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Supercritical extraction of essential oil from *Juniperus communis* L. needles: Application of response surface methodology

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ABSTRACT

The extraction of oil from *Juniperus communis* needles was investigated using supercritical CO_2. The extraction was carried out varying the pressure in the range of 10–30 MPa, the temperature within 308–328 K, with a solvent flow rate fixed at 0.42 kg h^{-1}, and a mean particle diameter equal to 0.5 mm or less than 0.315 mm. The operating parameters have been optimized using the response surface methodology where a second order polynomial expression was used to express the oil recovery, and the results were satisfactory. The maximum oil recovery relative to the initial mass was 6.55 wt%. It was obtained for an extraction under 328 K, 30 MPa and a particle diameter less than 0.315 mm. Selected samples of extracts were analyzed using gas chromatography–mass spectrometry (GC/MS) and the results show that the most concentrated compounds were germacrene D and 1-octadecene.

1. Introduction

Juniperus (*Cupressaceae*) is a plant widely cultivated in the northern hemisphere. This species grows as trees or shrubs. Traditionally, *Juniperus* has shown several applications, mainly related to its medicinal properties [1–3] and a highly specific flavor [4,5] which are associated to its volatile oil components. Most of the organs of this plant contain essential oils, but it is mainly extracted from the berries [5–10], needles [1,9], branches [1] and roots [2]. The berries contain 0.2–3.42% of volatile oil, depending on specific parameters such as the climate, the soil, the altitude, and the degree of ripeness. Traditionally the oil is collected by extraction using organic solvent: methanol [1,10], n-hexane [2], but the main used process is distillation of the crushed, dried, partially dried, or fermented berries [3–8]. The extracted oil is used in the production of medicinal products with antimycobacterial activity [1,2,9], antioxidant activity [10], diuretic and antiseptic activity as well as in food industry mainly for the production of alcohol beverages, cosmetic and perfume production [4].

To date, 68 species and 36 varieties of *Juniperus* are known [11], but there were few studies on the chemical composition of the local *Juniperus communis* oil extracted from the needles of the plants cultivated in the north regions of Algeria. To our knowledge, only one paper makes reference to the analysis of oils extracted from needles of *J. communis* grown in the National Park of Djurdjura in Algeria [9]. In this paper, the oils were obtained by hydrodistillation, analyzed by GC/MS, and showed high contents of sabinene, α-pinene and β-myrcene. The development of new separation techniques based on the use of supercritical fluids has been the motivating factor of the present study.

The extraction of essential oils from different parts of plants has known a great development due to the use of supercritical fluids in extraction processes where supercritical carbon dioxide (CO_2) is the mostly used since it is non-toxic, relatively inert, non-flammable and readily available as a by-product of the chemical industry. Supercritical CO_2 is considered as a GRAS (Generally Recognized As Safe) solvent. Under ambient conditions of temperature and pressure, CO_2 is gaseous. Thus, it allows a spontaneous and complete separation from extract and residue. Moreover, due to its low critical temperature (304.21 K), supercritical CO_2 can be used to extract thermolabile compounds. Furthermore, supercritical CO_2 can be quite selective and its solvent power can be improved by tuning on temperature and pressure. Finally, CO_2 is recycled at industrial scale, hence enabling a clean and compact operation [12–15]. Supercritical CO_2 extraction has been used as an efficient process in the production of essential oils from different parts of a plant with extracts having important pharmaceutical and food applications [16–20]. Some papers have dealt with supercritical CO_2 extraction of essential oil from the berries and/or the needles of *J. communis* [21,22] from Estonia and Serbia, and from berries

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of *Juniperus virginianna* from USA [23]. The composition of the oil extracted by supercritical CO_2 at 313.15 K and 11.8 MPa was similar to the oil extracted by n-hexane [21] and contained high contents of α-pinene and sesquiterpenes.

Barnislava et al. [22] obtained oils with supercritical CO_2 extraction under 313 K under pressures from 8 to 10 MPa containing monoterpene hydrocarbons, oxygenated monoterpenes, sesquiterpenes and oxygenated sesquiterpenes with compositions depending on pressure.

