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Comparison of the Performances of Hydrodistillation and Supercritical CO_2 Extraction Processes for Essential Oil Extraction from Rosemary (Rosmarinus Officinalis L.)

Mohamed Laid Ouzzar[a], Wahida Louaer[a], Ahmed Zemane[a,b], Abdeslam-Hassen Meniai[a]

[a] Laboratoire de l'Ingénierie des Procédés de l'Environnement (LIPE), Faculté du Génie des Procédés Pharmaceutiques Université Constantine 3, BP B60 Centre Djefaal Amar Khroub 25100 Algeria
[b] Université Larbi Ben M'Hidi, Oum Bouaghi, Algeria
meniai@yahoo.fr

In order to compare the extraction performances of two different techniques, essential oil was extracted from leaves of local rosemary by means of hydrodistillation and supercritical CO_2 extraction. However hydrodistillation is traditionally the most used one.
In the present work experiments were performed using a Clevenger-type apparatus well equipped to maintain the mass ratio plant/water to its initial level. The system was operated at atmospheric pressure, with a flow condensation rate of 4.5ml/min and a ratio plant/water of 1/10.
Supercritical fluid extraction runs were carried out using a dynamic extraction unit at the operating conditions of 100 bars for the pressure, 40°C for the temperature and 7g/min for the solvent flow rate.
In both methods the only parameter that was varied is the particle size, in order to investigate its effect on the processes.
The obtained extraction yields were 2.5 and 1.94% for the supercritical CO_2 extraction and the hydrodistillation, respectively. The results confirmed that the particle size had an important effect on the two processes where a decrease of the diameter enhanced mass transfer leading to better extraction yields. However hydrodistillation took at least two hours less time than Supercritical CO_2 extraction for a same essential oil extraction degree.

1. 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 (Petra et al., 2009) and (Carvalho Jr et al., 2005), its antibacterial, antimutagenic and antiseptic proprieties and as a chemoprentive agent (Adriana et al., 2013), (Zaouali et al., 201) and (Nabil et al., 2009). 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 Lawrence (1997), with the most active components being the phenolic diterpenes, primarily carnosic acid, and also carnosol, rosmanol, epi and isorosmanol (Pilar et al., 2004).
The extraction of essential oil from rosemary plants has been performed by means of various techniques like solvent free microwave extraction (Okoh et al., 2010), solvent extraction (Aruoma et al., 1996), fast controlled pressure drop process (Rezzoug et al., 2005), microwave hydrodiffusion and gravity (Nabil et al.,2009),

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hydrodistillation (Zaouali et al., 2010), (Nabil et al., 2009), (Okoh et al., 2010) and (Anton et al., 2010) and supercritical fluid extraction (Carvalho Jr et al., 2005), (Pilar et al., 2004) and (García-Risco et al., 2011), 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 (Rezzoug et al., 2005).

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 (Ensieh et al, 2007) and (Khajeh et al, 2010).

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.

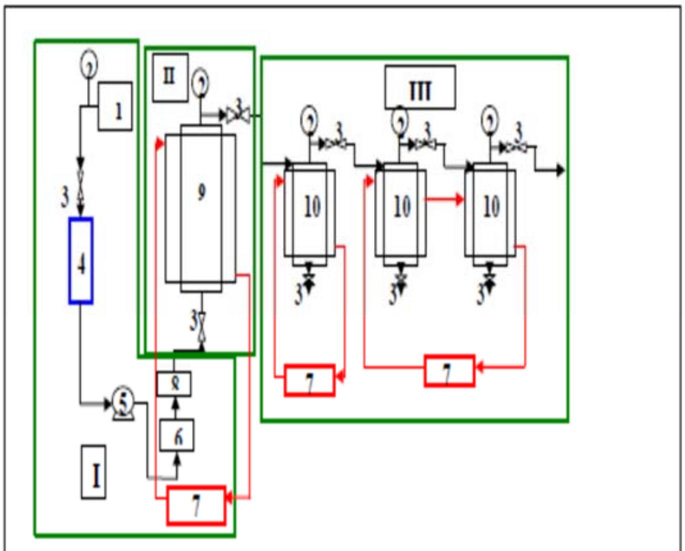
2. Materials and methods

2.1 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 sizes by passing through the sieve shakers with decreasing diameters.

2.2 Extraction methods

The supercritical CO_2 extraction experiments were carried out in the dynamic extraction unit previously conceived and assembled at the Chemical Engineering Sciences Laboratory in Nancy (LSGC, Nancy, France) and shown in Figure 1



1. Bottle of CO_2, 2. Pressure gauge, 3. Valves, 4.Cold exchanger, 5.Pump, 6.Pressure gauge, 7.thermostatedbath, 8. CO_2 Flow meter of, 9. Extractor,10. Separators. I : Preparation of supercritical CO_2 ; II : Part of extraction ; III : Extract recovery.

