Supercritical CO_2 Extraction of Essential Oil from Algerian Fennel (*Foeniculum vulgare Mill*)

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Abstract
The technology of supercritical C02 has real advantages qualitatively and ecologically. In fact, it does not use organic solvents or high temperatures, and does not generate wastes. Its solvent power allows the extraction of many molecules. From an environmental point of view, CO2 is a non-toxic gas which advantageously replaces many organic solvents subject to regulations getting ever severe. It does not contribute to the greenhouse effect, being used in a closed circuit.
The present work presents some findings particularly concerning the use of supercritical fluid in the extraction process of oil fennel at different temperatures and pressures. Fennel oil has been extracted using supercritical CO2, investigating the influence of pressure and temperature and representing extraction curves.

Keywords: *Supercritical extraction; Supercritical CO2; Fennel seeds, Critical state*

Résumé

La technologie du $C0_2$ supercritique présente d'incontestables atouts sur les plans qualitatif et écologique. En effet, elle n'utilise pas de solvants organiques, ni de fortes températures, et ne génère pas d'effluents. Son pouvoir solvant à géométrie variable, permet d'extraire de nombreuses molécules.

D'un point de vue environnemental, le CO_2-SC est non toxique, remplace avantageusement de nombreux solvants organiques soumis à des réglementations de plus en plus sévères. Il ne contribue pas à l'effet de serre, étant utilisé dans un circuit fermé.
Cette étude entre dans ce cadre, elle présente un des travaux réalisés, et concerne en particulier l'utilisation de fluide supercritique dans le processus d'extraction de l'huile de fenugrec à différentes températures et pressions, utilisant du CO_2 supercritique. L'influence de la pression et de la température en tant que variables dépendantes a été étudiée et les courbes d'extraction en représentées.

Mots-clés: Extraction supercritique ; CO2 Supercritique ; Graines de fenouil ; Etat critique.

1. Introduction

Supercritical fluid extraction is a technique where the solvent is a fluid at supercritical conditions. Supercritical fluids are characterized by a low viscosity close to that of gases, a density close to that of liquids and a high diffusivity. Thus, supercritical fluids may behave as solvents with a great solvent power enhancing the solubility of the compounds with adequate changes in the operating conditions of pressure and temperature.

Therefore many industrial fields are interested in the technology of supercritical CO_2 with its numerous applications such as decaffeination, removal of contaminants, purification of protein, extraction of flavors, extraction of essential oils, odor, discoloration, etc. Several other supercritical fluids are considered, particularly water and propane, but the most widely used one remains CO_2 upon which this technology is based due to its adjustable solvent power at the applied conditions of pressure and temperature, its great availability, non toxicity, low cost, etc. Also its supercritical state is reached at a pressure just over 74 bar and a temperature of 31 ° C, making very suitable for thermolabile compounds. CO_2 has also very particular properties like a high diffusivity of the order of that of a gas and a high density similar to that of a liquid, hence a good ability to diffusion, and good transport properties and solvent power, respectively, ensuring good extracting properties [1- 3].

An extraction process with supercritical CO_2 is operated in a closed loop, having pressurizing means (pumps) and heating means (heat exchangers) to bring it above its critical point. The product to be treated is placed in an extractor through which flows a supercritical CO_2 stream. The fluid charged with the extracted compound is then expanded to separate from the extracted compound. The latter is collected in a separator.

Fennel (Foeniculum vulgare Mill, family Umbelliferae) is an annual, biennial, or perennial aromatic herb, depending on the variety. It has been known since antiquity in Europe and Asia. The leaves, stalks, and seeds (fruits) of the plant are edible. The dried, aromatic fruits are widely used in culinary preparations for flavoring bread and pastry, in candies, and in alcoholic French liquors, as well as in cosmetic and medicinal preparations [4]

The present study is concerned with the supercritical CO_2 extraction of oil from local fennel seeds as well as the comparison of extraction yields and compositions of the extracts and distilled oil and the evaluation of its organoleptic characteristics obtained according to different methods [2].

2. Materials and methods

Solvents: Extractions were carried out with carbon dioxide of 99.7% purity supplied by Air Mediterranean sea liquid (France).

Fennel Seeds: The fennel seeds used were purchased from a local market in Algeria in the city of Constantine. The moisture content of the raw material was 7.5% (w/w). The seeds were ground to specific particle size before the extractions. A typical particle size distribution was studied.

Equipment and Extraction.

Analytical SFE Equipment

The experimental device shown in Figure 1 used at the laboratory scale (SFE20ml) was provided by Separex (champigneulles, France). It allows working with three autoclaves of capacity 5, 10 and 20 cm^3. In the present work the $5cm^3$ was used at a maximum pressure of 400 MPa and a flow rate of 0.5kg / hour.