Eller and Taylor [23] investigated oil extraction from *J. virginianna* using liquid and supercritical CO_2. The rate was higher under the supercritical extraction conditions (373 K and 41 MPa). The highest ratio cedrol/cedrene was obtained at 298 K and 10 MPa.

Supercritical CO_2 extraction was consequently applied in the present work in order to extract essential oil from needles of *Juniperus* cultivated in Algeria. The investigation of the effect of classical operating parameters such as pressure, temperature and particle size on the performance of supercritical CO_2 extraction was carried out. An experimental design through a modeling using the response surface methodology was used in order to optimize the experimental conditions, applying the same methodology used in a previous work carried out by the present authors for the extraction of essential oil still from a local plant, namely Myrtle [24]. Finally, the composition of the extracted oil was determined for a number of samples at different operating conditions.

2. Materials and experimental procedure

2.1. Materials

The used *Juniperus* was grown in Constantine (North Eastern Algeria) and sampled from the November 2013 local harvest at an altitude of 694 m above sea level. As a first step, dried *Juniperus* needles were ground in a mechanical grinder for a short but sufficient duration (15 s) to get a uniform particle size distribution. The obtained charge was then sieved using a Retsch-type vibrating system and only the fractions of diameter equal to 0.5 mm and less than 0.315 mm were kept. The water content of needles was determined as equal to 7.82 wt% by means of drying for 6 h in a vacuum oven at 378 K. CO_2 was supplied by Air Liquide Méditerranée (France) with a purity of 99.7%. Oil extracts were collected in 99.8% pure n-hexane (Carlo Erba, France).

2.2. Experimental procedure and conditions

The set-up used (Separex-4219) was supplied by Separex (Champigneulles, France). This apparatus has already been described in a previous work [24]. The SC-CO_2 extraction set-up is shown in Fig. 1 and was used as follows: the autoclave was filled with the dried needle powder and heated until the desired temperature was reached. Liquid CO_2 is cooled by a cryogenic bath at 277 K, filtered and pumped (using a constant flow pump, model Supercritical 24, Interchim) to fill the extractor until the working pressure was reached. The pressure was controlled by a pressure gauge. Then, the expansion valve was opened and a flow of CO_2 went through the biomass powder at a constant pressure, temperature and flow rate during predefined extraction duration. After passing through the extractor, the CO_2 was expanded through an expansion valve. The CO_2 became gaseous and extracted compounds were collected in a collecting vessel. The CO_2 flow rate was measured by a flow meter placed at the end of the extraction line. Oil extracts were collected in n-hexane and stored in a freezer (255 K). Samples were recovered every 15 min and the mass of essential oil was determined by double-weighing of the extraction cell. The plotted extraction curves represent the recovered mass of essential oil as a function of extraction duration (min) or as a function of solvent/biomass mass ratio (kg/kg). The dynamic extraction was continued for 1 h, after which it was noted that the extracted mass was no more significative.

Table 1
Factors and levels studied for the experimental design.

Parameter	Pressure, *P* (MPa)	Temperature, *T* (K)
Factor	X_1	X_2
Maximum parameter value	30	328
High level	(+1)	(+1)
Average parameter value	20	318
Medium level	(0)	(0)
Minimum parameter value	10	308
Low level	(−1)	(−1)

The reproducibility of the experiments using this extraction set-up and the procedure described above has already been demonstrated in a previous paper [24].

2.3. Experimental design

In this study, an experimental design has been performed in order to optimize two important operating variables of supercritical CO_2 extraction, pressure and temperature, at fixed particle sizes, and in order to achieve high yields of *Juniperus* oil. The other variables such as extraction duration and the solvent flow rate were fixed at 1 h and 0.42 kg h^{-1}, respectively.

The extractions were performed at temperatures and pressures in the ranges of 308–328 K and 10–30 MPa, respectively. This experimental domain corresponds to a commonly operating range encountered for the extraction of essential oils using supercritical CO_2.

Pressure and temperature were chosen for entry values of the experimental design and three levels (two values at the extremity and one value in the middle) were considered for each parameter; this study required thus 18 experiments, i.e. 3^2 for each considered particle size and the experimental domain is as shown in Table 1.

