Effect of Operating Conditions on Static/Dynamic Extraction of Peanut Oil Using Supercritical Carbon Dioxide

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ABSTRACT

Supercritical fluid extraction was successfully used to extract peanut oil from peanuts at temperatures between 40 and 80 °C and pressures of 5000-7000 psi. Static/dynamic cycling was used with a 10 minute static soak time, followed by a 10 minute dynamic interval. The overall extraction time was held constant at 3 hours. Peanut oil yield was determined gravimetrically. The crossover phenomenon was observed with the crossover pressure occurring at 6000 psi. Above the crossover pressure, an isobaric increase in temperature has a positive effect on the extraction yield, while below the crossover pressure an increase in temperature resulted in a decrease in oil yield. Yields between static/dynamic cycling and continuous runs were comparable, suggesting CO_2 usage could be reduced by half by static/dynamic cycling, creating a cost effective, greener process.

INTRODUCTION

Supercritical fluid extraction has emerged as an attractive separation technique for the food and pharmaceutical industries due to a growing demand for "natural" processes that do not introduce any residual organic chemicals. Supercritical CO_2 is by far the most commonly used supercritical fluid. The unique solvent properties of supercritical CO_2 have made it a desirable compound for separating antioxidants, pigments, flavors, fragrances, fatty acids, and essential oils from plant and animal materials. In the supercritical state, CO_2 behaves as a lipophillic solvent and so, is able to extract most nonpolar solutes. Separation of the CO_2 from the extract is simple and nearly instantaneous; leaving no solvent residue in the extract, as would be typical with organic solvent extraction. Unlike liquid solvents, the solving power of supercritical CO_2 can be easily adjusted by slight changes in the temperature and pressure, making it possible to extract particular compounds of interest. In addition, CO_2 is inexpensive, available in high purity; FDA approved, and is generally regarded as a safe compound (GRAS). CO_2 is also desirable for compounds that are sensitive to extreme conditions because it has a relatively low critical point, with a critical temperature of 31°C and a critical pressure of 1072 psi.

Supercritical fluids have unique solvent properties that are similar to both gases and liquids. Near liquid densities allow increased probability for interactions between the CO_2 and the substrate, similar to a liquid solvent [1]. The gas-like diffusivities of supercritical fluids are typically one to two orders of magnitude greater than liquids, allowing for exceptional mass transfer properties [2]. Moreover, near zero surface tension as well as low viscosities similar to gases, allow supercritical fluids to easily penetrate a microporous matrix material to extract desired compounds. The synergistic combination of density, viscosity, surface tension, diffusivity, and pressure and temperature dependence, allow supercritical fluids to have exceptional extraction capabilities.

The extraction of oil from peanuts, containing approximately 38% oil by weight, typically involves a series of steps including cracking into small pieces, cooking, mechanical pressing, and solvent extraction [2,3]. The mechanical pressing with screw presses or expellers removes approximately 50% of the peanut oil. The remaining oil is extracted using hexane, which is later removed through an evaporation-condensation system. The Code of Federal Regulations mandates that food grade oils should contain no more than 25ppm hexane [4]. Supercritical CO_2 extraction offers a greener alternative to the use of hexane in peanut oil extraction because it is less toxic and eliminates VOC emissions and solvent waste. In addition, energy costs associated with reaching the supercritical state for CO_2 have been shown to be less than energy costs associated with conventional solvent distillation [3].

Peanut oil is predominantly used in food applications; however, recent research has suggested that peanut oil extracted with supercritical CO_2 could be used as an sustainable alternative to diesel engine fuel [5]. As compared to hexane extraction, supercritical CO_2 is capable of producing higher quality oil because it can selectively extract the oil, leaving behind gums and other detrimental chemical residues.

The effect of temperature, pressure, particle size, and bed orientation on the extraction of peanut oil for a continuous system has previously been studied in order to determine the conditions that would yield an efficient oil extraction [5]. Temperatures between 25-120°C and pressures between 2000-10,000 psi were explored. This research found that above a pressure of 5800 psi, an increase in temperature increased the extraction rate. Below this pressure, an increase in temperature decreased the extraction rate. The maximum amount of oil was extracted at 10,000 psi and 100°C. A horizontal extractor achieved oil recoveries of 70%, while higher oil recoveries of 99% were approached in a vertically oriented bed [5]. Lower yields in the horizontal extractor were attributed to peanut meal settling in the vessel and solvent channeling across the top of the peanut meal.

