

Pilot Scale Extraction and Fractionation of Rice Bran Oil Using Supercritical Carbon Dioxide

Zhiping Shen,[†] Martin V. Palmer,[‡] Simon S. T. Ting,[‡] and Robert J. Fairclough^{*†}

Victoria University of Technology, Werribee, P.O. Box 14428, MCMC, Melbourne 8001, Australia, and Australian Food Industry Science Centre, Private Bag 16, Werribee, Victoria 3030, Australia

In the first stage of this two-stage process, crude rice bran oil was extracted with supercritical carbon dioxide (SC-CO₂) from a 300 g batch of rice bran. Oil-laden SC-CO₂ from the extractor (24.1 MPa/40 °C) passed continuously to a second-stage column where an oil phase (raffinate) separated from the SC-CO₂ at various controlled temperatures and pressures. Measurement of the compositions of raffinates and extracts allowed calculation of partition coefficients of triglycerides, free fatty acids (FFAs), α -tocopherol, sterols, and oryzanol and, hence, the selectivities of the fractionations. Fractionation removed almost all water and reduced the FFA concentration in raffinate by up to 50%. Oryzanol and α -tocopherol concentrations in the raffinate were not reduced by fractionation, but the sterol concentration was reduced under conditions favoring FFA removal. Under the flow rate conditions studied (3.5 kg of CO₂/h), the fractionations could be described by equilibria between oil and CO₂ phases.

Keywords: *Supercritical carbon dioxide; extraction; fractionation; rice bran oil*

INTRODUCTION

Rice bran oil is a valuable domestic oil resource in many countries, although its acceptability as an edible oil has been hampered because of its commonly high free fatty acid (FFA) content resulting from the high lipase activity of the bran (Nicolosi et al., 1994). Deacidification by conventional means (alkali or physical refining) is a relatively expensive process and may not be economically feasible if alternative vegetable oils are readily available. Furthermore, the use of conventional refining methods can result in significant losses of minor but nutritionally important components of rice bran oil, such as oryzanol (Nicolosi et al., 1994). In a previous study, Shen et al. (1996) demonstrated the feasibility of extraction of oil from rice bran using supercritical CO₂ (SC-CO₂) at various temperatures and pressures on single-stage pilot equipment and described some apparent partition coefficients for triglycerides, FFA, α -tocopherol, sterols, and oryzanol in SC-CO₂ under the conditions studied. These results indicated that there may be potential to develop a fractionating extraction system through exploitation of these apparent SC-CO₂ solubility differences among various components.

Partial deacidification of some other vegetable oils by SC-CO₂ has been reported previously, for example: soybean oil (Friedrich et al., 1982), palm oil (Brunner and Peter, 1982), olive oils (Brunetti et al., 1989; Bondioli et al., 1992), and peanut oil (Ziegler and Liaw, 1993). After comparing the solubility isotherms of fatty acids and vegetable oil, Maheshwari et al. (1992) suggested that separation of fatty acids from triglycerides might be possible by using SC-CO₂ at densities <0.7 g/mL. Chrastil (1982) measured the solubility of certain fatty acids and triglycerides in SC-CO₂ within the pressure range 8–25 MPa and the temperature range 40–80 °C and showed that at certain temperatures and pressures, CO₂ has a higher solvent power for fatty acids than for the corresponding triglycerides. Zhao et al.

(1987) performed the fractional extraction of oil from rice bran by SC-CO₂ with a single column holding 20 g of rice bran, producing rice bran oil low in FFA using pressures of 15–35 MPa at 40 °C. However, the apparent solubilities of rice bran oil and the partition coefficients of its components, especially FFA, in SC-CO₂ of lower density (0.25–0.69 g/mL) have not been investigated. In a previous study (Shen et al., 1996), we explored the time course of extraction of rice bran oil and its components using dense CO₂ at various temperatures and pressures. While the partition coefficients measured in that study are of general utility in the design of oil extraction and refining procedures, the time course data are directly applicable only to the design of batch separations. The present study is an extension of that research and was conducted to determine the feasibility of using SC-CO₂ to simultaneously extract and fractionate oil from rice bran, with particular reference to deacidification, by means of a second-stage on-line solvent density reduction step.

