ANISE ESSENTIAL OIL EXTRACTION BY SUPERCRITICAL CO_2

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abstract: The supercritical fluid extraction (SFE) of anise essential oil was studied using anise (Pimpinella anisum, fam. Apiaceae) seeds as raw material and CO_2 as solvent. The effect of operation conditions was analyzed in a series of experiments at temperatures between 40 and 50°C and pressures between 100 and 120 bar. The colected extracts were analyzed by GC-MS and the relative composition of the essential oil was determined. Trans-Anethole is the principal component extracted. The optimum conditions for trans-anethole extraction were 40°C and 120 bar; in these conditions, trans-anethole represents more than 83% of essential oil. We obtained an essential oil asymptotic yield of 1.52 wt % of the loaded material. Furthermore, the effect of CO_2 flow rate and mean particle size of coriander seeds was studied in the range of 0.5 to 1.5 kg/h and 0.5 to 1.0 mm, respectively.

Introduction

Partly in connection with the development of flavourings for new food products, there is need for renewed research into the alternative techniques available for extracting these compounds from plant material. The most widely used methods are based on hydrodistillation. These methods can result in damage to some of the more thermolabile compounds. Extraction with compressed CO_2 is an alternative approach, which is applied commercially to some extent [1,2]. The extracts obtained by this method contain a wider range of compounds than do the extracts obtained by hydrodistillation [3,4]. The pharmaceutical, cosmetic and perfume industries are also users or potential users of herb material extracts.

In the present work, extraction tests have been performed on anise seeds using supercritical CO_2 as solvent. The objectives were to study the influence of operation conditions on the composition of extracts and investigate the effects of mean particle size and solvent mass flow on the extraction yield of essential oils.

Experimental part

Tests on anise seeds were performed on a laboratory unit based on a 350 cm^3 extraction vessel equipped with two separators operated in series with a volume of 250 cm^3 each. A

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thermostated jacket allows regulating the temperature in the extractor by using of an electronic device with Pt thermometer control. Both separators were immerged in two 8 l Dewar vessels filled with a mixture of ethylene glycol and water. More details and a schematic representation of the apparatus have been given elsewhere [5]. About 300 g of comminuted anise seeds (with a mean particle size of 0.5 mm) were submitted to extraction in each run. A CO_2 flow rate of 1.5 kg/h and an extraction period of 120 min were used.[a]

First the SFE process was performed at various CO_2 densities. GC-MS data and sensory analysis were used to determine the extraction conditions that minimize the co-extraction of unwanted compounds; subsequently the optimum fractionation conditions to be used in the two separators were studied. The yield of the various fractions was measured by weight with respect to the dried material charged in the extractor.

GC-MS data were obtained using a Varian model 3400 gas chromatograph equipped with a fused silica DB-5 column (J&W; 30 m × 0.25 mm i.d., film thickness 0.25 μm) for the essential oil analysis. The GC apparatus was interfaced with a Finnigan-MAT 800 Ion Trap Detector (ITD, software version 4.1). GC conditions for the essential oil separation were as follows: oven temperature 50°C for 5 min, then programmed 50÷250°C at 2°C/min and subsequently isothermal at 250°C for 15 min. The samples were injected using the splitless sampling technique. The percentage composition of the essential oil was computed from the GC peak areas without using correction factors. The identification of the compounds was based on a comparison of retention times and mass spectra with corresponding data of components of reference oils and authentic compounds. Some mass spectra were compared with those of mass spectra libraries (NIST, version 4.0 and WILEY, version 5.0).

Extractions performed at various CO_2 densities showed that an extraction at p = 120 bar and T = 40°C was optimum in order to minimize the co-extraction of unwanted compounds. The best parameters to perform the fractionation were p = 90 bar and T = –5°C for the first separator and p = 15 bar and T = 10°C for the second one. Using this procedure, cuticular waxes were selectively precipitated in the first separator, in the second one the essential oil was recovered. Small quantities of water were obtained in the second separator and then separated by centrifugation. The amount of the oil collected in the separator was determined gravimetrically.