The response or output of the experimental design, noted *Y*, is the recovered mass of essential oil per mass of biomass (g oil/g dry *Juniperus* × 100).

The experimentally recovered mass of oil was analyzed by a response surface method to fit a second-order polynomial equation:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_{11}X_1^2 + b_{22}X_2^2 + b_{12}X_1X_2 \qquad (1)$$

where Y represents the response variable, b_0 is a constant, b_i, b_{ii} and b_{ij} are the linear, quadratic and interactive coefficients, respectively. The coefficients of the response surface equation were determined by using Nemrod-W software (LPRAI, Marseille, France) and the reliability of the model was assessed through the calculation of the correlation factor R^2.

The different operating conditions of the performed experiments are presented in Table 2 and for each set two series of experiments were carried out taking into account the two different particle sizes of the biomass powder: equal to 0.5 mm and less than 0.315 mm. The CO_2 density for those different operating conditions (see Table 2) varied from 395 to 910 kg m^{-3}.

3. Results and discussion

In this section, the results obtained from the present study are presented and discussed.

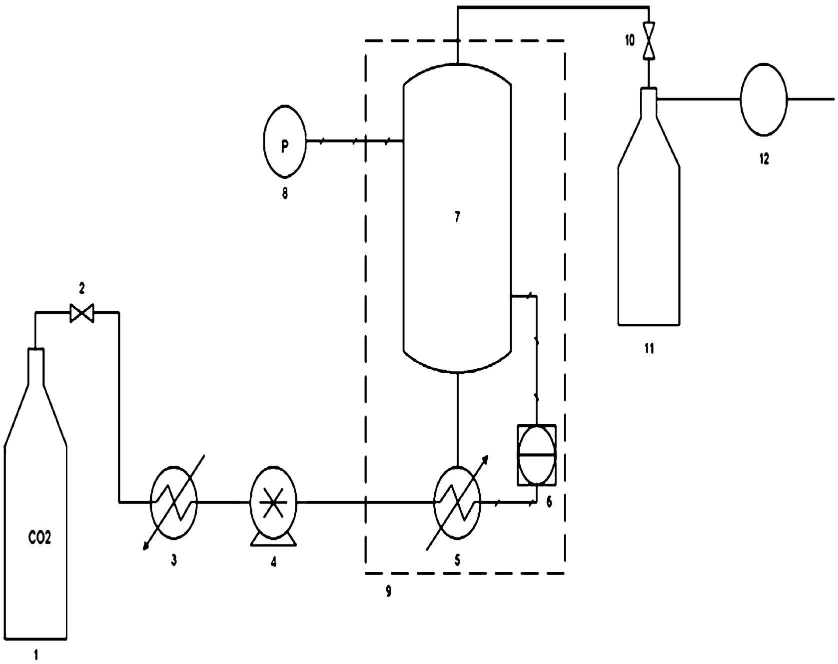

Fig. 1. Laboratory scale extraction set-up: (1) CO_2 tank; (2) valve; (3) cooler; (4) high pressure pump; (5) heat exchanger; (6) temperature regulator; (7) extraction cell; (8) pressure gauge; (9) Thermoregulated area; (10) Expansion valve; (11) Collector; (12) Flow meter.

Table 2
Experimental yields at different operating conditions.

Exp. no	Pressure (MPa)	Temperature (K)	CO_2 density ($kg\,m^{-3}$)	Yield (wt%)$D_p = 0.5$ mm	Yield (wt%)$D_p < 0.315$ mm
1	10	308	726	1.81	2.13
2	20	308	840	2.81	3.92
3	30	308	910	4.21	4.58
4	10	318	520	2.03	2.55
5	20	318	785	3.79	4.16
6	30	318	870	4.71	5.41
7	10	328	395	2.52	3.29
8	20	328	740	3.84	5.20
9	30	328	820	5.59	6.55