Reducing the particle size of the peanuts has also been shown to have a positive effect on the extraction [5]. Smaller particles have a larger amount of surface area as well as an increased number of ruptured cells resulting in a high oil concentration at the particle surface. Little diffusion into the particles takes place; therefore, the amount of oil available for extraction is proportional to the surface area. By decreasing the particle size range from 3.35-4.75 mm to a range of 0.86-1.19 mm, the total oil recovery was increased from 36% to 82% by mass [5].

Another study used static/dynamic supercritical CO_2 extraction to determine the effect of roasting temperature and time on the overall quality and flavor of the oil [6]. Flavor compounds were identified with GC-MS analysis. As roasting time increased, a number of flavor compounds were formed including hexanol, methylpyrrole, and a range of pyrazine compounds. Sensory analysis was performed by a group of panelists to rate the flavor and overall quality of the oil. Analysis showed that the panelists' perception of roasted flavor and overall quality corresponded to the concentration of methylpyrazine and other pyrazines in the peanut oil. As the concentration of these compounds increased, the flavor was reportedly bitterer. The relationship between extraction conditions to the yield of peanut oil was not present in this work.

Although supercritical fluid extraction of essential oils has been widely studied, few studies have focused on the use of static/dynamic cycling for oil extraction of peanuts. Supercritical fluid extraction is an equilibrium process, and does require some amount of "soak" time for the solute to reach an equilibrium concentration in the supercritical phase. This investigation will focus on the effect of temperature and pressure on the extraction of peanuts in a system operated in static/dynamic cycles.

THEORY

The transport mechanism that occurs in supercritical fluid extraction is considered a leaching process. In leaching, the solvent must first travel to the surface of the material and diffuse through the pores. The solute then dissolves in the solvent, and is transported to the surface of the particle. Finally, the solute is transferred into the bulk fluid. This process will proceed until an equilibrium concentration of the solute is reached in the bulk fluid [7].

A mass balance on the oil in the solid peanut phase can be derived for this system using a model that assumes no concentration gradient is present through the bed of peanuts.

$$\frac{MdC_{Oil}}{dt} = A_p k_L \left(C_{Oil,sc} - HC_{Oil}\right) \tag{1}$$

where

M is the mass of Peanuts, (g peanuts)

C_{Oil} is the concentration of oil in peanuts (g oil /g peanuts)

$C_{Oil,SC}$ is the concentration of oil in the supercritical phase (g oil/mL CO_2)

A_p is the surface area per mass of peanuts (m^2/g)

k_L is the mass transfer coefficient (m/s)

H is the equilibrium constant (g peanuts/mL CO_2)

The use of static/dynamic cycling in supercritical fluid extraction is similar to an equilibrium-staged separation. In essence, each static/dynamic cycle simulates a stage of the separation. During the static soak time, the system is allowed ample time to reach equilibrium, and then released during the dynamic interval. If enough oil is present in the peanuts, it can be assumed that equal amounts of oil will be extracted at each of the equilibrium stages (9 stages based on a 3 hour extraction). By performing this extraction process in cycles, equilibrium stages are simulated, allowing for an efficient extraction that uses half the amount of CO_2 that would be used in a continuous system.

MATERIALS AND METHODS

Extra large, whole, raw, and blanched peanuts, were obtained for this study from Neshaminy Valley Natural Foods (Ivyland, PA). The experiments were performed using a bench scale supercritical fluid extraction unit (SFT-150) that was obtained from Supercritical Fluid Technologies Inc. The unit is a nonrecirculating unit with a 100 mL pressure vessel rated up to 10,000 psi. Bone dry CO_2 with a purity of 99.8% was used for all the experiments, and was obtained from Messer GT&S. A flowsheet of the process is illustrated in Figure 2.

The peanuts were chopped in a food processor for 1 minute in order to increase the surface area. The particle size range of the peanuts was determined through a sieve analysis, and ranged between 0.85 mm and 2.36 mm. Next, the peanuts were weighed (60-62 grams), and loaded into the extraction vessel. Glass spheres were added to the top of the bed of packed peanuts in order to fill the remaining head space and give a completely packed vessel.

Before pressurization, the system was allowed to reach the preset operating temperature. In order to ensure a liquid feed to the diaphragm pump, CO_2 was fed from the cylinder into a chiller, where it was cooled to –5 °C. The chilled CO_2 was discharged from the pump into the bottom of the pressure vessel, and the pressure was adjusted to the desired operating pressure.