Results and Discussion

A further series of runs was performed to assess the optimal extraction conditions for the vegetable species considered. GC-MS analysis was used to characterize the extracted essential oils. Since oxygenated monoterpenes are considered the most desired essential oil flavour constituents, optimum extraction was fixed so that the maximum percentage of oxygenated monoterpenes with respect to the other compounds was produced. It was found that the optimum extraction pressure and temperature for anise seeds were in the ranges from 100 to 120 bar and from 40 to 50°C, respectively.

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Operating conditions of 120 bar, 40°C (called SFE-1) and 100 bar, 50°C (called SFE-2) were selected to evaluate process yields against time. The yield of anise oil was measured by weighting the oil recovered in the second separator at the various extraction times. The extraction results are summarized in Fig. 1.

The yield data show that the initial extraction rate of essential oils is high but tends to zero when solute concentration decreases. The essential oil yields obtained by SFE were compared. In the case of anise, the maximum yield was 1.52% by weight of the charged material, at SFE-1 conditions. Of course the two products are not completely comparable. Table 1 shows the identification and the quantification of extracted compounds (SFE-1 and SFE-2). The identified compounds are listed by increasing retention times.

The analysis of GC results given in Table 1 shows that the major contribution comes from trans-anethole, which represents 82÷83% of the oil composition. The hydrocarbon monoterpenes contribute less to the anise essential oil composition (1.29÷1.15%). Oxygenated terpenes are considered to be the main constituents of the aroma of many essential oils. In the anise oil extracted under SFE-1 conditions, oxygenated monoterpenes contribute with 7.37% to the total area.

Table 1. Percentage composition of anise oil isolated by supercritical CO_2 extraction (SFE-1 and SFE-2). The percentages are based on GC peak areas.

Compound	Rt[a]	SFE-1 (%)	SFE-2 (%)
α-Pinene	4.78	0.12	-
Camphene	4.97	0.10	0.14
Δ^3-Carene	5.18	0.22	0.19
Sabinene	5.30	0.13	-
β-Pinene	5.60	0.20	0.26
β-Myrcene	5.72	0.24	0.19
α-Phellandrene	5.91	0.08	0.09
o-Cimene	6.27	0.10	0.11
p-Cimene	6.35	0.91	0.77
Limonene	6.50	0.05	0.08
1,8-Cineole	6.96	0.81	0.70
γ-Terpinene	6.99	0.09	0.15
cis-Linalool oxide	7.21	0.08	0.11
trans-Linalool oxide	7.60	0.14	-
α-Terpinolene	7.72	0.06	0.05
Linalool	8.03	1.12	2.26
Fenchone	8.25	2.40	2.44
Camphor	8.74	0.22	0.25
cis-Menthone	8.84	1.38	1.39
Isomenthone	9.04	0.09	0.08
Neomenthol	9.29	0.07	-

Table 1. ***Continued.***

Compound	Rt[a]	SFE-1 (%)	SFE-2 (%)
cis-Menthol	9.30	0.75	1.05
Dihydrocarvone	9.47	0.16	0.24
Carvone	10.54	0.15	0.12
Estragole	10.75	1.38	1.67
p-Anisaldehyde	10.82	3.71	3.20
Fenchyl acetate	10.91	0.11	0.29
cis-Anethole	11.02	0.17	0.15
trans-Anethole	11.11	83.34	82.74
δ-Elemene	11.38	0.08	0.09
Dihydrocarveol acetate	11.40	0.15	0.08
Eugenol	11.73	-	0.05
Methyl Eugenol	11.91	0.15	0.07
β-Elemene	12.10	0.18	0.15
β-Caryophyllene	12.42	0.05	0.09
α-Bergamotene	12.76	0.05	-
cis-β-Farnesene	13.05	0.05	.014
Germacrene	13.65	0.34	0.27
β-Bisabolene	13.79	0.29	0.21
Farnesol	15.04	0.28	0.13

[a]Rt = retention time (min).

