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Supercritical Fluid Extraction of the Triglycerides Present in Vegetable Oils

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Abstract

The use of supercritical carbon dioxide to extract the triglycerides present in vegetable oils was studied over a temperature range of 40 to 80°C and at pressures of 100 to 300 bar. The solubility of the triglycerides was found to be dependent upon the solvent density and the solute volatility. Minimal selectivity for the different molecular weight triglycerides was observed at the conditions studied.

INTRODUCTION

Vegetable oils consist primarily of triglycerides covering a range of molecular weights, the range and distribution of which determines the physical properties of the oil and the uses for which it is suitable. Fractionation of oils is of interest because it allows the tailoring of a natural oil to particular specifications. Distillation is generally not suitable for vegetable oils because the triglycerides may break down at the temperatures required. Solvent residue inherent in solvent extraction, particularly hexane which is commonly used, is also becoming increasingly unacceptable in a product primarily used for human consumption. The high flammability of extraction solvents such as hexane also serves to make their use undesirable (*1*). Consequently an alternative fractionation technique without these shortcomings would be advantageous. Supercritical fluid extraction is therefore being considered as an alternative for the fractionation of vegetable oils, as well as for the extraction of the oil from oil-bearing plants (*2–4*).

A vegetable oil typically consists of a range of triglycerides, approximately 10% diglycerides, and a small fraction of free fatty acids and other minor constituents and impurities. A number of the minor components are of value as pharmaceuticals and food additives. Consequently, there is an economic incentive for the extraction or concentration of these components.

The use of supercritical fluids (SCF) in extraction processes is currently attracting intense interest, partly because of the potential energy savings offered by such processes (*5*). The inherent advantages of using a supercritical solvent as compared to other solvents are that SCF solvents may be nontoxic, inexpensive, and their solvating power can be manipulated by small variations in either pressure or temperature.

The present work involves the study of the solubility and selectivity, in supercritical carbon dioxide, of the various triglycerides found in vegetable oils. The information obtained will allow the determination of the applicability of supercritical fluid extraction to the extraction and fractionation of vegetable oils.

EXPERIMENTAL

All extraction experiments were performed in a countercurrent contacting column which is shown schematically in Fig. 1. Liquid CO_2 of industrial grade was delivered from a liquid supply cylinder [1], at approximately 50 bar, to the suction side of a Bran & Luebbe positive displacement metering pump [2], which was used to pump the liquid to the extraction pressure. The carbon dioxide pump head was cooled to ensure that the critical temperature was not exceeded. This precaution was necessary because the compressibility of the carbon dioxide increases dramatically at the critical point, thus reducing pump efficiency to a degree where effectively no pumping occurs. The flow rate of solvent was controlled by adjusting the length of the pump stroke. The liquid carbon dioxide was fed from the pump to a heating coil [3] located in the temperature control bath [9], where the liquid was heated through its critical point to the desired extraction temperature. From the heating coil the carbon dioxide, in the supercritical state, was directed into the bottom of the extraction column [4] and allowed to flow upward through the column, contacting the oil phase which flowed countercurrently downward through the column. The pressure of the system was measured by a pressure transducer [10] at the exit of the column. Dissolved solute in the supercritical phase was precipitated by reducing the fluid pressure to atmospheric through a heated control

