

Influence of the Operational Conditions on the Recovery of Volatile Oil Compounds in the Fractional Separation from Fennel (*Foeniculum vulgare*)

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In this paper, the effect of the operational conditions (temperature and pressure) on the recovery of anethole and fenchone in the fractional separation of fennel obtained by supercritical fluid extraction was studied. Dry fennel seeds were obtained from Fazenda Experimental Lageado of Unesp (Botucatu, Brazil). The SFE assays were done in a SFE unit containing two cyclone collectors. The experiments were divided into two steps: (i) Construction of the OEC and calculation of the kinetic parameters - to determine the operational time, (ii) Optimization of the temperature and pressure for the fractional separation. Throughout the process the pressure and temperature of the extractor were maintained at 250 bar and 313 K. The operational time, determined from the overall extraction curve, was $t_{CER} = 35$ min. The optimal operational conditions of separation, in order to obtain a volatile oil rich fraction and fatty acid rich fraction, were 80 bar and 313 K.

INTRODUCTION

The use of supercritical fluids to obtain extracts from vegetable matrix can be divided in two parts: (i) solubilization of the compounds in the supercritical fluid during its flow into the extraction column, and (ii) separation of the solute-solvent mixture in the separator. During the extraction stage, the temperature and pressure are selected in order to have the largest yield of the target compounds while in the separator the operational conditions are selected aiming the optimization of the solutes precipitation and solvent recycling. There are several papers in the literature dealing with the extraction stage [1]. However, there are only few references related to the separation stage [2]-[4].

The main importance of the separation stage is related to the solvent recompression cost, since the recovery of the solute is obtained by the decompression of the mixture. Although some sophisticated separation processes such as nanofiltration [5] and reverse osmosis [6] has been proposed in order to decrease the separation cost and to increase the process efficiency the most used separation process is still the reduction of the mixture pressure. Changes of solutes solubilities can be obtained at different conditions of temperature and pressure, however, one need to certify that there is a complete phase separation since some components can be volatilized with the CO₂, as in the case of the ginger oleoresin [7] and aniseed volatile oil [8]. The economical impact of the right selection of the separation condition was demonstrated by Bravi et

al [4]. The authors concluded that when the separation pressures are above or below the optimum one, the process global cost is high. In general, the operation condition of the separation stage is chosen in an arbitrary manner. In the orange essential oil deterpenation the selected separation conditions were pressure of 20 bar and temperatures from 273 to 290 K [9]. In the economical evaluation of the clove buds supercritical CO₂ extraction the separation pressure was set to 40 bar, considering that at this condition there was a complete phase separation [10]. One reason for this tendency is the lack of information about phase equilibria in real systems containing supercritical CO₂ [11]-[13]. Furthermore, there are some other parameters that must take into account in the separation stage such as solvent flow rate [14]. An increase in the solvent flow rate can force an incomplete phase separation with some small solute droplets been dragged by the depressurized CO₂. In order to decrease this factor, a better separation can be done using cyclones in series with steps of pressure decreasing (fractional separation). This operation is having some special attention [15]-[22]. Thus, the complete description of the separation process is a hard task since one need information of phase equilibria and processes hydrodynamics in order to determine the optimum temperature and pressure at the separation stage. There are two models present in the literature to describe the separation process: (i) the separator is considered to be a single theoretical stage [23] and, (ii) the phase equilibria is attained just after the expansion valve [24]. Camy and Condoret [24] compared both models and concluded that the second model describes better the separator.

Thus, the main goal of this paper was to study the influence of temperature and pressure on the yield and chemical composition of the fennel extract.

I. MATERIAL AND METHODS

Raw Material. The fennel (*Foeniculum vulgare*) was cultivated at the experimental farm of Lageado – UNESP (Botucatu, São Paulo, Brazil). The seeds were dried in a oven at 313,15 K, milled in a knife mill (Marconi, Model MA340, Piracicaba, Brazil) and storage in a freezer (Brastemp, Model 7501, São Paulo, Brazil) inside plastic bags.

Raw Material Characterization. The raw material humidity was determined using the xylol distillation method [25]. The particle size distribution was determine using a vibratory sieve system (Bertel, Model 1868, São Paulo, Brazil) and sieves of Tyler series mesh 16, 24, 32, 48 and 60. For the extractions the particles from 24-60 mesh were selected. The Sauter mean diameter was used to describe the particle size [26]. The particle real density was determined using a helium pycnometry. The porosity was calculated as 1 minus the ratio of the bed apparent density and the particle real density.

Extraction apparatus. The extraction apparatus used in the experiments was constructed at Technical University of Hamburg-Harburg as part of the SUPERNAT International Cooperation Agreement (CNPq/Brazil and DLR/German) and was previously described [27]. The system contains a 100 cm³ extractor (2 cm of inside diameter and 32 cm of height) and two cyclones to do the separation.

