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Survey on the extraction of oil from olive by supercritical fluid

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ABSTRACT

The high cost of organic solvents together with stricter environmental regulations and higher safety standards for medical and food industries emphasize the need for the development of new and clean technologies for the processing of food products. Supercritical fluid extraction (SFE), using carbon dioxide as a solvent, may be a viable alternative to the use of chemical solvents. The objectives of the project were to test the viability of extracting olive oil from dried olives with sc-CO2 by employing a laboratory-scale supercritical extractor; determine the composition of the extracted oil by means of a suitable analytical method; optimize the yield of extract by determining the optimum process conditions (temperature, pressure, time) with a statistical experimental design and surface response analysis and obtain a product which is free of harmful solvents and ready for human consumption without any subsequent refining, finally.

KEYWORDS

Supercritical fluid;
Oil;
Temperature;
Pressure.

INTRODUCTION

Extensive investigation in the mid-1800's on the phase behavior of carbon dioxide resulted in the values 30.92°C and 74 atm for the critical point of carbon dioxide, which are in close agreement to presently accepted values 31.1°C and 73.8 atm. The first industrial application of supercritical fluids is considered to be the de asphalting of heavy mineral oil fractions by means of dense propane in the petrochemical industry in the late 1930's. Since the 1950's, studies and development efforts have been focused on new ways of separating substances by making use of the unique properties of supercritical fluids[2]. Applying the concept of supercritical fluid extraction (SFE) to industry, scientists from the Max Planck institut fur Kohlenforschung studied the feasibility of using SFE in the food, petroleum and chemical industries. Zosel and coworkers from the Max Planck Institute were the first to characterize the use of sc-C02 as a solvent for caffeine[3]. In 1987 the first decaffeination plant was commissioned by Hag AG in Bremen. Following this a plant for hops extraction was constructed in 1982 in Germany and later in 1985 and 1988 facilities for hops (Pfizer) and coffee (General Foods) were commissioned in the United States[2].

In addition, there is an increasing public awareness of health, safety and environmental hazards associated with the use of organic solvents in food processing and possible solvent contamination of the final product. The high cost of organic solvents together with stricter environmental regulations and higher safety standards for medical and food industries emphasize the need for the development of new and clean technologies for the processing of food products. Supercritical fluid extraction (SFE), using carbon dioxide as a solvent, may be a viable alternative to the use of chemical solvents. One of the most popular and successful applications of SFE is the extraction of fats and oils with supercritical carbon dioxide (sc-C02). Almost all fats and oils lie within a polarity range extractable by CO2 or CO2 and an added modifier[1,2]. C02 is selected as solvent due to its non-reactive and non-toxic character, low cost, modest critical parameters, easy solute solvent separation and high selectivity[3].

Extraction by supercritical fluid

Supercritical fluid extraction has been traditionally applied in the food and pharmaceutical areas. Recent advancements in supercritical fluid technology are nutraceutical extracts (natural extracts from plants or natural products that exhibit physiological or health benefits)[12]. One of the most popular and successful applications of SFE is the extraction of fats and oils. Besides the ecological benefits, lipids have very high diffusion coefficients in supercritical fluids, much larger than in conventional liquid solvents. Thus, the extraction rates are enhanced and less degradation of solutes occurs[13].

History of olive

The olive is native of Palestine. It was known in Egypt in the 17th century B.C.[4]. The oil was used for cooking as well as for burning in lamps. In the 1900s pickling and canning procedures were developed in California[5]. Today the olive is the most extensively cultivated temperate fruit in the world and is produced in 39 countries worldwide, including all the Mediterranean countries, the south western United States, southern Australia and northern Africa. In South Africa olives has been commercially cultivated since the 20th century, residing mainly in the Western Cape[7]. More recently, cultivation extended to the drier summer rainfall regions.

