SUPERCRITICAL FLUID EXTRACTION OF PEACH (*PRUNUS PERSICA*) SEEDS

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ABSTRACT

The aim of this study is to investigate the extractability of peach seed oil using supercritical CO_2 and the effects of pressure (15.0 and 19.8 MPa), temperature (313.15 and 324.15 K) and cosolvent concentration (up to 5.0 mol % ethanol) on the extraction yield. Furthermore, preliminary results on the effect of kinetics parameters such as the geometry of the extractor and the solvent flow rate on the initial extraction yield are presented. The extracted peach oils are characterized with respect to fatty acids and tocoferols content by CG and HPLC, respectively.

INTRODUCTION

Spain is one of the main producers of peach in Europe (eight hundred thousand tons in 2006)[1]. A part of the peach harvested is processed in the food industry being the seed one of the subproducts. Peach seeds contain 40% wt of oils. The main fatty acids found in peach seed oil are oleic acid (18:1), ca. 58%, linoleic acid (18:2), ca. 32%, and palmitic acid (16:0), ca. 8%[2]. Linoleic acid is an example of the essential fatty acids that are necessary for human metabolism. It is known that a high content of polyunsaturated acids in vegetable oils reduces cholesterol level in the enriched diets[3]. So the peach seed can be considered as an important source of the oil for food and cosmetic industries.

Vegetable oil from seeds is traditionally processed by hexane extraction from ground seeds. The process is very efficient, but its major problem is the presence of hexane residues in the extract that must be removed. Steam and vacuum distillation are used to remove the hexane. The possible degradation of thermally labile compounds in the oil and the incomplete hexane elimination are the drawbacks of this process. Therefore, several authors have proposed the supercritical fluid extraction (SFE) as an environmentally benign alternative to conventional solvent extraction[4,5]. Carbon dioxide is the most widely used supercritical fluid. Carbon dioxide is non toxic, non flammable and is available at low cost with a high degree of purity. Its low critical constants (304.12 K and 7.38 MPa) allow supercritical operation of thermally labile compounds. CO_2 has adequate solvent properties for extraction of triglycerides. The addition of a small amount of a liquid modifier can enhance significantly the extraction of polar compounds. The aim of this study is to investigate the extractability of peach seed oil using supercritical CO_2 and ethanol-modified CO_2 and studying the effects of pressure, temperature, geometry of the extractor and solvent flow rate on the initial extraction yield. The extracted peach oils were characterized with respect to fatty acids (FA) and tocoferols content by CG and HPLC, respectively. Other seeds or their processing wastes have been the subject of several supercritical fluid studies. For instance, the kernel oil was extracted from apricot seed using supercritical CO_2[6] or propane[7]. However, to the best of our knowledge, SFE of the peach seeds has not been attempted.

MATERIALS AND METHODS

CO_2 (99.99 mol%) was supplied by Air Liquide. Ethanol absolute, used as cosolvent, (99.9 mol %) and hexane (99.0 mol %), used in the Soxhlet extraction, were supplied by Panreac and Carlo Erba, respectively. Diethyl ether, used to collect the extracts was supplied by Fluka (99.8 mol %). Peach seeds (*Prunus persica*, red variety) were supplied by a peach processing company from Murcia, Spain. Unshell peach seeds were ground into small pieces using a kitchen-type grinder (Ufesa, Spain). The ground seeds were mixed with 2 mm glass beads and were packed in a cylindrical net.

