

SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF ROSEMARY COMPARISON WITH STEAM DISTILLATION AND HYDRODISTILLATION

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ABSTRACT

Supercritical fluid extraction (SFE), steam distillation and hydrodistillation were used to extract the essential oils from rosemary (*Rosmarinus officinalis*) and a comparative study of extracts obtained using SFE, SD and HD is presented.

Supercritical fluid extraction of natural products show that many factors have impacts on the oil yield, such as extraction pressure, temperature, particle size, addition of co-solvent and the distribution of material in the extractor.

For the extraction process (SFE) of rosemary the conditions were as follows:

- extraction pressure of 80 - 100 bar
- extraction temperature of 35- 40°C
- $d_p > 0.270$ mm
- ethanol was added directly to the material (3% mass)
- the raw material is charged with a packing into the extraction vessel.

Under such a condition the yield obtained by SFE is higher compared to the others methods.

GC analysis shows that the extracts obtained using the three methods were no similar in composition.

INTRODUCTION

In recent years supercritical fluid extraction (SFE) has become an alternative to more conventional extraction procedures, chiefly because the dissolving power of supercritical fluids can be adjusted by regulation the pressure and the temperature conditions employed. By using SCCO₂ instead of steam distillation or extraction with organic solvent, contributes to solve the problem of toxic residual solvent in the products, and allows to use lower temperatures leading to lesser deterioration of the thermally labile components in the extract [1, 2].

Rosemary occupies 100.000 hectares of the Algerian territory [3], it is an aromatic plant used in flavouring of food, cosmetic and folk medicine, the composition of rosemary (*Rosmarinus officinalis*) extracts vary due to climate factors during cultivation, humidity and extraction process, there are three principal chemotypes of *Rosmarinus officinalis* : cineole, camphor/borneol, verbenone.

Arthur et al [4] used 23 cultivars of rosemary and they observed that all cultivars could be grouped into six chemotypes based upon the composition of their essential oils,

Boelens [5] concluded that two types of Rosemary oils existed one high in 1,8 cineole (from France, Greece, Tunisia and parts of Italy) and one low in 1,8 cineole (from Spain, Yugoslavia and other parts of Italy).

Few studies concerning the rosemary from Algeria have been reported, Boutekedjiret et al [6] observed that the Rosemary of east Algeria origin content 30-50 percents of 1,8 cineole, our experiments showed the existence of an other chemotype: camphor/borneol.

Several authors have compared the essential oil obtained by steam distillation and the product obtained by SFE, they found that steam distillation oil contained higher percentages of terpene hydrocarbons. In contrast, the SFE oil contained a higher percentage of oxygenated compounds [7, 8, 9].

In the present study SFE was used to extract the essential oil from Rosemary leaves. Extraction conditions were adjusted to obtain the highest yield. Extracts were analyzed by GC and compared with Rosemary oil isolated by steam distillation (SD) and hydrodistillation (HD).

1- MATERIALS AND METHODS

1-1 Materials

Rosemary leaves (*Rosmarinus officinalis*) were collected from plants growing in university garden, the leaves were air dried.

1-2 Extraction procedures

The supercritical extraction apparatus mainly consisted of a 125 ml extractor (inside diameter 23mm and length of 300mm) and three separation vessels, operated in series. CO₂ (99.8 % pure, Carboxyque française, France) circulation was assured by volume metering pump (Dosapro Milton Roy. Milroyal D) assuming a liquid flow rate up 3.2 kg/h and pressure up to 250 bar. A schematic representation of the apparatus is given in figure 1.

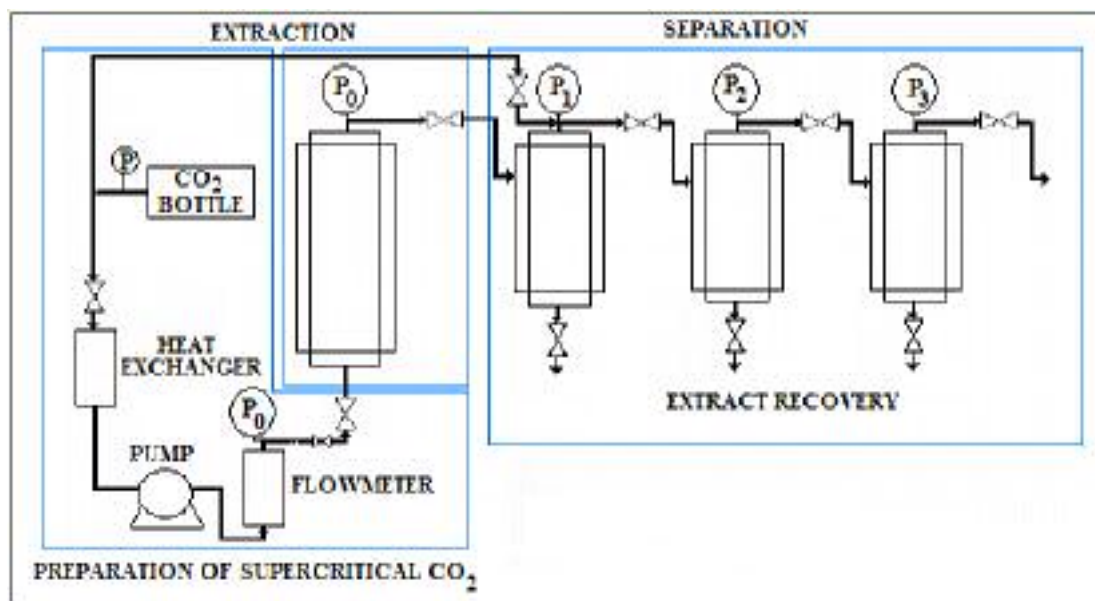


Figure 1 : Experimental Apparatus

For some experiments the extraction cell was filled with 10g of ground Rosemary (dried) and 60g of glass bead, in the extraction with ethanol as modifier, 3 % of ethanol was added directly to the material. The analysis of particle size distribution was performed by passing the ground plant material through sieves of various mesh size and weighing the fraction taken from each tray.