The extraction autoclave was filled with an homogeneous mixture of fennel powder. The liquid CO_2 was a priori cooled by a cryogenic bath over (0°C), filtered and then pumped into the extractor until the working pressure was reached. Before entering the extraction autoclave, CO_2 was pre-heated to the desired extraction temperature. Supercritical CO2 then came into contact with the dried seed. The pressure and the flow rate were maintained constant by using the expansion valve.

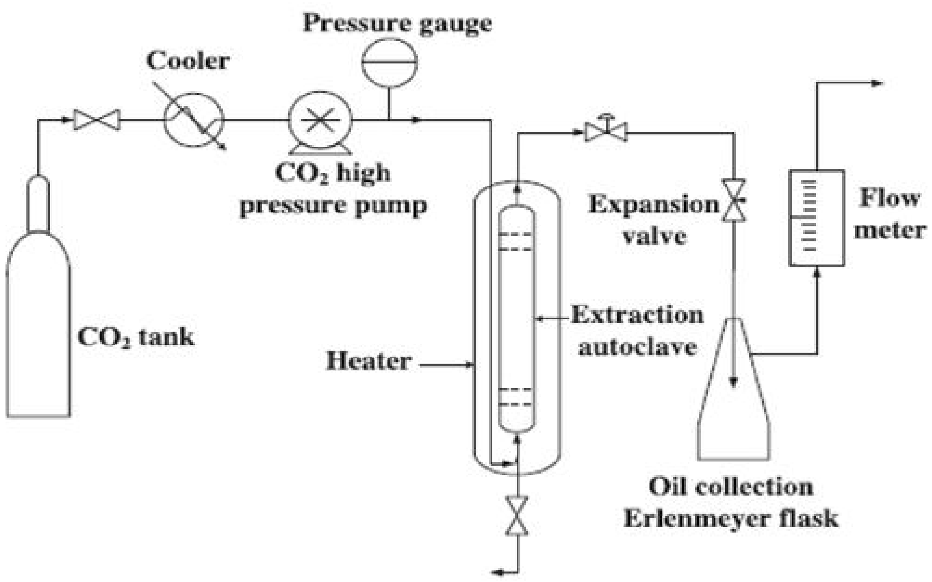

Fig.1. SC-CO2 extraction apparatus.

3. Results and discussion

In order to obtain the best conditions for the SC-CO_2 extraction of fennel seeds, experiments were performed at different pressure–temperature settings of the extractor. The selection of pressure and temperature ranges was based on the fact that a great change in the density and dielectric constant of CO_2 occurred between 100 and 400 bar, and in order to prevent the thermal degradation of some volatile oil compounds, temperatures up to 55°C were applied. The pressure varied from 100 to 400 bar and temperature from 35 to 55°C.

The Extraction yields expressed as grams of extracted oil/grams of seeds are represented in Figure 2. And Table 1 shows the experimental conditions which prevailed in each performed experiment. The effects of pressure and temperature on the supercritical CO2 extraction yield were studied. The extraction yield was found to vary significantly with temperature and pressure.

Table 1. SFE experimental conditions for fennel seeds extraction

Run	Pressure (bar)	Temperature (c°)	Time (min)	Flow (g/min)
1	100	35	120	50
2	100	45	120	50
3	100	55	120	50
4	250	35	120	50
5	250	45	120	50
6	250	55	120	50
7	400	35	120	50
8	400	45	120	50
9	400	55	120	50

