A COMPARATIVE STUDY OF ESSENTIAL OIL EXTRACTION YIELDS FROM ALGERIAN ROSEMARY (ROSMARINUS OFFICINALIS L.) BY SUPERCRITICAL CO_2 EXTRACTION AND HYDRODISTILLATION PROCESSES

Ouzzar M. L., Zermane A., Louaer W., Meniai A-H*

meniai@yahoo.fr

ABSTRACT

The extraction of essential oil from Algerian rosemary leaves was carried out by hydrodistillation and supercritical CO_2 extraction.
The hydrodistillation extraction experiments were performed using a Clevenger-type apparatus, equipped with a cohoba permitting to maintain the mass ratio plant/water to its initial level. The system was operated at atmospheric pressure, with a flow condensation of 4.5ml/min and a ratio plant/water of 1/10. In both methods the only parameter that is changed is the particle size, in order to know its effect on the processes.
The supercritical fluid extraction was carried out using a dynamic extraction unit at a pressure of 100 bars, a temperature of 40° C and a solvent flow rate of 7g/min.
The comparison of the yields of the two processes showed that the supercritical CO_2 extraction led to a better yield, with a value of 2.54% compared to 1.94% obtained for the hydrodistillation. The results also showed that the particle size had an important effect on the two processes, and a decrease of the diameter enhanced mass transfer leading to better extraction yields.
Keywords: Essential oil yield; Rosemary; supercritical CO_2; Hydrodistillation; comparative study

INTRODUCTION

Rosemary (*Rosmarinus officinalis* L.) is a Mediterranean plant growing abundantly due to the favorable coastal climate. It also can be cultivated in arid and rocky areas and can grow in calcareous rich soil. Rosemary is a wild shrub belonging to Labiates family, one to two meters high and with small and always green leaves. It is relatively rich in essential oil which can be extracted from the flower itself or from the leaves, where most of oil glands are located. However, the highest quality of essential oil is obtained from the leaves.
This oil can be used as an aroma in food, and it is also known medicinally for its powerful antioxidant activity [1, 2], its antibacterial, antimutagenic and antiseptic proprieties and as a chemoprentive agent [3-5]. The oil chemical composition depends largely on the influence of extraction conditions and generally the main components of rosemary essential oil are: 1,8-cineol, α-pinene, camphor, verbenone and borneol, whereas others, such as: terpinene-4-ol, α-terpineol, β-caryophyllene, 3-octanol, geranyl-acetate and linalyl-acetate [6], with the most active components being the phenolic diterpenes, primarily carnosic acid, and also carnosol, rosmanol, epi and isorosmanol [7].

The extraction of essential oil from rosemary plants has been performed by means of various techniques like solvent free microwave extraction [8], solvent extraction [9], fast controlled pressure drop process [10], microwave hydrodiffusion and gravity [5], hydrodistillation [4, 5, 8, 11] and supercritical fluid extraction [2, 7, 12], etc. However each technique has an effect on the extraction yield as well as on the oil properties. For example, for steam and hydrodistillation, the elevated temperatures can cause chemical modifications to the oil components and often a loss of the most volatile molecules. When using the solvent extraction, it is very difficult to obtain totally solvent-free products and there is also a loss of the highly volatile components. In contrast, extraction by supercritical fluids generally leads to high-quality and solvent-free products [10].
An analysis of the oil obtained by supercritical fluids extraction and that by steam and hydrodistillation revealed qualitative differences; it has been found that the supercritical CO_2 extraction gives a better selectivity for compounds of interest [13, 14].

The objective of the present work is to compare two different techniques, namely hydrodistillation and supercritical CO_2 extraction, with respect to the extracting yield and also process time. The study was also an opportunity to investigate the effects of the particle size of the plant material on the process performance.

MATERIALS AND METHODS

- Plant material

The used rosemary leaves (Rosmarinus Officinalis L.) were collected from plants growing in Constantine (north east of Algeria). A priori the leaves were air dried in the dark and the moisture content was 5.92 %. Thereafter, the leaves were ground and classified according to their granulometry by passing through the sieve shakers with decreasing diameters.