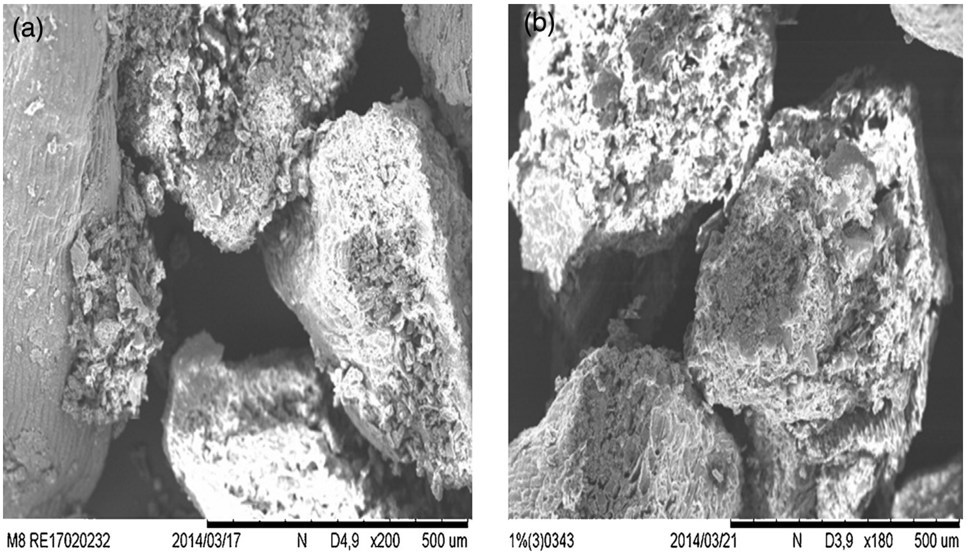

Fig. 2. Scanning electron microscope images of the surface of dry *Juniperus*: (a) biomass before extraction and (b) “smashed” biomass after extraction.

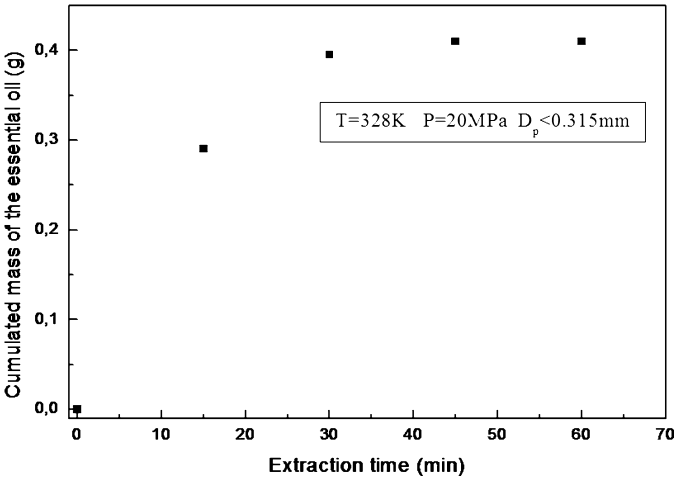

Fig. 3. Cumulated mass of the essential oil of *Juniperus*, as function of extraction time. Extraction performed using CO_2 under 20 MPa and at 328 K with a flow rate fixed at $0.42\,kg\,h^{-1}$ and a particle size diameter less than 0.315 mm.

3.1. Observations of samples

Some micrographs were performed before and after extraction using a Fujitsu electronic scanning microscope (TM3000). The observation and the comparison of the different micrographs show that the extraction process produced certain structural changes in the *Juniperus* solid support. Fig. 2 presents two micrographs of needle powder before extraction (a) and after supercritical extraction (b).

The initial *Juniperus* needles (a) show glandular trichomes mainly of peltate type, which are filled with essential oil. The needle powder underwent damage during the supercritical CO_2 extraction process and trichomes may be destroyed. The whole structure seems more porous after extraction [19].

3.2. Kinetics study

Fig. 3 shows the cumulated recovered mass of essential oil represented as a function of time at conditions: $T = 328$ K, $P = 20$ MPa and $D_p < 0.315$ mm. Generally, the shape of extraction curve illustrates that two possible mechanisms may be acting on the supercritical CO_2 extraction process. During the first period of extraction, corresponding to the first part of the curve, the solutes to be extracted are readily available at the solid surface and hence are easily extracted by the supercritical fluid at a fast and constant rate. For this step, the extraction process is controlled by the external mass transfer resistance [19] and by the solubility of the extracted solutes in SC-CO_2.