More specifically, the aim of the present study was to continuously produce a rice bran oil of enhanced composition using a second-stage expansion column after primary SC-CO₂ extraction and to utilize the data from the expansion column to calculate the solubility of rice bran oil, the partition coefficients, and the selectivities of its components, as functions of temperature, pressure, and density under these lower density conditions.

MATERIALS AND METHODS

Materials. Medium-grain rice bran was provided by the Ric growers' Co-operative Ltd., Leeton, Australia. The moisture content and total hexane extractable matter in the bran were 8.48% and 17.59%, respectively.

Extraction Methods. A schematic diagram of the pilot plant extraction and fractionation unit (Distillers MG Ltd., U.K.) is shown in Figure 1. Food grade pure liquid carbon dioxide (CO₂; 99.8% purity; CIG, Melbourne) was cooled and pressurized by a piston pump to a pressure of 24.1 MPa, which was regulated and checked by a variable pressure indicator controller. The pressurized CO₂ passed through a heater and

[†] Victoria University of Technology.

[‡] Australian Food Industry Science Centre.

Table 2. Distribution of Minor Components of Rice Bran Oil, Extracted at 24.1 MPa/40 °C and Fractionated at Various Temperatures and Pressures

pressure (MPa)	temp (°C)	oryzanol (mg/g of oil)		campesterol (mg/g of oil)		stigmasterol (mg/g of oil)		β -sitosterol (mg/g of oil)		α -tocopherol (mg/g of oil)	
		raffinate	extract	raffinate	extract	raffinate	extract	raffinate	extract	raffinate	extract
8.6	50	10.85	ne	1.80	ne	1.60	ne	1.40	ne	0.25	ne
8.6	45	12.06	5.20	1.75	1.49	1.55	1.29	9.89	7.10	0.24	nd
8.6	40	11.20	6.43	1.65	3.40	1.50	3.10	9.30	18.50	0.22	0.00
9.9	40	12.15	6.36	1.45	2.70	1.25	2.45	7.76	15.09	0.19	0.10
11.2	40	12.65	5.43	1.45	2.35	1.20	2.15	6.90	13.48	0.19	0.23

^a ne, not enough sample to detect; nd, not detected.

which the respective recoveries were 72.3%, 31.0%, 85.9%, and 68.0%. The present method has achieved a greater reduction in FFA than that by the method of Zhao et al. (1987). Furthermore, the consumption of CO₂ per gram of rice bran in the present method was only 26% of the consumption in the work of Zhao et al. (1987).

In the present study, after 13.9 kg of CO₂ had been used, only 83.39% of hexane extractable oil was recovered, whereas in our previous extraction trials (Shen et al., 1996) 92.97% of hexane extractable oil was recovered after 13.2 kg of CO₂ was consumed. Since, in the present study, a higher average flow rate of 3.5 kg/h of SC-CO₂ was used rather than the 2.5 kg/h of SC-CO₂ in our former work (Shen et al., 1996), one possible explanation for these different results is that after about 75% of hexane extractable oil has been recovered, mass transfer difficulties become important and the yield of oil decreases with increased CO₂ flow rate. In other words, at the higher CO₂ flow rate the later stages of extraction deviate more from equilibrium since the contact time between the solvent and the oil is reduced.

The distribution of other oil components between the raffinate and extract is shown in Table 2. These mostly followed the previously reported trends in the partition coefficients between oil and SC-CO₂ phases (Shen et al., 1996). The sterols (campesterol, stigmasterol, and β -sitosterol) were concentrated in the extract. Oryzanol was preferentially distributed to the raffinate, which is consistent with the respective partition coefficients reported by Shen et al. (1996). However, it appears that in the present study, because of the lower densities of CO₂ at 8.6 and 9.9 MPa, α -tocopherol was concentrated in the raffinate and not preferentially extracted as occurred with CO₂ at higher densities (Shen et al., 1996).