Figure 1: The dynamic extraction unit

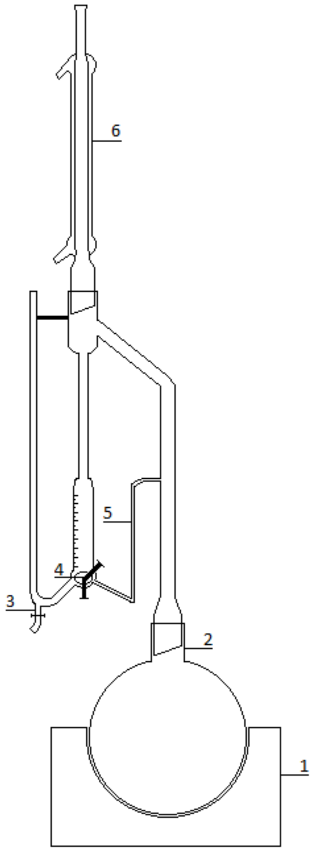


Figure 2: The hydrodistillation unit

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.
In order to investigate the effect of the particle size on the hydrodistillation process performance of t, a first set of experimental runs were performed at atmospheric pressure for a mass ratio plant/water and a condensation rate of 1/10 and 4.5 ml/min, respectively. Similarly the effect of this parameter was also examined for a supercritical fluid extraction using the dynamic extraction unit shown in Figure 1, at a pressure, a temperature and a flow rate of Carbon dioxide of 100 bars, 40°C and 7g/min, respectively.

The hydrodistillation experiments were carried out in a Clevenger-type apparatus as described in the 10th edition of the French Pharmacopeia (Pharmacopée Française); Figure 2 shows schematically such a system which operates at atmospheric pressure equipped with a device permitting to maintain the mass ratio plant/water on 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 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.

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.