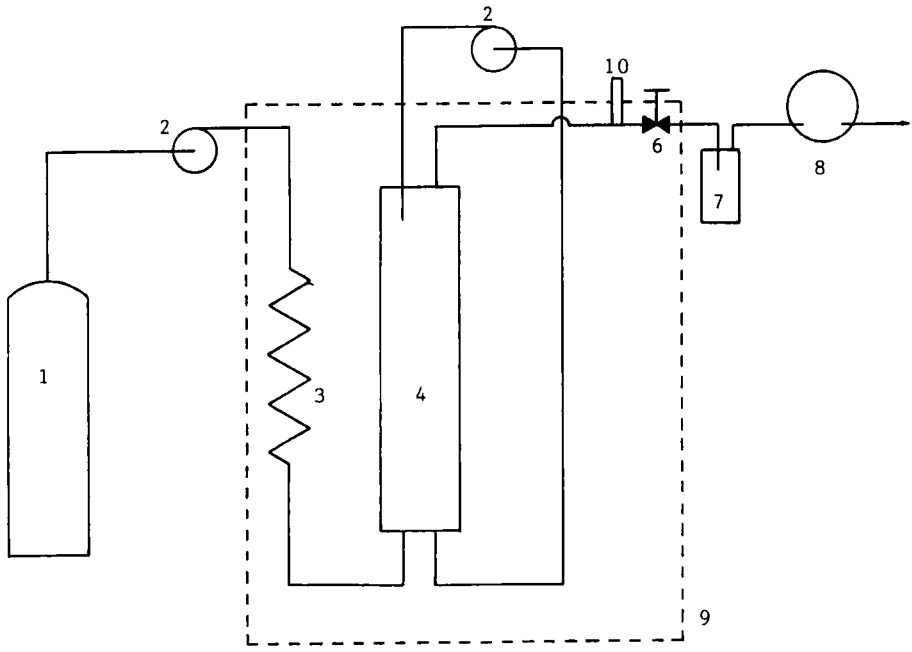

FIG. 1. Diagram of experimental apparatus.

valve [6], and the precipitate was collected in a sample trap [7]. The control valve was heated to prevent it from freezing as a result of the Joule-Thomson effect. Pressure control was achieved through manual manipulation of the control valve. The flow of carbon dioxide was measured by using a wet test gas meter [8] connected to the sample trap outlet. The amount of solute collected and the gas volume passed through the system enabled the solubility of the oil to be determined. The oil phase was circulated downward through the column by the second head of the pump [2]. The extraction column was approximately 40 cm in height and had a volume of approximately 1.5 L. Column packings of 12 mm diameter were used to increase the contact area available for transfer of oil into the solvent. The preheat coil and the extraction column were contained in a constant temperature water bath [9] to control the extraction temperature.

All components of the system in contact with the fluid were manufactured from either 316 stainless steel or Teflon. The equipment was rated to a working pressure of 340 bar.

As the solubility of oils in carbon dioxide can be drastically reduced by the presence of small quantities of nitrogen, the system was thoroughly flushed with pure carbon dioxide after any dissassembly of components and prior to the commencement of an experiment.

The system was equilibrated at its operating temperature for a number of hours to ensure a constant temperature throughout the extraction column. The attainment of equilibrium solubility was verified by reducing the flow rate of carbon dioxide passing through the system until further reduction showed no change in solubility.

Samples of the extracted oil were esterified and subsequently analyzed by capilliary gas chromatography to determine the selectivity for the different triglycerides.

The oil used was a mixture of crude palm oil (50%), safflower oil (25%), and linseed oil (25%). This mixture was used to provide a larger range of triglycerides than would be obtained with a single oil. It also served to reduce the viscosity of the palm oil which was difficult to handle in its pure form.

RESULTS AND DISCUSSION

Initial experiments were conducted by using the extraction apparatus as a spray column, that is, without packing. Doubts about the efficiency of the fluid–liquid contact area and mass transfer were raised by the low extraction rates obtained. These extraction rates were obtained at a constant carbon dioxide flow rate and a number of pressures and temperatures. A number of different column packings were then tested to increase the efficiency of the mass transfer. The results obtained are shown in Fig. 2. The packings used were 1/2″ ceramic Raschig rings and 1/2″ stainless steel Pall rings. As is illustrated by the data in Fig. 2, greater mass transfer efficiency was obtained with the Pall rings.

On the basis of these preliminary studies, subsequent extractions were undertaken using the Pall rings as column packing. The results obtained, plotted as extraction rate versus pressure at temperatures between 40 and 80°C, are shown in Fig. 3. It is clearly shown from all of these isotherms that increasing the solvent pressure increased the solubility of the oil in carbon dioxide. This graph also shows a maximum extraction rate at a temperature of 60°C.