Global yield determination. The global yield was determined by an exhaustive supercritical CO₂ extraction at 250 bar and 313 K. This condition was selected from Moura et al. [28]. The CO₂ flow rate was $6.8 \pm 0.7 \times 10^{-5}$ kg of CO₂/s. The extracts were collected in glass flasks immersed in a bath maintained at 268 K in order to decrease the amount of volatile compounds that are presented at gas CO₂. The obtained samples were kept in a freezer at 268 K.

Process time determination. The extraction time was defined as the Constant Extraction Rate period (CER) calculated from the overall extraction curve (OEC). The fennel apparent bed density was 497 kg/m^3 . The bed height was 16 cm, been the empty space of the column at the CO_2 entrance filled with glass beads (2 mesh). A static period of 5 minutes was used in the experiments. The samples were collected in 5, 10 or 20 minutes interval. The experimental OEC was adjusted by two splines as described by Rodrigues et al. [29].

Influence of the operational condition in the separation stage. The bed characteristics and operational conditions were the same used in the extraction time determination. The tested conditions of the first separator were 20, 80, 100, and 120 bars at 313 K and 80 bar and 263 K. The samples were collected at the end of each experimental run. In order to collect the extract on cyclones inner surfaces it was rinsed with hexane. The hexane was separated from the extract in a rotovap system (Heildoph Instruments, model Laborota 4001, Viertrieb, Germany) with a vacuum control (Heildoph Instruments, model Rotovac Control, Viertrieb, Germany).

Identification and quantification of the extract components. The extracts were analyzed in a GC-FID system (Shimadzu, model 17A, Kyoto, Japan) equipped with a fused silica capillary column DB-5 (30m \times 0.25mm \times 0.25 μm , J&W Scientific, Folsom, USA). The carrier gas was helium (1.7 mL/min, 99.9% purity, White Martins Gases Industrials, Campinas, Brazil); a split ratio of 1/30 was used. The temperatures of the injector and of the detector were 240 and 280 $^\circ\text{C}$, respectively. The column was heated to 50 $^\circ\text{C}$ for 5 min and programmed at 5 $^\circ\text{C}/\text{min}$ to 280 $^\circ\text{C}$, and heated for 5 min. One microliter of the samples was injected (5×10^{-6} kg of extract diluted in 1×10^{-6} m 3 ethyl acetate P.A., Lot 55893, LabSynth, São Paulo, Brazil). The anethol and fenchone content were quantified by the external standard method [30] using the anethol and fenchone standards (Aldrich).

II. RESULTS AND DISCUSSION

Global yield

The global (X_0), anethol, and fenchone yields were 10.07 ± 0.02 , 0.9 ± 0.1 , and $0.033 \pm 0.003\%$ (dry basis, d.b.), respectively. The relative purity (ratio between the component and global yield multiplied by 100) of anethol and fenchone were 9.6 ± 0.9 and $0.34 \pm 0.04\%$ (m/m), respectively.

Process time determination

The fennel OEC is presented in Figure 1. Rosa and Meireles [10] showed that the operational time is fundamental to evaluate the extraction process cost, concluding that the manufacturing cost increased for extraction times larger than CER period (t_{CER}). Using the experimental data, the OEC was fitted by a spline with two straight lines, been the slope of the first straight line identified as t_{CER} . The results are presented in Table 1. The operation time was the t_{CER} as represented in Figure 1.

Table 1 – Kinetic parameters at CER period

M_{CER} (kg extract/s) $\times 10^8$	8.6 ± 0.6
T_{CER} (min)	35 ± 2
Y_{CER} (kg extract/kg CO_2) $\times 10^3$	12 ± 1
R_{CER} (%)	7.70 ± 0.03
R_{total} (%)	9.90 ± 0.20

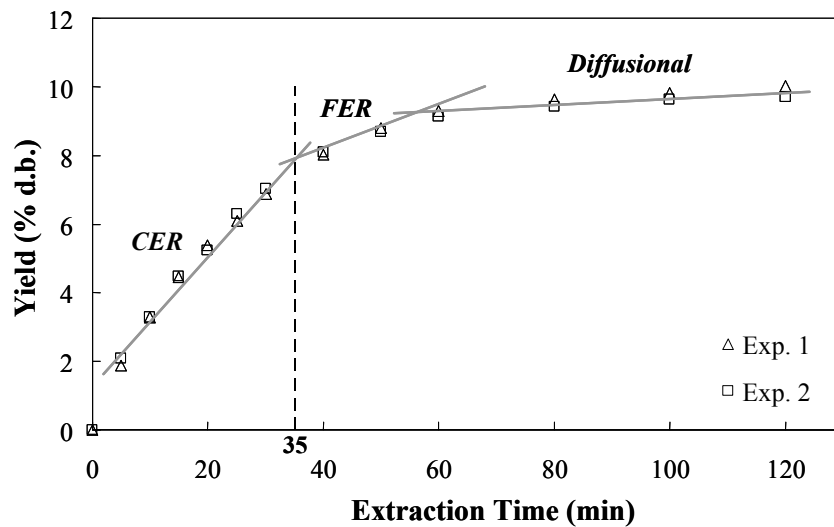


Figure 1 – Fennel OEC at 250bar/40°C/ 6.8×10^{-5} kg CO₂/s.