After pressurizing the vessel, the peanuts were statically soaked for 10 minutes. After the ten minutes were completed, the static/dynamic valve was opened to a flowrate of approximately 85 ml/minute for 10 minutes. Typically, 7.5 volume exchanges are swept through the vessel during the dynamic interval [6]. In a 100 mL vessel, 750 mL should be swept, however, in the current experiments, 8.5 volume exchanges were used to ensure that all the oil would flow out of the pressure vessel. The CO_2 containing the extracted oil exitsed through the top of the vessel and passed through the static/dynamic valve. The unit is equipped with a restrictor valve, which is a valve that regulates the release flowrate of the CO_2. Due to the large decrease in pressure from inside the vessel to atmospheric pressure, the restrictor valve is heated to prevent the valve from freezing.Experiments were conducted in static/dynamic cycles, each interval being 10 minutes, for a total time of 3 hours. The static interval allows the peanuts to soak so that the CO_2 can penetrate the matrix and extract the oil. During the dynamic interval, CO_2 carrying the peanut oil flowed out of the unit and into a pre-weighed collection flask, where the CO_2 was vented to a fume hood. In a commercial process, the CO_2 would be compressed and recycled back to the process.

A range of operating conditions were tested. Experimental temperatures included 40, 50, 60, 70, and 80°C, while operating pressures included 5000, 6000, and 7000 psi. The percent yield of peanut oil (% by weight) was determined gravimetrically, and was taken to be the mass of oil collected, divided by the mass of peanuts loaded into the extraction vessel multiplied by 100.

RESULTS AND DISCUSSION

In each experiment, a light yellow, transparent oil with the characteristic peanut scent was extracted. A few suspended particulates were also present, which could be removed through a simple filtration step. The resulting peanut cake varied in color ranging from a yellow-brown tone for operating conditions that removed only a small fraction of the oil to a brittle chalky white color for conditions that removed a large percentage of the oil content. A color gradient was observed in the packed bed, with the lighter colored peanuts being at the bottom of the bed, and the more yellow tones at the top of the bed. This could be due to the fact that the equipment is an upflow unit and the peanuts at the bottom of the bed are more exposed to fresher CO_2 entering the vessel.

The yield of peanut oil exhibited a strong dependence on temperature and pressure. Figure 2 shows the yield of peanut oil verses temperature at constant pressures. The highest yield was obtained at the highest temperature (80°C) and highest pressure (7000 psi), and the lowest yield was obtained at the lowest pressure (5000 psi) and highest temperature (80°C).

At the lowest pressure, 5000 psi, the highest yield was obtained at 40 °C and the lowest at 80°C. The highest pressure, 7000 psi, showed an inversion in the effect of temperature as compared to 5000 psi. At 6000 psi, all temperatures yielded approximately the same value, ranging between 21.3 % and 22.1%.

Figure 3 shows the inversion effect that was observed above and below 6000 psi. These results correspond to the trend previously reported for peanuts in a continuous system [5]. This type of behavior is typical of binary solid-fluid systems, and is referred to as the crossover phenomena [2]. Below the crossover pressure of 6000 psi, an isobaric increase in temperature will decrease the solubility. Conversely, above the crossover pressure an isobaric increase in temperature will increase the solubility and overall yield.

There are two different factors that significantly contribute to the crossover effect, density and volatility [2]. At higher densities, the supercritical CO_2 is capable of contacting more surface area, thus causing more oil to dissolve and be extracted. An increase in temperature at isobaric conditions will decrease the density and solubility. The opposing effect is the volatility effect. At higher temperatures, the oil becomes more volatile, which allows more peanut oil to be extracted. Below the crossover pressure, the density effect is more prominent, which gives way to higher solubility and yields at lower temperatures. Above the crossover pressure, the volatility effect controls, giving higher yields at higher temperatures.

In order to compare the yields of static/dynamic system to a continuous system, a continuous experiment was performed at 80°C and 7000 psi. The yield from the static/dynamic run at these conditions yielded 25.4%, while the continuous run yielded 27.8% oil by weight. These results are reasonably comparable. Since CO_2 flowed through the system for the entire 3 hours during the continuous run, twice as much CO_2 was used compared to the static/dynamic run that flowed CO_2 through the system for 1.5 hours.