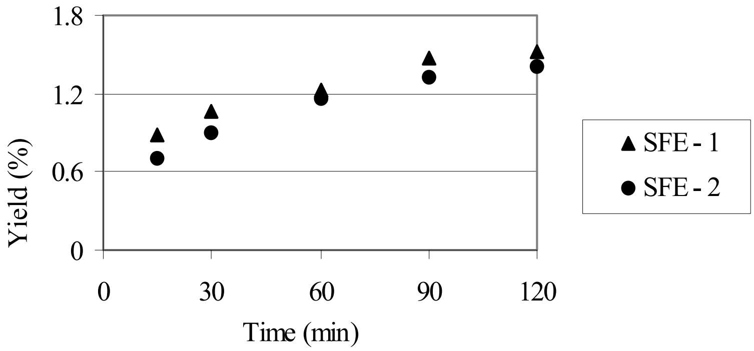

Fig. 1: *Anise oil yield at various extraction times.*

To study the influence of solvent mass flow and particle size of anise seeds on extraction rate, two series of experiments were designed in the range of 0.5 to 1.5 kg/h and 0.5 to 1.0 mm at 120 bar and 40°C (see Figs. 2 and 3). The average particle size of anise seeds employed in the first series was 0.5 mm and the solvent mass flow employed in the second series was 1.5 kg/h.

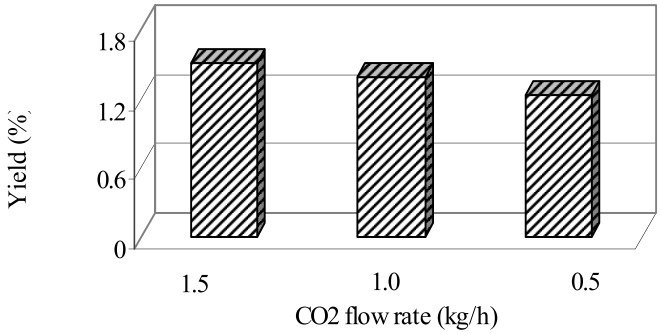

Fig. 2: *Influence of CO2 flow rate on the yield of anise essential oil extraction.*

The Fig. 3 shows the extraction yield as a function of time for mean particle sizes respectively of 0.5, 0.8 and 1.0 mm. These results confirm the importance of particle size in SFE of essential oils. By the other end, it is not possible to operate with the smallest particle size possible because comminution techniques can induce degradation of some thermolabile compounds.

The changes of the mean particle size have a relevant effect on the extraction yield and can be utilized to better use the SFE technology. In other words, it is possible to have a more efficient use of the extractor and a lower CO_2 and utilities consumption.

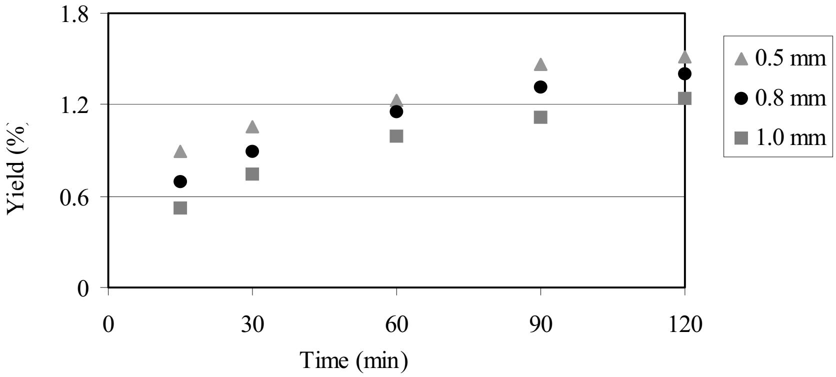

Fig. 3: *Anise essential oil yield against extraction time, at different particle sizes.*

Conclusions

Trans-anethole is the principal component extracted. At 120 bar and 40°C the trans-anethole content in the essential oil extracted is greater than 83%.

The particle size, extraction time and solvent flow rate should be taken into account to acquire a complete knowledge of the SFE process. These parameters influence the extraction rate and the yield of the process.

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