(a) Economical significance

Worldwide 15 724 187 million tons of olives are produced on an area of over 8 million hectares. The United States industry value was $60.7 million in 2002, and has varied between $34 and $102 million over the last decade[5]. In 2004 South Africa's total olive oil production was 490 tons, compared to the total world output of about 3 million tons. The advantage South African producers have, is that oil is pressed during the European off-season, when oil is scarce and northern demand is high[8]. In addition, the local olive market shows a 10% growth in demand each year for table olives, and 20% annually for oil[9]. South African olive oil does very well in international competition. In 2004 Kloofenburg Estate olive oil won a prestigious award in the Italian world olive oil guide, which cited it as one of the best 15 olive oils in the world[8].

(b) *Olea europaea* as medicinal plant

Natural products and their derivatives represent more than 50 % of all drugs in clinical use in the world[l]. About 119 plant derived chemical compounds of known structure were identified as currently being used as drugs or biodynamic agents that affect human health, including morphine, atropine, codeine and digoxin. It has been estimated that 80% of people living in developing countries are almost completely dependent on traditional medicinal practices for their primary health care needs, which means that about 64% of the total population of the world utilizes plants as drugs[2]. Research in medicinal plants is thus of immense global importance. Olive oil derived from the ripe fruit of *Olea europaea* is high in monounsaturated fatty acids and antioxidants, which correlates strongly with the low rates of chronic diseases and particularly coronary hart disease (CHD) seen in Mediterranean countries where the majority of fat calories consumed are derived from olive oil. Western countries in contrast, where diets are high in saturated fatty acids, have a high incidence of CHD. This suggests that olive oil, through its beneficial effects on lipid metabolism, blood pressure, diabetes and clotting mechanisms, plays a major role in health preservation[3]. In addition, a variety of organic liquids and a selection of inorganic substances, noble gases and water may be used as supercritical fluids[4]. The choice of supercritical fluid is determined by the polarity of the substance to be extracted and the technical feasibility of the conditions required existing as a supercritical fluid. Corrosive, environmentally hazardous, flammable and explosive substances are typically unsuitable as supercritical fluids[5]. The relatively mild critical conditions, abundance, low cost, non-toxicity and un-reactive nature of C02 make it a suitable supercritical fluid for a variety of processes[6]. C02 can be used for the removal or extraction of non-polar and weakly polar compounds like alkenes, terpenes, aldehydes, esters, alcohols and fats[7]. Variation of temperature and/or pressure, or density, allows the solvent strength of sc-C02 to be adjusted to dissolve specific substances better than common organic solvents. The addition of small amounts of co solvent allows sc-C02 to dissolve more polar compounds[8]. Highly polar compounds are insoluble in C02, though water is soluble up to 0.3 mass % in C02 at 250 atm and 50°C. Two classes of polymers are notable exceptions, viz. amorphous flouro polymers and silicones. These materials, which have been found to be C02-phillic, serve as essential building blocks for surfactants designed for application in near-critical and sc-C02. The solubility of both polar and nonpolar solids in a supercritical fluid may be enhanced through the use of a modifier. Modifiers are added to the fluid in low concentrations (5% or less on a v/v basis) and are either polar (acetone, methanol) or non-polar (propane, octane). C02 has a small polarisability and no dipole moment, making it possible for additives to increase the polarisability of the substance. Modifiers have been shown to increase the solubility of a solute in the sc-C02 by an order of magnitude. While it is known that the polarisability of C02 is affected by the modifier, its interaction with the solute is still a matter of investigation. Methanol and acetone have been the modifiers most often studied. Methanol can act as either a Lewis acid or a Lewis base. During SFE the methanol may interact with functional groups on the solute or it may only be involved in solvent sphere formation. Solvent sphere formation seems to be more a function of methanol concentration rather than its ability to gain or lose electron density. Acid-base interactions between sc-C02 and an aqueous system cause pH to have a definite influence on any process occurring in such a medium. The fact that water is present in a large variety of extraction matrices stresses the importance of acid-base interactions within supercritical fluids.