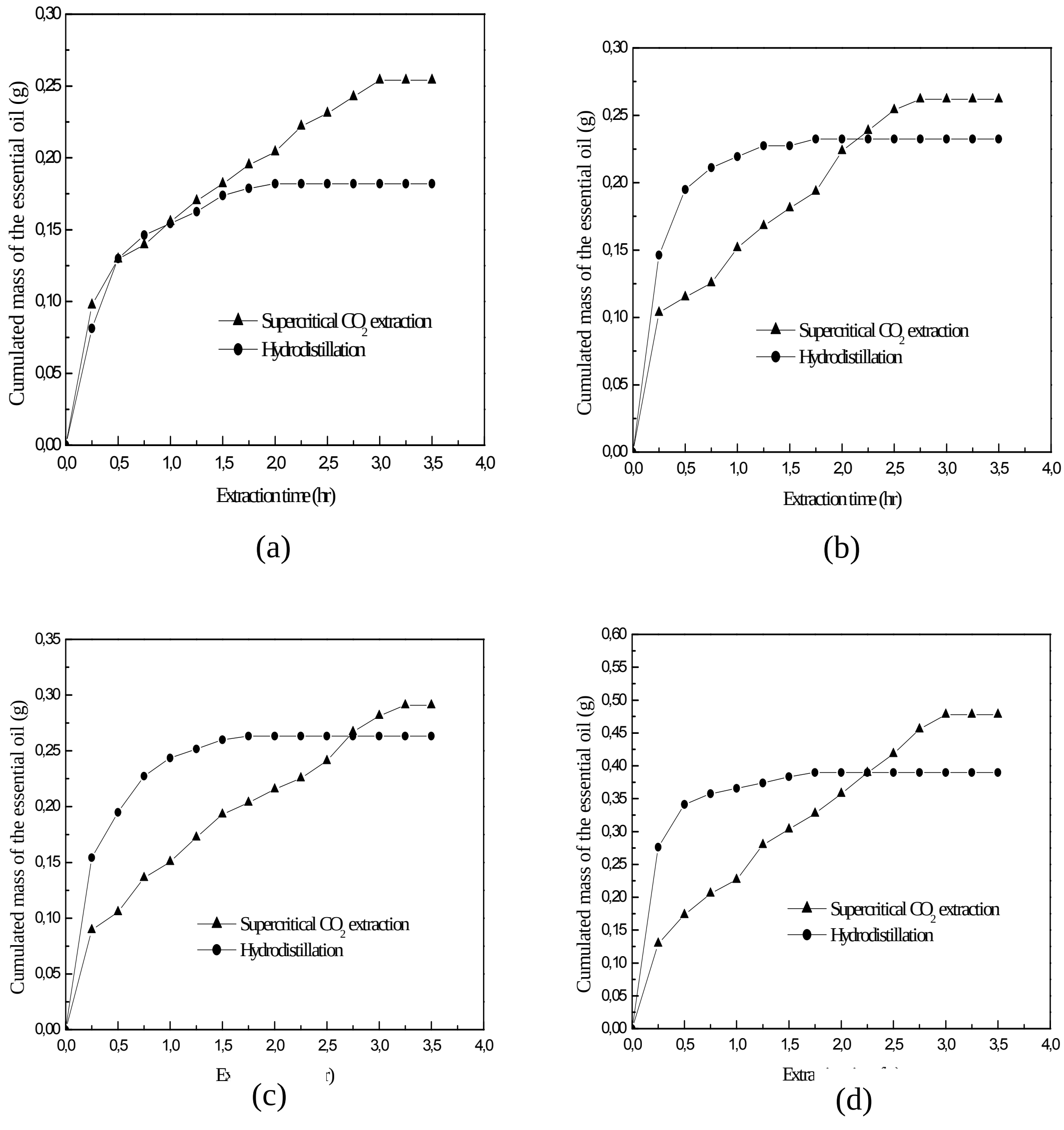


Figure 2: Accumulated mass of essential oil as a function of time obtained by Hydrodistillation and Supercritical CO_2 for different particle size: (a) 1 mm, (b) 0.5 mm, (c) 0.25 mm, (d) 0.18 mm

3. Results

3.1 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 2:

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 2b, c & d, contrarily to Figure 2a, 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.

3.2 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 3:

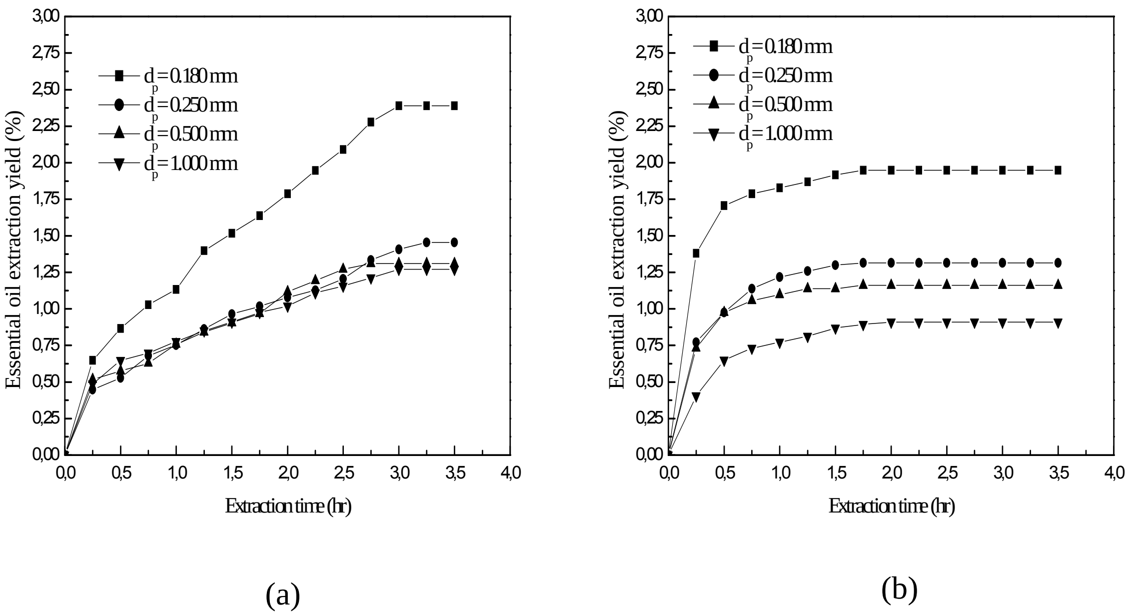


Figure 3: Essential oil extraction yield as a function of extraction time for different particle size, (a) Supercritical CO_2, (b) Hydrodistillation.

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 0.250 mm increase progressively the extraction yield, nevertheless, the decrease to less than 0.180 mm 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.

4. 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, and it was also found that smaller particle diameters enhanced mass transfer hence increasing the extraction yield.

The results are in agreement with the fact that the supercritical fluid extraction generally leads to relatively high extracting yields for systems involving the extraction of essential oil from plants, as reported in the literature (Ensieh et al, 2007) and (Khajeh et al, 2010). However the major drawback of the former one *i.e.* is mainly due to the relatively high cost of the required high pressure equipment, compared to the second one *i.e.* Hydrodistillation which is still considered as a traditional process.

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