Steam distillation and hydrodistillation were performed for 3h with a conventional apparatus, all experiments were realized with 10 g; of fresh Rosemary.

1-3 Analysis

Chemical composition of extracts was determined by gas chromatography method using a fused silica capillary column with a bonded stationary phase CP Sil 5CB, and flame ionisation detector. The identification was performed by comparison the retention time of the available pure products with the retention time of the extracted Rosemary oil.

RESULTS AND DISCUSSION

The raw material and drying process applied to the Rosemary plants were based on previous data obtained in our laboratory.

The supercritical fluid extraction conditions were investigated in the range $P = 80-100$ bar and $T = 35 - 40^{\circ}\text{C}$; they were found to be optimum at $P = 100$ bar and $T = 40^{\circ}\text{C}$. The separator conditions were kept constant for all experiments : $P_1 = 80$ bar, $P_2 = 40$ bar, $P_3 \sim P$ atm., $T_1 = T_2 = T_3 = 22^{\circ}\text{C}$. CO_2 flow rate is kept constant near 1. g/min.

The effect of following process parameters on the percentage yield were studied: particle size, packed cell, and addition of co-solvent in material leaves. All the results are summarised on table 1.

Table 1: Parameters and experimental results of SFE at $p = 100$ bar and $T = 40^{\circ}\text{C}$

Experiments	Particle size (mm)	Mass feed (g.)	Glass bead (g)	Ethanol (mass %)	Yield (%)
1	0.224 >dp>0.160	10	0	0	Trace
2	> 0.270	10	0	0	1.03
3		10	60	0	1.16
4		4	60	3	2.44
5	>0.315	10	60	0	1.06
6		10	60	3	2.38

Examination of table 1 resulted in the conclusion that the most operating conditions for SFE are: $P = 100$ bar, $T = 40^{\circ}\text{C}$, $d_p > 0.270$ mm.

The addition of ethanol (3%) as modifier increase the extraction yield, although carbon dioxide is a relatively good solvent for the extractions, it has some limitations for the extraction of polar substances from plant matrix. Ethanol was used as modifier in this study, because it is environmentally kindly and relatively safe to human health.

The extraction time is the main parameter that contribute to optimum extraction, i.e. a maximum yield at a minimum extraction time, figure 1 represents the yield obtained using the SFE, SD, and HD of Rosemary oil.

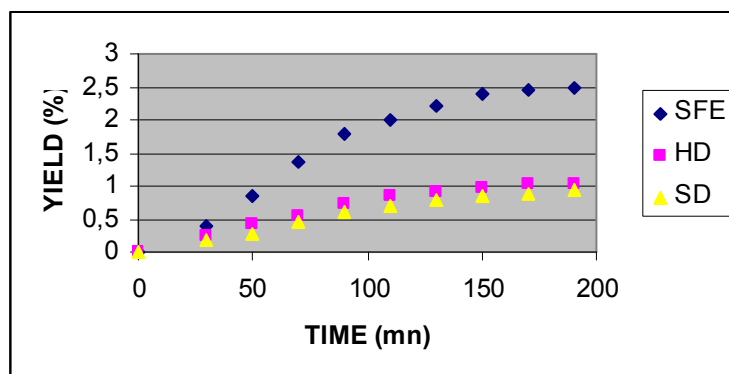


Figure 2: Yield oil versus time for SFE(experiment n°4), HD and SD from Rosemary

The yield obtained by SFE is higher compared to yield obtained by HD (1.02) and SD (0.95).

Figure 2 shows that in the first part of the extraction the yield curve is linear. As already mentioned [10,11], this is consistent with the hypothesis that in the first part of the extraction the fluid leaving the system is at the equilibrium conditions. The initial extraction rate of Rosemary oil is high but tends to zero when solute concentration decreases. An extraction period around 120 mn were the most suitable for the three procedures used.

A quantitative composition of the main constituents present in the SFE, SD and in the HD Rosemary oil was realized; the results are summarized in table 2.

Table 2: Percentage composition of Rosemary leaf oils isolated by supercritical CO₂ extraction (SFE), steam distillation (SD) and hydrodistillation (HD), respectively

Components	SFE	SD	HD
α - Pinene	6.75	4.76	14.03
1,8-Cineole	9.24	6.53	4.03
Camphor	15.96	7.51	11.99
Borneol	22.01	15.00	3.80
Bornylacetate	3.52	6.07	0.50

The examination of composition data for Rosemary (*Rosmarinus Officinalis*) oils reveals that an other type of rosemary (Camphor/Borneol) existed in Algeria, however the wide variation in these oils indicates genetic variability in this genus.

The extract obtained using the three methods contain the same components. Although the concentrations are different, a somewhat higher level of α -Pinene was found in the HD oil while the concentrations of Camphor and borneol were higher in SFE product.

The SFE oil contained higher percentages of oxygenated monoterpenes which strongly contribute to the fragrance. Therefore, the supercritical fluid extraction oil should give better reproduction of the natural aroma of the Rosemary leaves than the distilled oil.

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