- Extraction methods

The supercritical CO_2 extraction experiments were carried out in a dynamic extraction unit previously conceived and assembled at the Chemical Engineering Sciences Laboratory in Nancy (LSGC, Nancy, France). Such an apparatus mainly consists of a CO_2 reservoir, an extractor vessel and three separator vessels in series, accompanied by a thermostatic bath, a metering pump, a cryostat, the necessary instrumentation to control the pressures, temperatures, mass flow rates and valves for the extract collection.
The operating temperature and pressure can reach up to 80° C and 25 MPa, respectively, with a maximum gas mass flow rate of 3.2kg/h.
A mass of 20g of the plant material was packed into a sample unit, with glass wool placed at its top and bottom in order to prevent the entrainment of the rosemary during the extraction process, to homogenize the gas flux in the extractor and to fill any dead volume. The glass wool mass used was of the order of 2g. The void fraction of the particle bed was 0.54 and its height was measured before the introduction of the sample unit in the extractor (volume of 125 cm^3, 23mm inside diameter, and 300mm height). This operation was carried out with care in order to avoid any rosemary mass loss. The sample was then allowed to reach the constant extraction temperature before charging CO_2 into the high-pressure pump from the storage cylinder. The CO_2 gas was further compressed to the desired pressure of the pump. After 1h, a time corresponding to the static extraction, the extractor valve was opened and the intermediate valves between the separators were continuously adjusted in order to regulate the pressure and, hence, to keep a constant flow rate. Samples were taken every 15min, by means

of the valves placed at the bottom of the separators, and weighed to obtain the mass of the essential oil. The dynamic extraction was pursued for 3.5 hr, after which it was noted that the extracted mass was very low. Finally, the glass containing the extracted essential oil was kept in a freezer, ready for chromatographic analysis.
The operating conditions such as pressure, temperature, supercritical fluid flow rate and the particle diameter were fixed as shown in the following Table 1.

Table1: Operating conditions (supercritical CO_2 extraction method).

T[°C]	P [MPa]	Q[g/min]	d_p [mm]
40	10	7	1.00
40	10	7	0.50
40	10	7	0.25
40	10	7	0.18

The hydrodistillation experiments were carried out in a Clevenger-type apparatus as described in the 10^{th} edition of the French Pharmacopeia [15]; the system operates at atmospheric pressure equipped with a device permitting to maintain the mass ratio plant/water to its initial level. In every experiment, 20g of rosemary leaves and water were placed, in different proportions, in two liters capacity ball glass. The mixture is conducted to the boiling temperature with a determined flow condensation for 3.5hr. The liberated steams cross up the column and come out of the condenser in the liquid state.
The system enables hourly sampling (every 15min) and the samples weighing indicated the mass of the extracted essential oil which was collected in a glass was kept in a freezer, ready for chromatographic analysis.
The operating conditions such as flow condensation, mass ratio plant/water, and the particle diameter were fixed as shown in Table 2

Table 2: Operating conditions (hydrodistillation extraction method).

Mass ratio plant/water	Flow condensation [ml/min]	d_p [mm]
1/10	4.5	1.00
1/10	4.5	0.50
1/10	4.5	0.25
1/10	4.5	0.18

In order to obtain the best conditions for the hydrodistillation extraction process, preliminary experiments were performed at different experimental parameters, such as: the mass ratio plat/water and the flow condensation.

RESULTS

Comparison of the hydrodistillation and supercritical CO_2 extraction yields

The accumulated mass of essential oil extracted from Rosemary plant leaves by means of hydrodistillation and supercritical CO_2 extraction, with different particle size are shown in the following figure 1:

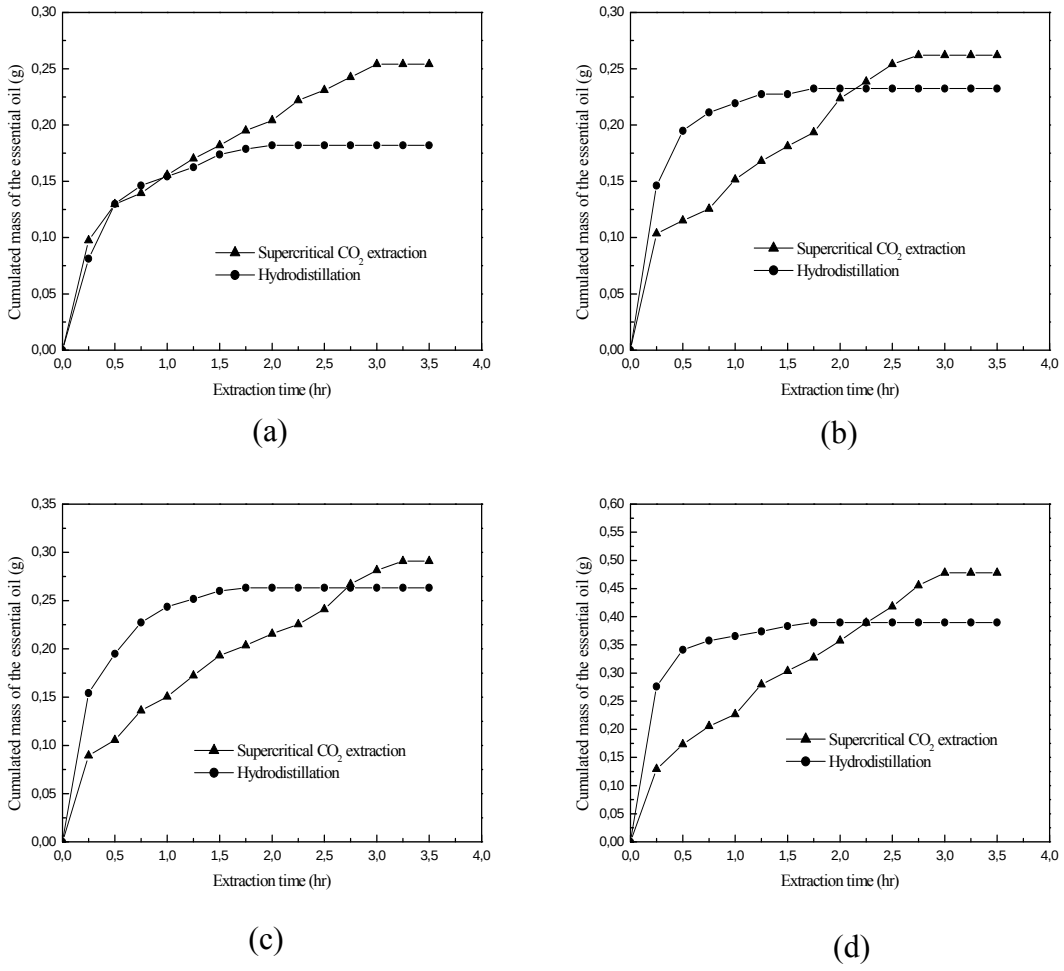

Figure 1: Accumulated mass of essential oil as a function of time obtained by Hydrodistillation and Supercritical CO_2 for different particle size: (a) 1 mm, (b) 0.5 mm, (c) 0.25 mm, (d) 0.18 mm.

It is clear from the above figures that for a fixed particle size, supercritical CO_2 extraction led to a greater amount of the accumulated essential oil, comparatively to that obtained by means of hydrodistillation, in most cases. However for a fixed amount of extracted essential oil, the hydrodistillation process exhibited a shorter extraction time than the supercritical fluid extraction as shown in Figures 1b, c & d, contrarily to Figure 1a, where the extracting time is much longer. Therefore it is necessary to investigate further the effect of the particle size as shown in the following section.

Effect of the particle size on the Rosemary essential oil extraction yield

The essential oil extraction yield is defined as the percentage of the recovered essential oil mass ratio with respect to a mass of dried leaves (taken as 20g in the present work). From the above figures 2, it is clear that this parameter i.e. the extraction yield is influenced by the sizes of the particles which control the mass transfer area. Therefore this effect was studied for both supercritical CO_2 and hydrodistillation processes, fixing all parameters but the particle diameters where four different values of 1.0, 0.5, 0.25 and 0.18mm, and the experimental results are shown in the following figures 2.

