0.026	2.115	0.93	3.5	1.64	19.343	254.933	1.235	3.60

Table 4

Tocopherols concentration in the extracted oils.

P (bar)	T (K)	t (min)	α tocopherol (mg/kg extract)	γ tocopherol (mg/kg extract)	δ tocopherol (mg/kg extract)	Total tocopherol (mg/kg extract)
200	313	231	55.9	575.1	52.7	683.6
	323	246	80.6	941.9	68.0	1090.5
	333	316	119.3	1471.3	97.9	1688.6
300	313	472	33.9	454.9	27.1	515.9
	323	610	24.3	346.2	19.2	389.7
	333	524	33.3	490.1	31.9	555.4
400	313	471	28.9	394.4	25.2	448.5
	323	405.8	27.7	399.8	23.0	450.5
	333	336	28.0	383.6	21.9	433.5
Soxhlet		483	34.0	446.6	24.4	505.0
Roasted		305	27.5	366.2	18.9	412.6
Argapur*		-	35.8	484.7	32.8	553.2

* commercial food oil.

produced by ‘‘Moroccan organic’’ company. β -tocopherol was not detected in the extracts in agreement with other studies [3,21,29]. To our knowledge, only Gharby et al. [30] found a very low concentration of β -tocopherol in argan oil: between 2 and 7 mg/kg_{extract} depending on the conventional extraction method applied (Soxhlet, mechanically pressed and traditionally pressed).

For all extraction experiments, the extracts were composed in average of 6.7 % of α tocopherol, 87.6 % of γ tocopherol and 5.7 % of δ tocopherol. A similar ratio was found in the literature when conventional extraction methods were applied [3,21,29,30]. For all extraction experiments, the amount of total tocopherols is at the same order of magnitude than the one reported by Taribak et al. [3]. Nevertheless, the values reported in this study are slightly lower probably due to SC-CO₂ extraction conditions and harvest location [20,24]. The oil extracted from roasted kernels have a lower concentration of tocopherols than the commercial one, the order of magnitude is however similar. This lower concentration may be not only due to harvest location but also to the differences in roasting methods and conditions [31,32].

The highest concentration of tocopherols in the extracts were obtained at 200 bar due to a low amount of extracted oil E compared to the ones obtained at higher pressure. Indeed, at 200 bar the extraction could not have been performed until its end due to very slow extraction kinetics contrary to the extracts obtained at pressure higher than 200 bar (Fig. 4). This interesting result means that tocopherols were mainly extracted at the beginning of the extraction period.

When pressure was higher than 200 bar, the concentration of tocopherols in the extracts was found to be close than the ones obtained after Soxhlet extraction. The closest concentrations were found for the extracts obtained at 300 bar and 313 K. The concentrations of total tocopherols were found to range between 389.7 and 555.4 mg/kg which is in the same order of magnitude than the results reported in the literature when conventional extraction methods were applied [3,21,29,30], as well. Nevertheless, the concentrations of tocopherol reported by Haloui et al. [21] were higher probably due to a different harvest location or period [20,24]. The highest concentration of γ -tocopherol was obtained at 300 bar and 333 K.

5. Conclusions

The extraction of argan oil by SC-CO₂ is very promising. The

extraction kinetics established in this study show that regardless of the pressure and the temperature, the maximal extraction yield (0.63 kg_{oil}/kg_{biomass}) could be reached. Extraction conditions of 200 bar exhibit very slow extraction kinetics (the maximal extraction yield can be reached after an estimated time between 17 and 44 h depending on the temperature) and a retrograde solubility zone. The best extraction kinetics were found at 333 K at 300 and 400 bar, the highest solubility of argan oil in SC-CO₂ was obtained at 400 bar and 333 K. A mean particle diameter of 750 μm leads to the best extraction kinetics, a lower mean particle diameter leads to channelling due to a very fatty biomass.

The application of Sovová’s mathematical model gave access to mass transfer coefficients which are very useful for scale-up studies. The model shows that solute-matrix interactions occur during the SC-CO₂ extraction probably due to oil desorption from porous biomass (confirmed by SEM analysis). The model was also applied to predict the complete shape of the extraction curves at 200 bar.

Tocopherols were mainly extracted during the first period of SC-CO₂ extraction. The ratio and the composition of tocopherols were close and of the same order of magnitude than the one obtained after conventional extraction methods. When pressure was higher than 200 bar, the extraction yield was higher than those obtained by mechanical pressing or traditional extraction and the extraction yield was at the same order of magnitude than organic solvent extraction. Nevertheless, for the fastest extraction kinetics conditions (400 bar and 333 K) the extraction time for reaching the maximum yield was about 4 h, two times lower than Soxhlet extraction, and no separation step between oil and solvent is needed (contrary to Soxhlet or organic solvent extractions) as CO₂ become gaseous at ambient condition.

Considering all the data reported in this study, SC-CO₂ extraction performed at 400 bar and 333 K is the best compromise between yield, extraction duration and concentration of total tocopherols.

Author contribution

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors contributed equally.

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Declaration of Competing Interest

The authors report no declarations of interest.

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