In this study the extraction of olive oil from dried olives with sc-CO2 was investigated. Extraction of olive oil with sc-C02 has the potential advantage of obtaining high yields of oil within relatively short extraction times and a final product that is free of organic solvents and compares favorably with commercial olive oil without multiple refinements. Several authors have reported solubility data for certain components of olive oil, as well as sc-C02 extraction of olive oil from olive husk (solid residue left after first extraction of oil) and from polishing earths used in the refining process. SFE has been applied to the de-acidification of olive oil, which has a high content of free fatty acids when extracted mechanically. The possibilities of using sc-C02 to de-acidify olive oil without modifying its triglyceride composition and nutritional quality have been suggested.

MATERIALS AND METHOD

This study was aimed at extraction of olive oil with sc-C02 from dried olive fruit and analysis of the obtained oil, as well as at a comparison of the quality of the obtained oil with that of commercial olive oil. The equipment, materials, methods and procedures utilized to achieve this, are highlighted in this section. Figure 1 shows the supercritical setup.

RESULTS AND DISCUSSION

The effect of operating temperature is investigated on the extracted palmitic acid. The pressure varies from 200 and 400 atmosphere. In addition the oil recovery is evaluated in different operating temperature. The operating pressures are 200 and 400 atmosphere in this run.

Effect of temperature on extracted palmitic percentage

In this section the effect of temperature on the basic parameters in supercritical fluid extraction is investigated. All of the experiments are hold at 200 and 400 atmosphere. Operation safety restrictions are considered in high pressure working and high temperatures. So, temperatures up to at 400 atm

$$\mathbf{PalmiticAcid\% = 0.029T + 6.7667}$$
$$\mathbf{R^2 = 0.9279, P = 200atm} \qquad (1)$$

$$\mathbf{PalmiticAcid\% = -0.045T + 10.6}$$
$$\mathbf{R^2 = 0.9643, P = 400atm} \qquad (2)$$