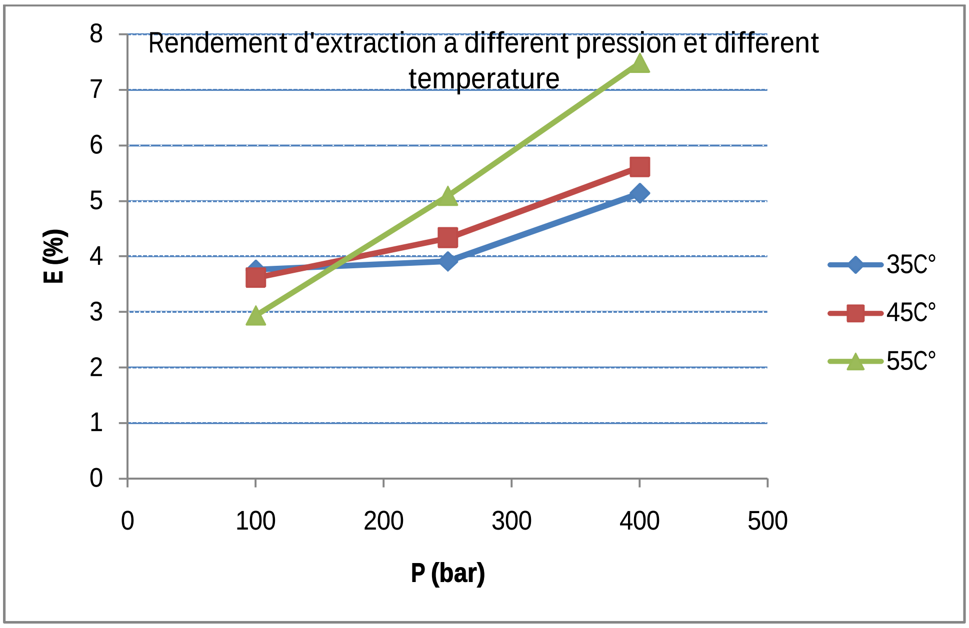

Fig. 2. Effects of the extraction pressure and temperature on the extraction degree of the essential oil

At 100 bar, the total amount of the obtained extract was unusually small but, as pressure increased, the amount of extracted material increased (Fig. 2). It was found that at higher pressures (250 and 400 bar) the solubility of some compounds from vegetable matter changed from negligible to significant. This is explained by the fact that the density and viscosity of supercritical CO_2 changed and, therefore, its extracting power increased. However, the high pressure resulted in greater cost for the extraction operating system.

It should also be noted that the appearance of the extracts changed slightly with the increase of temperature and pressure. The color, which was straw yellow at lower pressure and temperature, became darker, particularly with increasing temperature. Increased temperature at pressure of 250 and 400 bar, had a favorable effect on the extraction efficiency although the change was not significant.
At 100 bar, **the** effect of temperature on the extraction was negative, the effect of temperature on density was less pronounced and the solute vapor pressure effect dominated, leading to oil solubility and an increase in the yield with temperature. At 400 bar and 55°C the decrease in the diffusivity led to a reduction in the interaction between the supercritical fluid and the solute contained within the matrix and this in turn led to a decrease in the yield of the extraction process. The extraction yields obtained by SFE at 55°C and 400 bar were higher and reached 7.5%.

4. Conclusion

The supercritical CO_2 technology makes use of the supercritical fluid solvent power that can be modulated according to the applied pressure and temperature conditions, allowing selective extractions. The resulting products do not contain solvent residues, an important advantage towards the environment. This is a clean technology without wastes. Furthermore, the use of co-solvents modifies the solvent power of supercritical CO_2 and allows additional opportunities for this extraction process.

References:

[1] Ruberto, G., Tiziana Baratta, M., Deans, S. G., & Damien Dorman, H. J. (2000). Antioxidant and antimicrobial activity of Foeniculum vulgare and Crithmum maritimum essential oils. Planta Medica, 66,687–693.

[2] Reverchon, E., Daghero, J., Marrone, C., Mattea, M., & Poletto, M. (1999). Supercritical fractional extraction of fennel seed oil and essential oil: Experiments and mathematical modelling. Industrial & Engineering Chemistry Research, 38, 3069–3075.

[3] Gullie´n, M. D.; Manzanos, M. J. Contribution to Study Spanish Wild-growing Fennel (*Foeniculum vulgare* Mill.) as a Source of Flavour Compounds. *Chem. Mikrobiol. Technol. Lebensm.* **1994**, *16*, 140-144.

[4] Sima´ndi, B., Dea´k, A., Ro´nyai, E., Yanxiang, G., Veres, T.,Lemberkovics, E´ ., et al. (1999). Supercritical carbon dioxide extraction and fractionation of fennel oil. Journal of Agricultural and Food Chemistry, 47, 1635–1640.

[5] Gullie´n, M. D.; Manzanos, M. J. A Study of Several Parts of the Plant *Foeniculum vulgare* as a Source of Compounds with Industrial Interest. *Food Res. Int.* **1996**, *29*, 85-88.

[6] Gupta, K.; Thakral, K. K.; Gupta, V. K.; Arora, S. K. Metabolic Changes of Biochemical Constituents in Developing Fennel Seeds (*Foeniculum vulgare*). *J. Sci. Food Agric.* **1995**, *68*, 73-76.

[7] Marrone, C., Poletto, M., Reverchon, E., Stassi, A., “Almond oil extraction by supercritical CO2: experiments and modelling,” *Chemical Engineering Science*, vol. 53, N°. 21, pp. 3711–3718, 1998.

[8] Palazoglu, T. K., Balaban, M. O., “Supercritical CO2 extraction of lipids from roasted pistachio nuts,” *Transactions of the American Society of Agricultural Engineers*, vol. 41, N°. 3, pp. 679–684, 1998.

[9] Salgin, S., Salgin, U., “Supercritical fluid extraction of walnut kernel oil,” *European Journal of Lipid Science and Technology*, vol. 108, N°. 7, pp. 577–582, 2006