Extraction rate is plotted against temperature in Fig. 4 at pressures of 210 and 270 bar. These data clearly show the maximum occurring at 60°C. The reason for this maximum is that as the temperature is increased, the

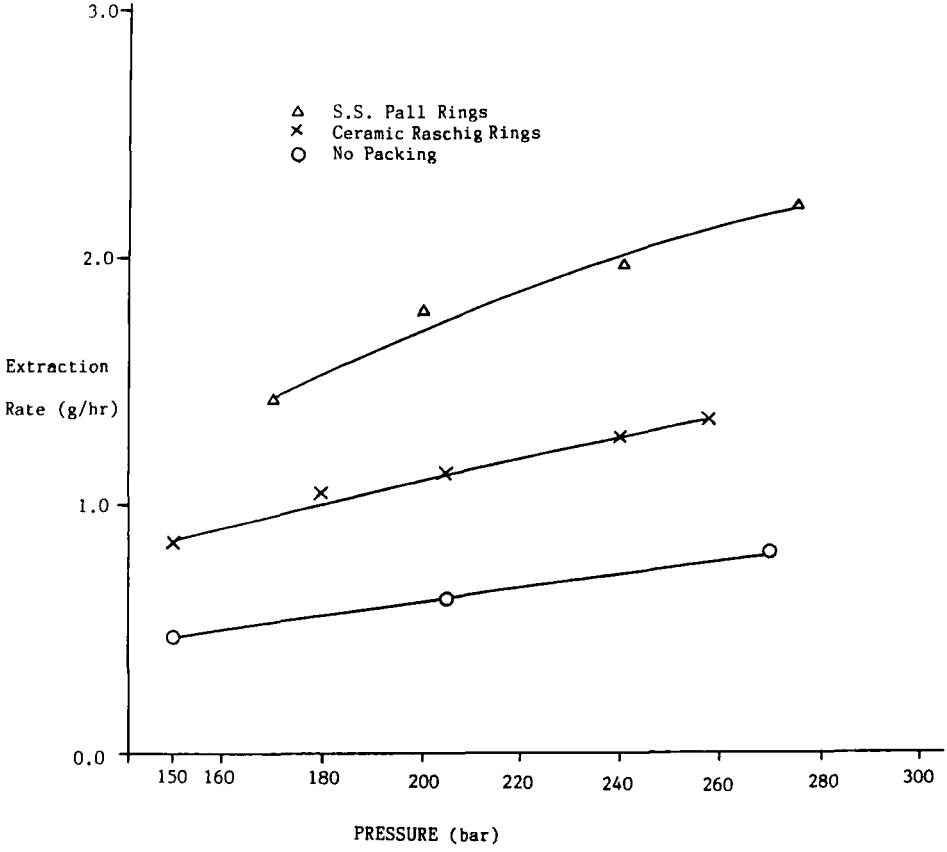

FIG. 2. The effect of column packing on the extraction rate.