In the next stage, the extraction yield of the solutes increases in a much slower manner, tending to a practically constant value at the end of the extraction process. This second part of the curve can be explained by the fact that the superficial solute gets exhausted and then it is extracted from deeper sections of the solid substrate by the solvent. At this point, diffusional and internal mass transfer resistances dominate the extraction process [19]. At considered extraction conditions, the CO_2 mass flow rate being constant and equal to $0.42\,kg\,h^{-1}$, an extraction time of 60 min corresponding to a mass ratio CO_2/biomass of 50. It is clear that the extraction was completed after 30 min of extraction. The mass of essential oil extracted was calculated equal to 5.20 wt% (g oil/g dry *Juniperus* × 100) with respect to the dry-mass fraction of the *Juniperus*. The kinetic study explains why, within the experimental range of 30–60 min, time did not show significant effect on oil yield.

Table 3
Coefficients of the response surface equation ($D_p = 0.5$ mm).

Coefficient	Value	Standard error	Significance %
b_0	3.512	0.180	0.0294**
b_1	0.518	0.099	1.34*
b_2	1.360	0.099	0.0824**
b_{11}	−0.048	0.171	79.5
b_{22}	−0.003	0.171	98.6
b_{12}	0.170	0.121	25.4

* $\alpha < 0.05$.
** $\alpha < 0.001$.

Table 4
Coefficients of the response surface equation ($D_p < 0.315$ mm).

Coefficient	Value	Standard error	Significance %
b_0	4.268	0.099	<0.01**
b_1	0.735	0.054	0.0876**
b_2	1.428	0.054	0.0121**
b_{11}	0.238	0.094	8.5
b_{22}	−0.342	0.094	3.60*
b_{12}	0.202	0.067	5.6

* $\alpha < 0.05$.
** $\alpha < 0.001$.

3.3. Optimization of SC-CO_2 extractions

The effects of operating conditions, namely pressure and temperature, on the supercritical extraction of *Juniperus* essential oil were investigated using the response surface methodology.

Analyses were performed by using experimental oil yields to identify the constants and coefficients of variables, and to investigate the effect of variables. The estimated constants, for both considered particle sizes $D_p = 0.5$ mm and $D_p < 0.315$ mm are presented in Tables 3 and 4, respectively.

Substituting the coefficients values into Eq. (1) for both considered particle sizes $D_p = 0.5$ mm and $D_p < 0.315$ mm, gives the following polynomials:

$$Y(\%) = 3.512 + 0.518X_1 + 1.360X_2 - 0.048X_1^2 - 0.003X_2^2 + 0.170X_1X_2 \tag{2}$$

$$Y(\%) = 4.268 + 0.735X_1 + 1.428X_2 + 0.238X_1^2 - 0.342X_2^2 + 0.202X_1X_2 \tag{3}$$

The response equation fits the experimental data with correlation factor values R^2 of 0.992 and 0.998 for $D_p = 0.5$ mm and $D_p < 0.315$ mm, respectively, indicating a good representation of the variation of the essential oil extraction yield. The fitting between the model and the experimental data is shown in Fig. 4a and b.

However, it is clear that the obtained results could also be fitted with a first order equation, probably due to the limited variation within the considered pressure and temperature ranges of 10–30 MPa and 308–328 K, respectively. However with two parameters (pressure and temperature) and three levels a higher polynomial order would lead to a more accurate representation. For the present work the number of the obtained experimental data points enabled the calculation of the coefficients of a second order model which has also the advantage of involving explicitly the interaction terms (X_1X_2).

The response surface equations indicate that oil yield increases when the pressure increases as well as when the temperature increases.