CONCLUSIONS

In this study, it was shown that performing supercritical fluid extraction in static/dynamic cycles is capable of achieving high yields comparable to continuous operation. In addition, operating in static dynamic cycles reduces CO_2 usage by half. The use of static/dynamic cycling in supercritical CO_2 extraction of peanut oil was demonstrated to be a safe, efficient, and a cost effective alternative to pressing and hexane extraction.

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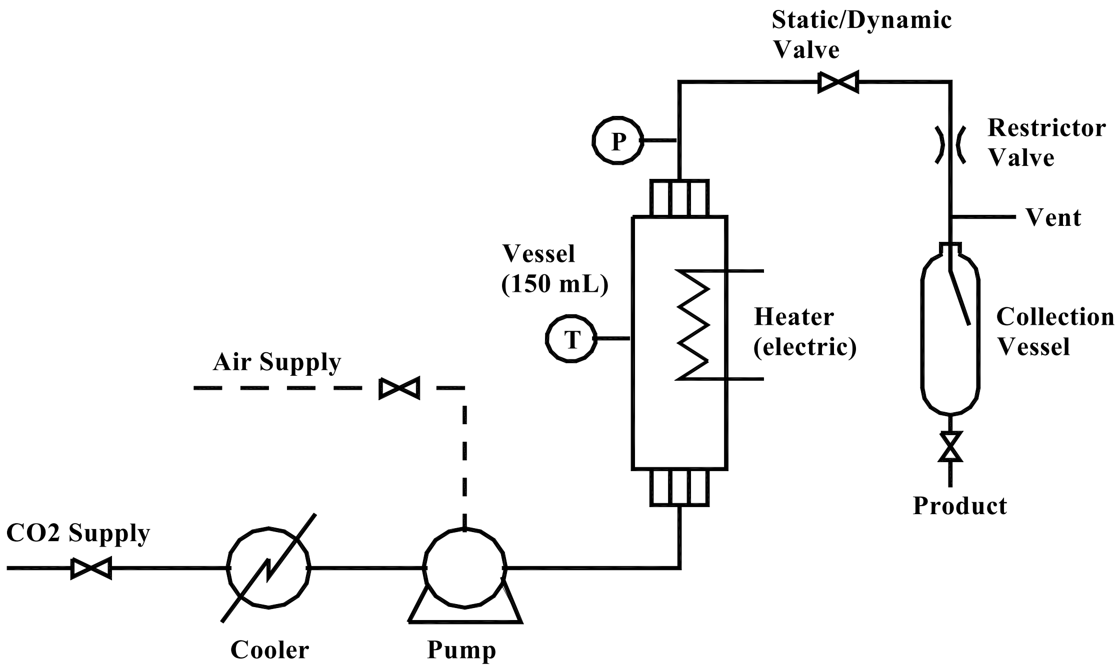