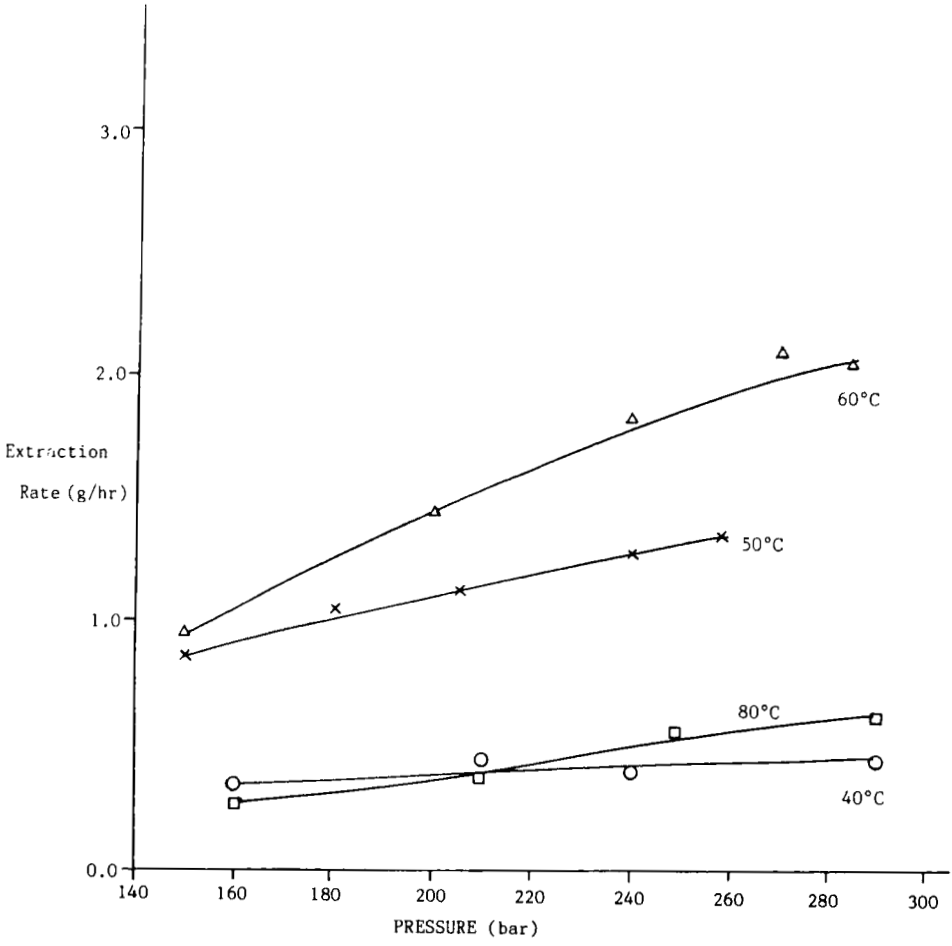

FIG. 3. The effect of pressure on the extraction rate.

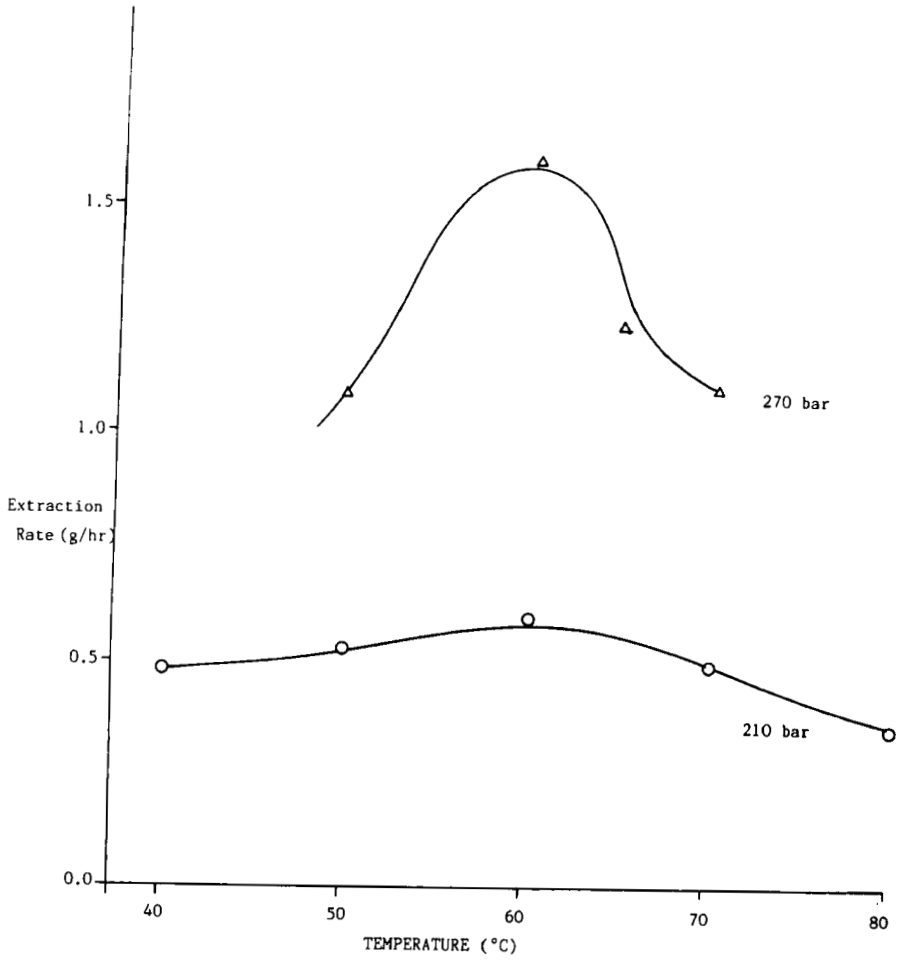

FIG. 4. The effect of temperature on the extraction rate.

solute volatility increases, which tends to increase solubility; however, the solvent density decreases, which tends to decrease the solubility. These two effects compete with each other, and one of them will normally be dominant in a particular temperature region. In this case the solute volatility effect is dominant at temperatures below 60°C and the solvent density effect is dominant above 60°C. The effect is more pronounced at higher pressures and tends to disappear at lower pressures. This phenomenon is generally referred to as retrograde behavior.