Fig. 5 illustrates the response surface for particles size equal 0.5 mm (a) and for particles size $D_p < 0.315$ mm (b). These figures

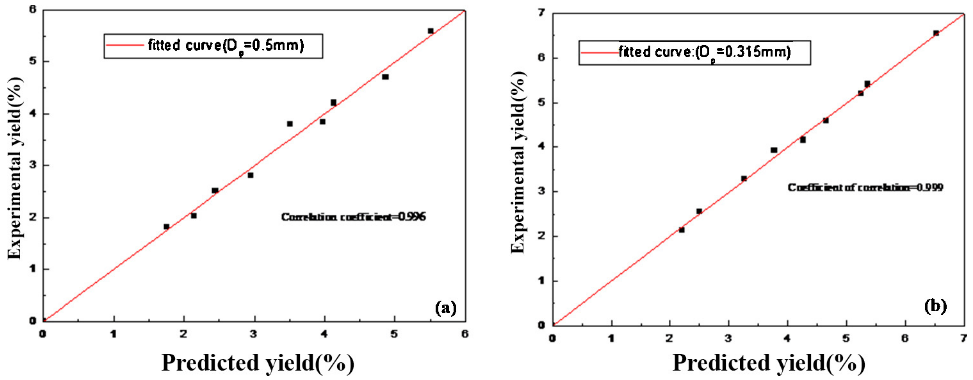

Fig. 4. Reliability of the modeling of experimental data. (a) $D_p = 0.5$ mm and (b) $D_p < 0.315$ mm.

show the influence of temperature and pressure on the yield of *Juniperus* oil. For both particle sizes, the influence of the variation of pressure and of temperature is similar.

In fact in the chosen experimental field of measurements, whatever the temperature, an increase in pressure leads to an increase in oil recovery. This is due to a higher solubility of the different solutes at higher pressures. At a constant pressure, the increase in temperature also leads to an increase in oil recovery, and this for both considered particle sizes equal to 0.5 mm and less than 0.315 mm. Therefore the two corresponding independent models were coherent for both granumetries and did not show any retrograde effect even in the low pressure/high temperature zone. This could probably be explained by the fact that for the considered pressure and temperature ranges, the improvement of CO_2 solvency due a pressure increase is not exactly counterbalanced by an increase in temperature. Different pressure and temperature ranges would perhaps show a possible retrograde zone where an increase in temperature would lead to a decrease in the extraction yield.

3.4. Chemical components of SFE Juniperus extract

Chemical component profiles of *Juniperus* extracts produced under different operating conditions are presented in Table 5. Extracts were analyzed by gas chromatography coupled with mass spectrometry column (HP5MS, 30 m × 0.25 mm × 0.25 μm; inj. split 1 μL). The identified compounds are mainly sesquiterpenes and are listed in Table 5 from the most concentrated to the less concentrated. The most concentrated compounds are 1-octadecene and germacrene D. This latter molecule belongs to the sesquiterpenes family and is known to have antimicrobial and insecticidal properties.

Table 5 gives the different constituents present in the extracts obtained at different operating conditions and also shows the influence of the operating conditions (temperature, pressure and particle size) on the compositions of these recovered extracts as well as on the corresponding yield values.

The highest yield value of 6.55% obtained in the present work at 328 K, 30 MPa and $d < 0.315$ mm is significantly higher than most of the values reported in the literature, at similar conditions, for the essential oil extraction from Juniper needles and where in some cases they are about three times lower [21]. However as reported in the literature extraction yields of 12.5% were also achieved for the extraction of essential from juniper fruit at a pressure and temperature of 12.5 MPa and 323.15 K, respectively [25].

As shown in Table 5, 1-octadecene and D-germacrene are present at relatively high concentrations in the different extracts. However many research works in the literature showed different oil compositions and in most of them α-pinene was the constituent with the highest concentration. For instance an analysis of essential oil extracted from wild Greek *J. communis* L. showed that α-pinene was the major constituent with a mass percentage of 27% followed by, sabinene (13%), germacrene-D (10%) and myrcene (9%) [26].

Similar analyses of a number of Macedonian juniper essential oil samples obtained by hydrodistillation identified 74 components with a presence of monoterpene hydrocarbons ranging from 39.11 to 73.38%. [27]. Therefore all these large extraction yield and oil composition differences observed at comparable extraction