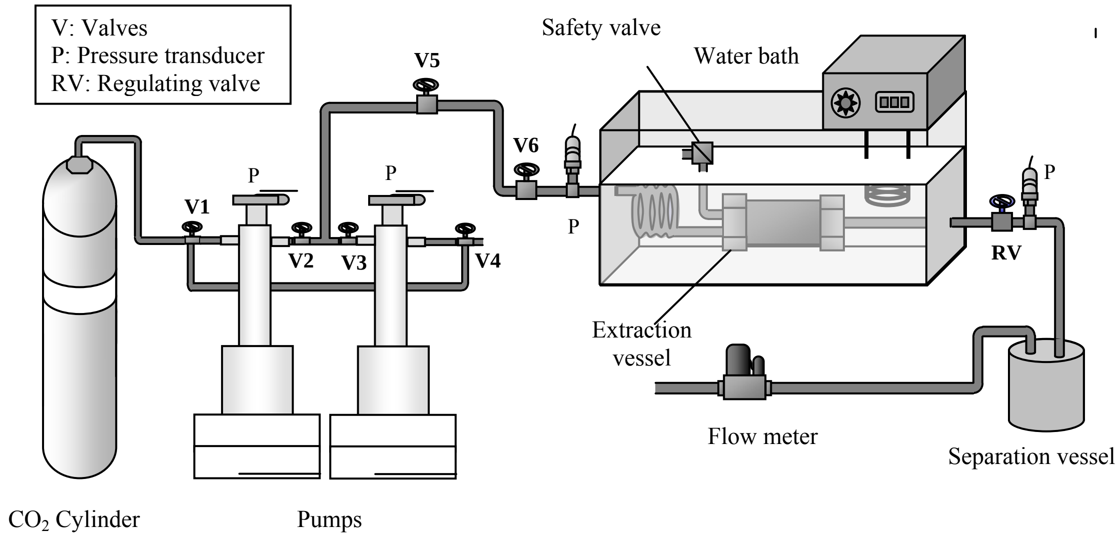

Figure 1. Experimental apparatus

The supercritical extraction was carried out in a semi-batch flow extraction apparatus built at our laboratory. The flow diagram of the equipment is shown in figure 1. This apparatus can operated at temperatures between 293 y 333 K and pressures up to 20.0 MPa. CO_2 was pumped at constant pressure into a 230 mL extraction vessel, using an ISCO pump (260D model). The vessel was filled with the seed sample (10-20 g) and glass beads. The pressure was measured in three points of the apparatus using DRUCK relative pressure transducers. The extraction vessel was immersed in a water bath (SELECTA, TECTRON 3000543 model) in which temperature was controlled within ±0.05 K. The CO_2 flow was controlled by means of a regulating valve (Swagelok, SS-31RS4). A flow meter (BROOKS, model 5851E) was used to measure the total amount of CO_2 used. The extracts were collected in glass tubes (previously weighed) placed in the separator at ambient temperature and pressure. The amount of extract obtained was established by weight. The extracts obtained from the supercritical fluid extraction of the peach seeds were analysed for their content in fatty acids by gas chromatography using the IUPAC 2301 method[8]. The extraction conditions were 313 and 324 K and 15.0 and 19.8 MPa, CO_2 flow rate was 0.40 Ln/min. Experiments with CO_2 modified with 2.5 or 5 % mol ethanol were carried out at 324 K and 15.0 and 19.8 MPa, at the same CO_2 flow rate. A second pump was used to introduce ethanol in the CO_2 pump and premix both components.

RESULTS

The supercritical extraction curves obtained are presented in figure 2. The yield is expressed as g of extracted oil$\times$100/g of seeds. The effect of pressure and temperature on the supercritical CO_2 extraction yield was studied at 313 and 324 K and 15.0 and 19.8 MPa (figure 2 (a)). Extraction of peach seeds with supercritical CO_2 modified with 2.5 % and 5 % mol ethanol was also carried out at 324 K and different pressures (figure 2(b)). In both cases the extraction yield varies significantly with temperatures and pressure with values ranging from 3 to 30 % or from 10 to 35 % for pure CO_2 or ethanol-modified CO_2, respectively. As expected, at constant temperature the yield increases with pressure, due to the increase in density of CO_2 or CO_2 + ethanol mixtures and, thus, in the solvent power.

The effect of pressure on the extraction yield is more pronounced when pure CO_2 is used. The change in density with pressure is higher in pure CO_2 than in the mixture of CO_2 + 5% mol ethanol under those conditions[9]. At each pressure, the extraction yield using supercritical CO_2 decreases as temperature increases, this effect is attributed to the decrease of the CO_2 density which dominates over the increase of the solute vapour pressure. In figure 2, the effect of cosolvent concentration in CO_2 on the extraction yield at 324 K is shown. The yield increases as the ethanol concentration gets higher due to the increase of solvent polarity.

Extraction yield in liquid hexane (Soxhlet) was 48 % w/w. In comparison, the highest yield in supercritical fluid extraction was 32 % for the experiment conducted at 324 K and 19.8 MPa using CO_2 modified with 5% ethanol. Assuming that the oil extraction using hexane is complete, this value represents a 70 % of the maximum value. Similar yields have been reported for other seeds oils [10,11].