In Table 1 the fatty acid composition of the oil mixture which was extracted is shown. The analyses of the extracted samples reveal minimal change in the fatty acid compositions.

The low selectivity obtained can be partly explained by a phenomenon reported by Bamberger and coworkers (*1*). The solubility of the most soluble component in a mixture of triglycerides was similar to its pure component solubility. The less-soluble components, however, were found to have their solubility enhanced by the presence of the more-soluble components. This effect would reduce the selectivity obtained in a triglyceride mixture over that which would be expected from examination of the pure component solubilities.

The solubility data are plotted as a function of carbon dioxide density in Fig. 5. The purpose of plotting the data as a function of density is to separate the effects of solute volatility, which is not a function of density, and the solvent attraction forces, which are primarily density-dependent. Thus deviations from a linear relationship are due to solute volatility effects. The data show the solubility increasing monotonically with increased solvent density due to the solvating forces becoming greater as the distances over which they have to act becomes smaller. At constant density the higher solubility is obtained at the higher temperature as the volatility of the solute increases. These data show trends similar to the data of Fattori et al. (*6*) for canola seed oil plotted on similar axes, thus indicating that the oil mixture used in this work had a triglyceride composition similar to that of canola oil. As shown in Fig. 6, the pressure depen-

TABLE 1
Fatty Acid Composition of Oil

Temperature (°C)	Pressure (bar)	^{14}C:0	^{16}C:0	^{18}C:0	^{18}C:1	^{18}C:2	^{18}C:3
Starting oil		0.6	27.2	3.3	27.6	28.5	12.2
60	262	0.8	30.5	3.2	29.8	25.1	9.1
60	285	0.8	30.0	3.1	28.0	26.3	11.0