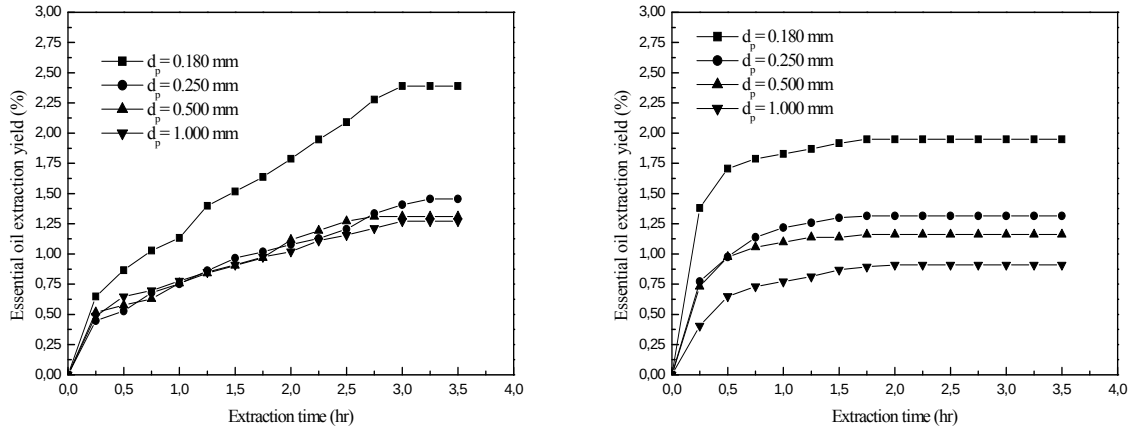

Figure 3: Essential oil extraction yield as a function of extraction time for different particle size, (a) Supercritical CO_2, (b) Hydrodistillation

As figure 3 shows, for the supercritical CO_2 extraction the decrease of the particle size from 1 to 0.250mm did not have a noticeable effect on the extraction yield, however, the decrease to less than 0.180mm increase significantly the yield extraction.
For the hydrodistillation process, the decrease of the particle diameters from 1 to 0.250mm increase progressively the extraction yield, nevertheless, the decrease to less than 0.180mm increase significantly the yield extraction.
This may be explained by the increase of the mass transfer area, and to the smaller intraparticle diffusion resistance due to shorter diffusion paths. It may be concluded that the decrease of the diameter enhanced mass transfer leading to a better extraction yields.

CONCLUSION

Rosemary essential oils were extracted by means of Supercritical CO_2 and Hydrodistillation processes, with particles of various sizes. The results indicated that the supercritical fluid process was more performing in extracting the essential oil than the hydrodistillation. This latter process was rather faster. This confirms the literature where the supercritical fluid extraction generally leads to relatively high extracting yields for systems involving the extraction of essential oil from plants [13, 14].
For the particle size effect, it was found that smaller diameters enhance mass transfer hence increasing the extraction yield.

REFERENCES

[1] PETRA, T., MIRAN, B., HELENA, A., Food chemistry, Vol. 115, **2008**, P. 740.
[2] RAUL, N.C-Jr., LUCINEWTONS, M., PAULO, T.V-R., M. ANGELA, A.M., Supercritical fluids, Vol. 35, **2005**, p. 197.
[3] ADRIANA, M.O-S., CATALINA, M.V-B., MIGUEL, A.E., MIGUEL, A.J., SILVIA, M., Food control, Vol. 31, **2013**, p. 189.
[4] YOSR, Z., TAROUB, B., MOHAMED, B., Food and chemical toxicology, Vol. 48, **2010**, p. 3144.

[5] NABIL, B., MARYLINE, A.V., MOHAMED, A.F., EMMANUEL, P., BRAHIM, Y.M., FARID, C., Food chemistry, Vol. 144, **2009**, p. 355.
[6] LAWRENCE, B.M., Progress in essential oil, Rosemary oil, Perfumer and flavorist, Vol. 22 (5), **1997**, p. 71.
[7] PILAR, R., FRANCISCO, J.S., ELENA, I., GUILLERMO, R., Chromatography A, Vol. 1057, **2004**, p. 241.
[8] OKOH, O.O., SADIMENKO, A.P., AFOLAYAN, A.J., Food chemistry, Vol. 120, **2010**, p. 308.
[9] ARUOMA, O.I., SPENCER, J.P-E, ROSSI, R., AESCHBACH, R., KHAN, A., MAHMOOD, N., MUNOZ, A., MURCIA, A., BUTLER, J., HALLIWELL, B., Food and chemical toxicology, Vol. 34, **1996**, p. 449.
[10] REZZOUG, S.A., BOUTEKEDJIRET, C., ALLAF, K., Food engineering, Vol. 71, **2005**, p. 9.
[11] ANTONI, S., ADAM, F., ANTONIO, G-O., ANGEL, A.G-B., Food engineering, Vol. 97, **2010**, p. 253.
[12] MONICA, R.G-R., ELVIS, J.H., GONZALO, V., TIZIANA, F., FRANCISCO, J.S., GUILLERMO, R., Supercritical fluids, Vol. 55, **2011**, p.971.
[13] ENSIEH, G., YADOLLAH, Y., NADER, B., FATEMMEH, S., Food engineering, Vol. 79, **2007**, p.306.
[14] MOSTAFA, K., YADOLLAH, Y., SHAHAB, S., Food and bioproducts processing, Vol. 88, **2010**, p. 227.
[15] Pharmacopée française. 10ème édition, V, 4.4. Paris: Maisonneuve. **1983**.