In this study, preliminary results about of the influence of the extractor geometry on the supercritical CO_2 extraction yield of peach seeds at 313 K and 19.8 MPa are presented. For this purpose, a smaller tubular extractor of 17 mL was used. The influence of the solvent flow rate on the initial yield was studied. It is found that the initial extraction yield is independent of the extractor geometry and the solvent flow; however, the extraction time is smaller for the 17 mL extractor. The weak dependence of the initial yield on these kinetics parameters seems to indicate that the process is solubility controlled.

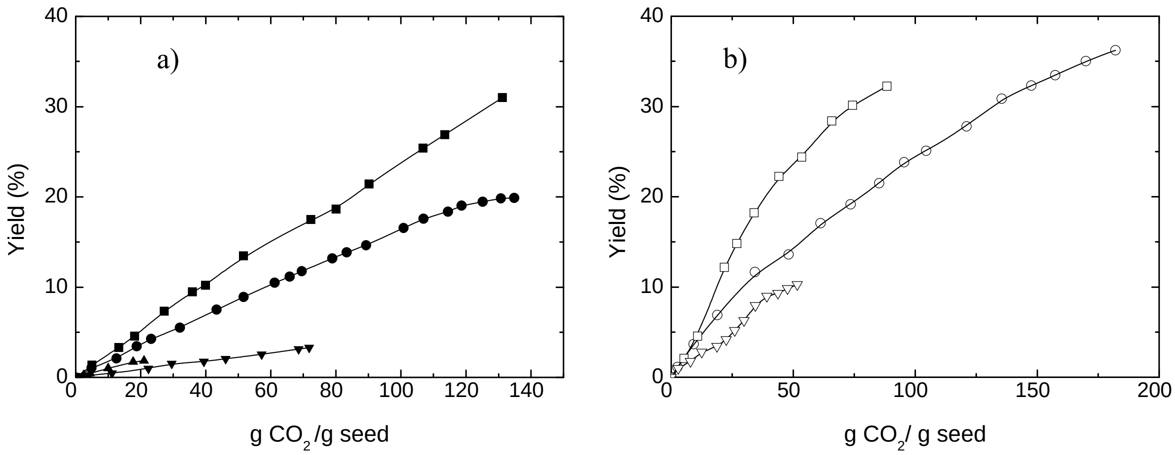

Figure 2. Extraction yield of peach seed as a function of g CO_2/g seed. a) Pure supercritical CO_2 at 313 K and 15.0 MPa (▲); 313 K and 19.8 MPa (■); 324 K and 15.0 MPa (▼); 324 K and 19.8 MPa (●). b) Supercritical CO_2 modified with ethanol at 324 K: 15.0 MPa and 5 % mol ethanol (∇); 19.8 MPa and 2.5 % mol ethanol (O); 19.8 MPa and 5% ethanol (□).

The peach seed oil extracted are analysed for their content in FA by CG. No significant differences are observed in the composition among the oils obtained using supercritical CO_2 or modified CO_2 and the Soxhlet extraction using hexane. The oils obtained contain mainly palmitic acid (5.5-6.6 %), oleic acid (72 -78 %) and linoleic acid (16-18 %). These results are similar to those previously obtained using organic solvents by Kamel and Kakuda[2].

The amount of tocol (tocopherol and tricotrienol) in the seed peach oil obtained using supercritical CO_2 at 313 K and 19.8 MPa was determined by HPLC. The γ-tocopherol and γ-tocotrienol contents of the oil extracted are 44 and 150 mg/kg, respectively. The γ-tocopherol content is lower than that obtained in other oils extracted using supercritical carbon dioxide, while the γ-tocotrienol content is higher.

CONCLUSIONS

Supercritical CO_2 both pure and modified with ethanol showed to be effective in the extraction of oil from peach seeds. For the same solvent ratio, the highest initial yield is obtained at 324 K and 19.8 MPa with CO_2 modified with 5 % mol ethanol which represents 70% of the maximum yield obtained from this seed. The initial yield increases with pressure and decreases with temperature at the conditions of this study. Increasing the ethanol concentration in the solvent increases the extraction yield due to the increase in solvent polarity. Based on the FA composition, the oil obtained by supercritical extraction contained mainly palmitic acid (5.5-6.6 %), oleic acid (72 -78 %) and linoleic acid (16-18 %). There is no change in terms of fatty acid distribution in all the extracted peach seed oils at the conditions of this study.

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