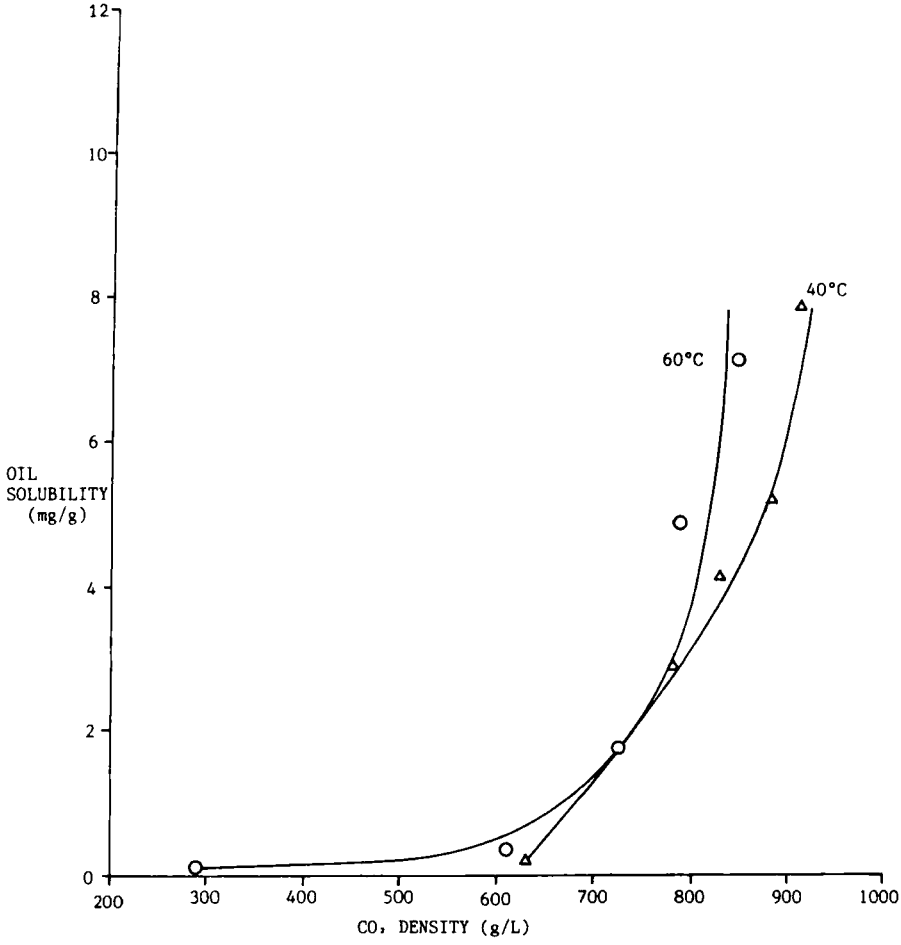

FIG. 5. Oil solubility as a function of carbon dioxide density.

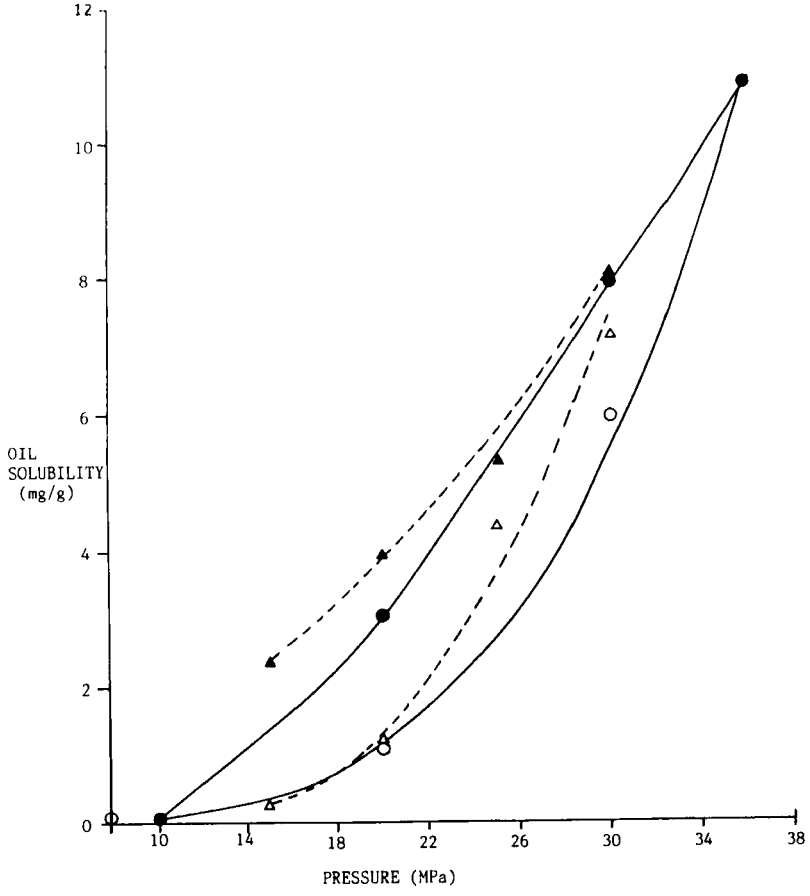

FIG. 6. Oil solubility as a function of pressure. Data of Fattori et al. (*6*): (○) 70°C and (●) 40°C. Data of the present study: (△) 60°C and (▲) 40°C.

dence of the solubility obtained in this study is also similar to the canola oil data of Fattori et al. (*6*). The solubilities obtained in this work, however, are slightly higher, which indicates a higher concentration of the more soluble, lower molecular weight triglycerides. It should be noted that the solubilities in Fig. 6 tend to converge as the pressure is increased beyond 250 bar. At higher pressures the effect of temperature is reversed so that increasing temperature resulted in increased solubility. This is due to the effect of the temperature on solute volatility being more pronounced than its effect on density at higher pressures.

CONCLUSION

The solubility of triglycerides in supercritical carbon dioxide was measured and found to have values ranging up to 8 mg oil/g carbon dioxide. The analysis of the extracted oil showed minimal selectivity for any of th individual triglycerides over the range of conditions studied.

Acknowledgments

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