Isobaric Fractionation at 8.6 MPa. Table 1 shows the effect of temperature in the fractionation column on the distribution of the major components of rice bran oil between the raffinate and extract at 8.6 MPa. By increasing the fractionation temperature from 40 to 45 °C and then to 50 °C, the SC-CO₂ density and hence its solvent power were progressively decreased. This resulted in a progressively increasing yield of raffinate and corresponding decreasing yield of extract. The FFA concentration in the raffinate increased with increasing temperature, while the FFA concentration in extract initially increased and then decreased. In SC-CO₂ fractionation of olive oil, Bondioli et al. (1992) reported that with temperatures of 40 and 60 °C at a pressure of 13 MPa there was an increase in raffinate yield and FFA concentration in both the raffinate and extract at the higher temperature. The trends in our fractionation are in accord with this study except for the reduced FFA concentration in the rice bran oil extract at higher temperatures. Table 2 shows the effect of the temperature in the fractionation column on the distribution of

rice bran oil minor components between the refined oil fraction and extract. When the temperature was increased from 40 to 45 °C and then to 50 °C at constant pressure, resulting in decreased density of CO₂, the concentration of all minor components increased in the refined oil with the exception of oryzanol. The reason for this behavior of oryzanol is still uncertain. The densities of CO₂ at 50 °C/8.6 MPa were too low to produce sufficient material for analysis of any extract component other than FFA.

Selectivities and Partition Coefficients. In our previous paper on the extraction of rice bran oil in dense CO₂ (Shen et al., 1996), the results were presented as partition coefficients calculated on a mass fraction basis. In the present study, ratios of the partition coefficients are used to derive "selectivity" (*S*), which provides a useful basis for comparison with respect to the fractionation process. *S* values were calculated for different extraction conditions according to the equation (Brunetti, 1989)

$$S = \frac{W_E^I/W_R^I}{W_E^T/W_R^T}$$

where W_E^I and W_R^I are the weight fraction of the component (I) in the extract and refined oil and W_E^T and W_R^T the weight fraction of triglycerides in the extract and refined oil, respectively. The "separation factors" calculated by Arul et al. (1994) are actually ratios of partition coefficients calculated on a mole fraction basis. Brunetti (1989) had earlier used the term "distribution coefficient or solvent selectivity" to refer to a ratio of partition coefficients calculated on a mass fraction basis. Nilsson et al. (1991, 1992) have consistently used partition coefficients calculated on a mass fraction basis and have defined the term "selectivity" as the ratio of such partition coefficients.

Table 3 shows the selectivities for some minor rice bran oil components isothermally at 40 °C and isobarically at 8.6 MPa, respectively. In every case, FFA had the highest selectivities, meaning that the FFA were preferentially enriched in the extract under all CO₂ conditions used, compared with the other components. The selectivities of oryzanol decreased with increasing CO₂ density, meaning that the best separation of oryzanol from triglycerides was obtained at 11.2 MPa/40 °C among all of the conditions used, while α -tocopherol was preferentially retained in the refined oil under most conditions.

Figure 2 plots the partition coefficients versus CO₂ density for triglycerides, FFA, sterols, and oryzanol. Data from a previous study (Shen et al., 1996) are included with data from the present work. The data from Shen et al. (1996) were determined at high pressure at which the assumed equilibrium condition is approached by passing CO₂ over dispersed oil droplets in rice bran. In the present study data were determined

Table 3. Selectivities for Some Minor Components of CO₂ Extracted Rice Bran Oil

pressure (MPa)	temp (°C)	FFA	oryzanol	campesterol	stigmasterol	β -sitosterol	α -tocopherol
8.6	50	2.23	ne ^a	ne	ne	ne	ne
8.6	45	27.82	1.29	2.55	2.49	2.14	<0.06
8.6	40	15.64	1.08	3.90	3.91	3.76	0.02
9.9	40	9.00	0.75	2.66	2.80	2.78	0.75
11.2	40	7.73	0.57	2.14	2.36	2.58	1.62

^a ne, not enough sample to detect.