Figure 1: Flowsheet of Supercritical Fluid Extraction Setup

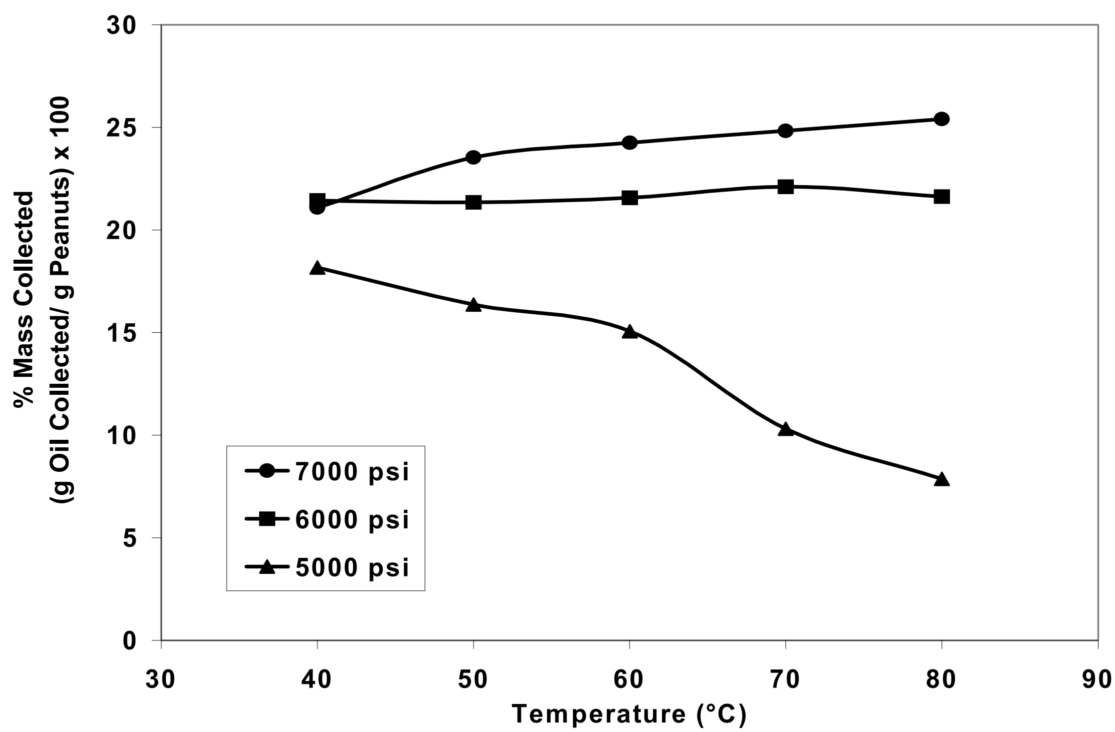

Figure 2: Peanut Oil Isobars: static (10 minutes):dynamic 10 (minutes), time=3 hours

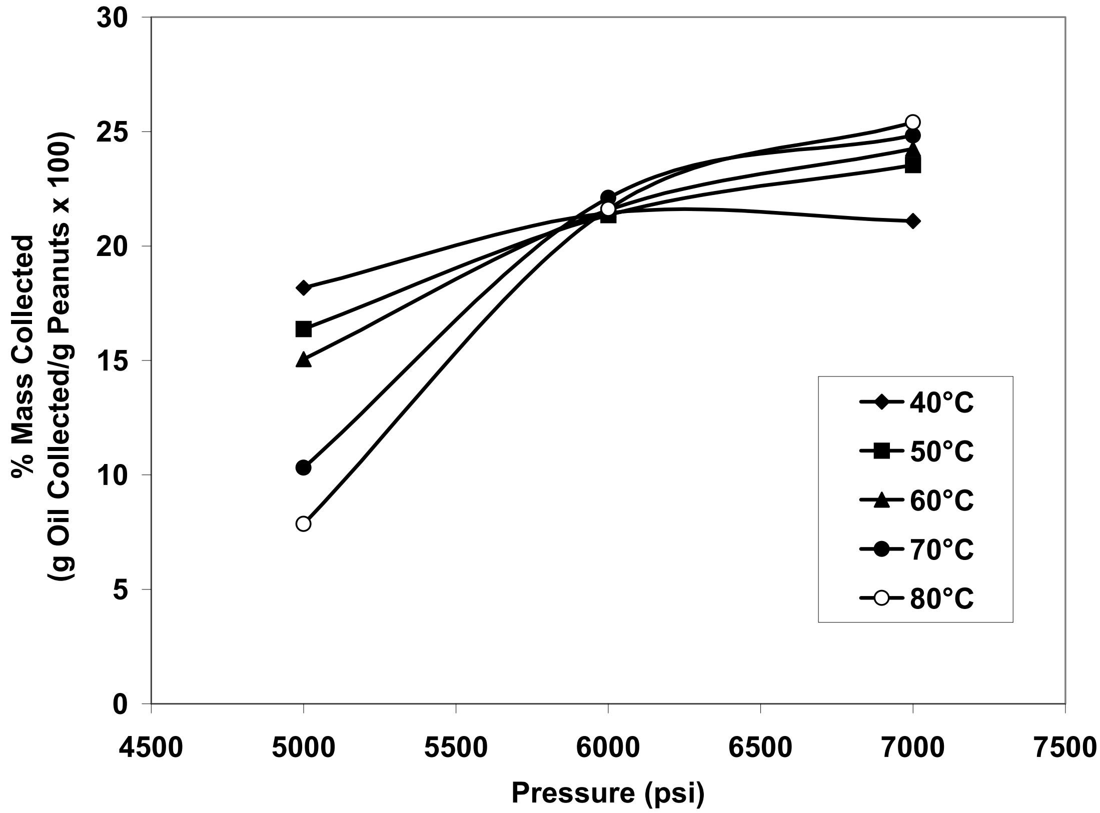

Figure 3: Peanut Oil Isotherms: static (10 minutes):dynamic 10 (minutes), time=3 hours