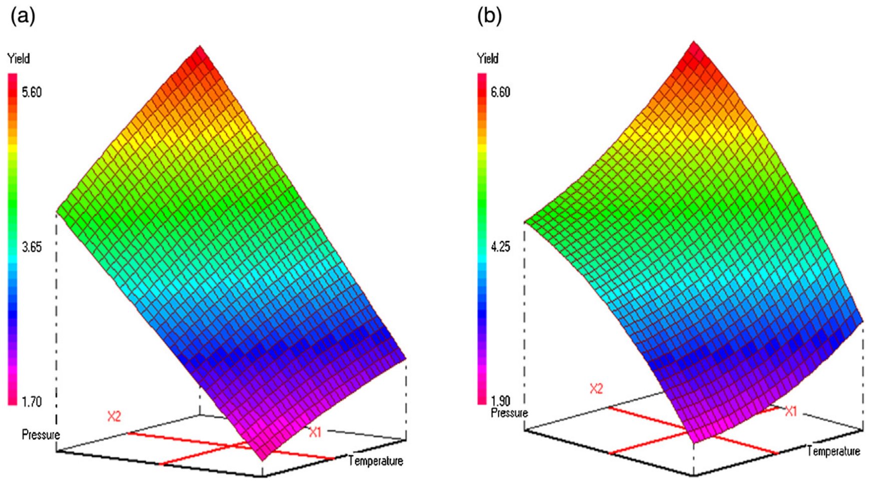

Fig. 5. Response surface plot showing the effect of temperature and pressure on oil yield at a fixed particle diameter: (a) $D_p = 0.5$ mm and (b) $D_p < 0.315$ mm.

Table 5
Composition of main components in some extracts (%).

Compounds	Extract recovered at 318 K; 20 MPa $d = 0.5$ mm Yield of 3.79 wt%	Extract recovered at 328 K; 30 MPa $d < 0.315$ mm Yield of 6.55 wt%	Extract recovered at 308 K; 10 MPa $d < 0.315$ mm Yield of 2.13 wt%	Extract recovered at 318 K; 20 MPa $d < 0.315$ mm Yield of 4.16 wt%
1-Octadecene	7.912	10.060	15.997	15.275
Germacrene D	4.623	3.225	5.570	6.700
α-Cubebene	1.506	1.470	2.831	3.185
Retinol	1.500	1.831	1.904	3.048
Trans caryophyllene	1.929	1.337	2.349	2.772
Palmitic acid	1.049	1.911	2.354	1.961
γ-Cadinene	1.127	0.985	1.766	1.390
α-Humulene	1.550	0.856	1.513	1.776
Manoyl oxide	0.635	0.749	1.192	1.439
α-Cadinène	1.113	0.745	1.367	1.493
Germacrene B	1.253	0.728	1.756	1.687
Citronellylphenylacetate	0.471	0.615	1.037	1.495
α-Pinene	1.787	0.581	0.554	–
Cycloisolongifolene	0.686	0.641	1.248	1.279
α-Copaene	0.488	0.499	0.898	0.928
α-Hylangène	0.569	0.407	0.756	0.744
Calamenene	0.384	0.393	0.661	0.922

conditions justify and encourage the assessment of the extraction performance on each particular plant species like the Algerian Juniper and confirms the results reported in [28].

Finally it should be noted that in the present work no cosolvent was used with the supercritical CO_2 and therefore whatever the percentage of water in the raw material it would not dissolve in supercritical CO_2 since the former i.e. Water is a dipolar constituent and hence is not soluble in a non polar solvent like supercritical CO_2, explaining the reason why only global extract compositions were measured.

4. Conclusion

In this study, the effect of two parameters, temperature and pressure, was investigated for the supercritical carbon dioxide extraction from Algerian *Juniperus* needles for particle diameters of 0.5 mm and less than 0.315 mm. Extractions were performed at temperature and pressure ranges of 308–328 K and 10–30 MPa, respectively, and a solvent flow rate fixed at 0.42 kg h^{-1} during 1 h of extraction. The maximum oil recovery 6.55 wt% (relative to the initial mass of dry biomass) has been obtained for an extraction under 328 K, 30 MPa and the lowest mean particle diameter. The results were analyzed by a response surface methodology in this experimental range and a good agreement was observed between RSM and experimental oil yields. GC–MS analyses of *Juniperus* oil extracted by SC-CO_2 showed that the dominant extracted compounds are germacrene D and 1-octadecene, except for the extract obtained under the conditions leading to the highest yield (30 MPa and 328 K, for a particle diameters less than 0.315 mm).

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