Table 4. Comparison of Partition Coefficients of Triglycerides with Solubility of Vegetable Oil

CO ₂ density (g/mL)	0.6941	0.7767	0.8087	0.8406	0.8732	0.9159
temp (°C)	40	60	40	40	40	40
pressure (MPa)	11.2	24.1	17.2	20.0	24.1	31.0
partition coefficient of triglycerides ($\times 10^3$)	0.66 ^a	3.52 ^a (3.1) ^e	2.50 ^a		5.52 ^a	6.93 ^a
solubility of vegetable oil and triolein (g/kg of CO ₂)	0.6 ^b	3.1 ^e	2.0 ^b	2.9 ^c (3.1) ^d	5.0 ^b	7.2 ^b

^a This work. ^b Fattori et al. (1988) (Figure 5 for canola oil). ^{c,d} Stahl et al. (1980) (Figure 4 for sunflower oil and Figure 5 for soybean oil). ^e Nilsson et al. (1991) solubility and partition coefficient of pure triolein.

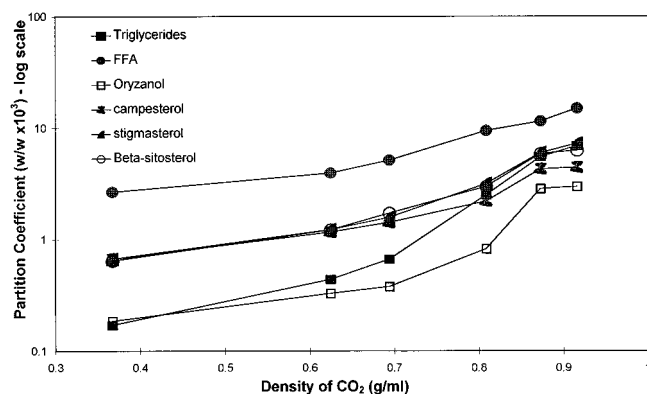


Figure 2. Partition coefficients for some components of rice bran oil at 40 °C plotted on a logarithmic scale. Single points represent the mean values of data from duplicated experiments.

at lower pressures, at which the assumed equilibrium is approached by condensing oil from solution in CO₂. The two sets of data are approximately contiguous, indicating that the assumption of equilibrium is justified in both sets of experiments.

The selectivities are ratios of partition coefficients and determine the maximum possible degree of separation of any pair of components under given conditions in a simple batch or concurrent process. For optimal separation the selectivity must be maximized (or minimized, depending on how it is defined). This condition is best shown by maximum distance between the respective partition coefficient curves when plotted on a logarithmic scale. Figure 2 has been plotted on a logarithmic scale to illustrate the possibilities and limitations of CO₂ as a fractionating solvent for rice bran oil.

The vertical distances between the curves clearly show that FFA are best separated from triglycerides at low CO₂ densities (<0.7 g/mL), which is in agreement with the data of Maheshwari et al. (1992). The curves for sterols are all very close to each other, indicating the poor ability of CO₂ alone to separate the sterols from each other at 40 °C in the CO₂ density range tested. This could be expected because of the similarities of the molecular structures of these sterols. Since the sterol curves are located between the FFA and triglyceride curves at CO₂ densities <0.8 g/mL, it is inevitable that any simple process to separate FFA from triglycerides at 40 °C and a CO₂ density of <0.8 g/mL will also partially remove sterols from the triglycerides. In other words, at 40 °C, to preserve the sterol content of rice bran oil, it is necessary to conduct the deacidification at densities higher than optimal. It is possible that