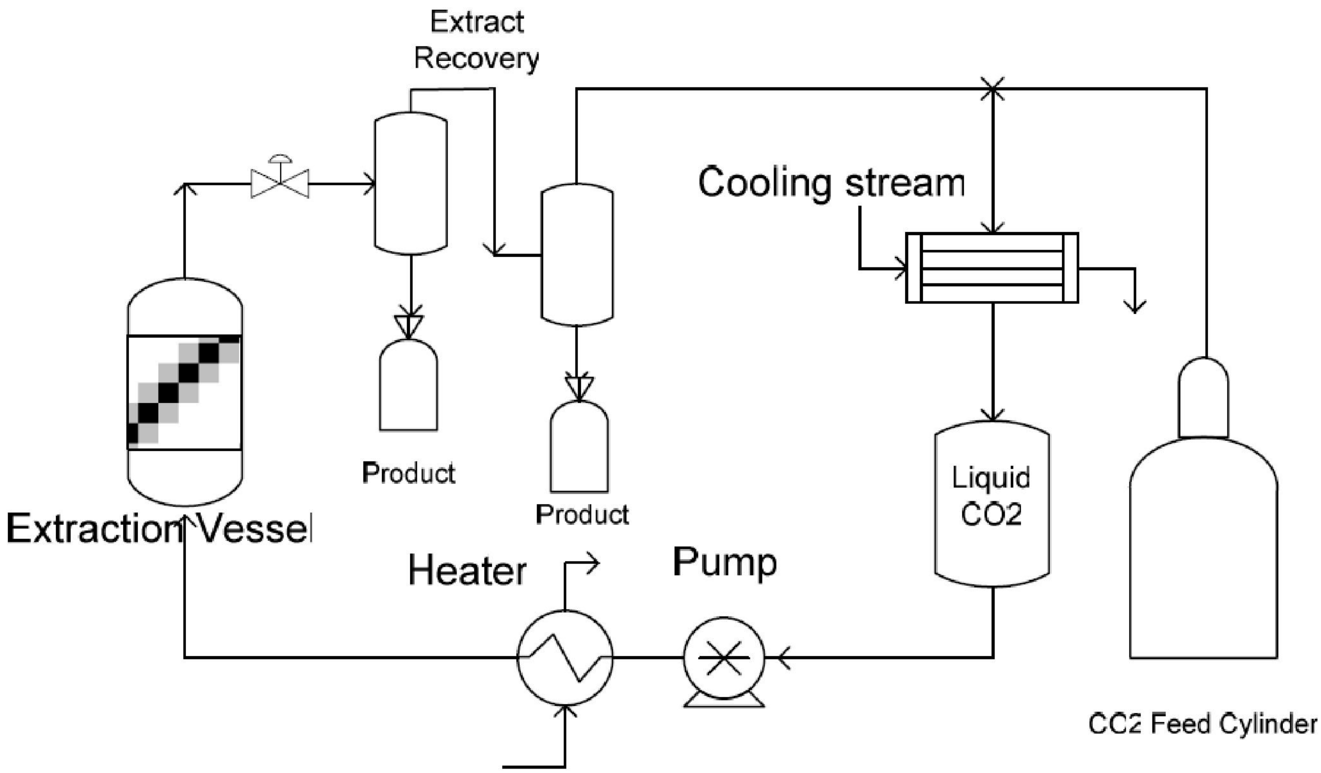

Figure 1 : Schematic of supercritical fluid extraction set up

Correlations 1 and 2 show the increase in temperature increases the percentage of extracted palmitic acid at 200 atm pressure. This may relates to the increase in the amount of diffusion coefficient due to temperature augmentation. However when the pressure increases into two times, 400 atm, the increase in temperature higher than 50 C, declines the amount of extracted palmitic acid.

Effect of temperature and moisture content on the oil recovery

$$\text{Oil Recovery\%} = 0.0224T^2 + 1.96T + 49$$

$$R^2 = 1, \text{Moisture content} = 7.5\% \qquad (3)$$

$$\text{Oil Recovery\%} = 0.0288T^2 - 2.44T + 117$$

$$R^2 = 1, \text{Moisture content} = 4.5\% \qquad (4)$$

$$\text{Oil Recovery\%} = 0.11T + 59.833$$

$$R^2 = 0.9973, \text{Moisture content} = 2.5\% \qquad (5)$$

Correlations 3, 4 and 5 state the effect of moisture content on the oil recovery versus temperature. Three different moisture contents, 2.5%, 4.5% and 7.5% are surveyed. The increase in the temperature from 20 C to 75 C shows different trends of oil recovery at different moisture content. The higher amount of oil recovery is obtained at lower temperatures (25 and 50) with the higher moisture contents (7.5% and 4.5%). At 70 C temperature the moderate amount of moisture 2.5% shows the higher oil recovery about 98%. The higher moisture expands the seeds and makes them more permeable and improves the oil recovery. But at 75 C and 7.5% moisture content, the seeds may be overheated and the amount of oil recovery decreases. So, 7.5% moisture content at 50 C is the best operation condition. The amount of residual oil content is important in the evaluation of supercritical fluid extraction.

CONCLUSION

Several aspects of supercritical carbon dioxide (sc-Co2) extraction of olive oil were investigated. These included a viability study using a laboratory-scale supercritical extractor, optimization of the extraction conditions. Satisfactory results were obtained in the investigated areas and several shortcomings were identified. The successes and shortcomings are briefly discussed in the results and discussion section. Results show the pressure and temperature affects the extraction yield. The higher moisture expands the seeds and makes them more permeable and improves the oil recovery. But at 75 C and 7.5% moisture content, the seeds may be overheated and the amount of oil recovery decreases. So, 7.5% moisture content at 50 C is the best operation condition.

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