The fennel overall extraction curve and the variation of anethol purity with time is presented in Figure 2. From Figure 2 one can observe that the select process time (35 minutes) should be adequate if the target compound was anethol since it is possible to extract almost all of the anethol present in fennel during this time. Thus, an extraction time of 35 minutes was selected for the study of the operational conditions influence on the separation stage.

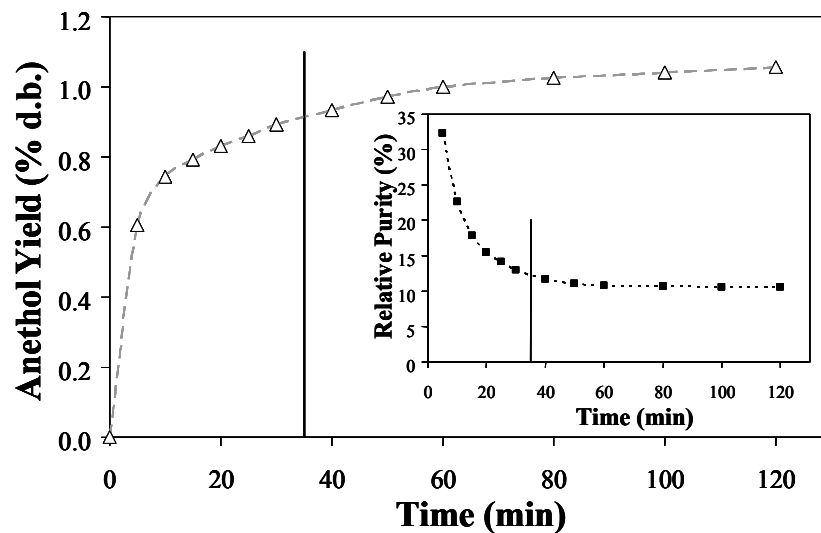


Figure 2 – Fennel OEC and anethol relative purity at 250 bar, 40°C and 6.8×10^{-5} kg CO₂/s.

Influence of the operational condition in the separation stage

The global yield of extract, anethol, and fenchone for several operational condition of the first separator is present in Table 2. The second separator was always operated at ambient pressure and 263 K.

Table 2. Extract, anethol and fenchone yields (% d.b.) in the separators
(Extraction condition: 250 bar / 40 °C / 6.8×10^{-5} kg CO₂/s).

Operational Condition (1 st separator)	Yield (% d.b.)					
	1 st separator			2 nd Separator		
	Extract	Anethol	Fenchone	Extract	Anethol	Fenchone
20 bar / 313 K	7.554	0.677	0.0781	0.019	0.010	0.0003
80 bar / 313 K	7.303	0.435	0.0469	0.232	0.195	0.0095
100 bar / 313 K	7.541	0.313	0.0013	0.173	0.153	0.0153
120 bar / 313 K	6.137	0.262	0.0009	1.386	0.259	0.0096
80 bar / 263 K	7.535	0.449	0.0520	0.106	0.102	0.0214

From Table 2 is possible to observe that the extract global yield (sum of both separator) was approximately constant (7.60 ± 0.08 % d.b.) and is close to the CER yield (Table 1). However, the anethol and fenchone yields vary from 0.466 (100 bar/313 K) to 0.687 (20 bar/313 K) and from 0.010% (120 bar/40°C) to 0.078% (20 bar/313 K), respectively.

In general it was observed that global, anethol and fenchone yields decreased with the increase of the pressure in the first separator, while it was observed an increase of global and anethol yields in the second separator. The decrease of temperature at 80 bar resulted in a increase of extract, anethol and fenchone yields in the first separator.

Although was possible to observe an increase of extract and anethol yields with an increase in the first separator pressure, the anethol relative purity decrease from 84.1 % (80 bar/313 K) to 18.7 (120 bar/313 K). The largest anethol purity in the extract was observed at 80 bar and 263 K (96.0%).

CONCLUSION

The optimal extraction time to obtain anethol from fennel at 250 bar and 313 K was 35 minutes. At this extraction time almost 80% of the anethol can be extracted. The tested operational conditions of the first separator resulted in extracts with distinct contents of anethol and fenchone. The anethol yield in the second separator increased with first separator pressure, but the anethol purity decreased. The extract with higher content of anethol (96%) in the second separator was obtained using 80 bar and 263 K as operational condition of the first separator.

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