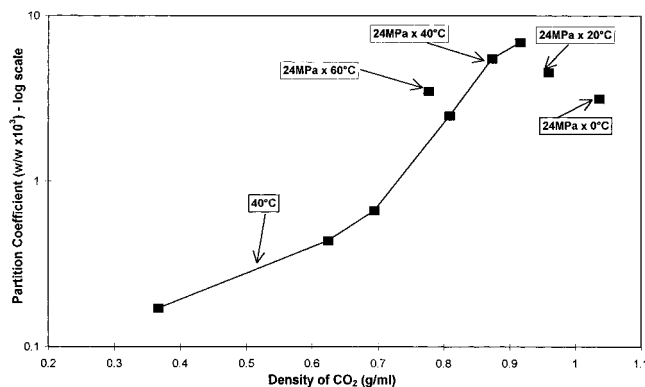


Figure 3. Partition coefficients of triglycerides in rice bran oil plotted on a logarithmic scale. Single points represent the mean values of data from duplicated experiments.

another temperature could be more favorable or that the use of entrainers or adsorbents could overcome this difficulty.

Oryzanol had a partition coefficient that was less than or equal to the partition coefficient of triglycerides under all CO₂ conditions at 40 °C. At CO₂ densities >0.6 g/mL it would be possible to separate rice bran oil into a high oryzanol fraction and a low oryzanol fraction. The high oryzanol fraction would also inevitably have a reduced FFA content compared with the unfractionated oil.

In the present study, partition coefficients were also measured at temperatures of 45 and 50 °C and a CO₂ pressure of 8.6 MPa. These conditions produced extremely low partition coefficients that are outside the useful range. However, our earlier work (Shen et al., 1996) included some measurements at 60, 20, and 0 °C using higher CO₂ densities, which show the direction and magnitude of temperature effects. These measurements are included with the triglyceride and FFA partition coefficient isotherms of the present study in Figures 3 and 4, respectively. The use of density rather than pressure as the independent variable simplifies the understanding of the temperature effect. This approach has also been taken by del Valle and Aguilera (1988), who measured and compiled the solubility data of vegetable oil in SC-CO₂ over a range of temperatures from 20 to 80 °C and plotted them on a logarithmic scale against CO₂ density to show a family of parallel straight lines. The solubility isotherms of canola oil in CO₂ as a function of CO₂ density at temperatures from 25 to 70 °C measured by Fattori et al. (1988) displayed four parallel curves. Maheshwari et al. (1992) reported the predicted solubilities of five free fatty acids as a function of temperature and density of SC-CO₂. When plotted

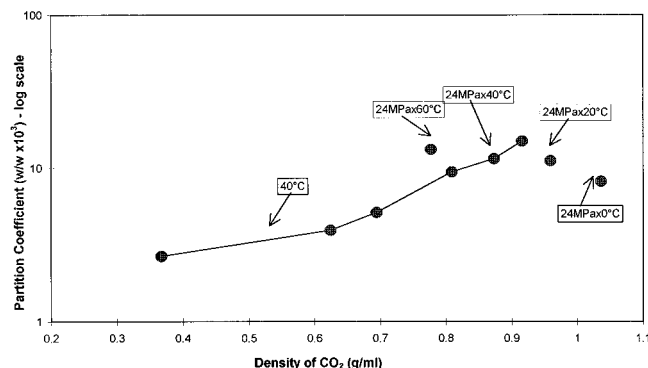


Figure 4. Partition coefficients of FFA in rice bran oil plotted on a logarithmic scale. Single points represent the mean values of data from duplicated experiments.

on a logarithmic scale, these appeared as a group of parallel straight lines in all cases. The data plotted in Figures 3 and 4 of the present study are consistent with the partition coefficient isotherms being families of parallel curves. For comparison, Fattori et al. (1988) also plotted their data using pressure as the independent variable and showed that the isotherms exhibited crossover points. Yun et al. (1991) reported that solubility curves of cholesterol in CO_2 plotted on a logarithmic scale versus CO_2 density showed a parallel linear trend of data at temperatures from 40 to 60 °C. Examination of the data points of Figure 3 of the present study indicates a complex relationship between isotherms if they were plotted against pressure. The use of density as the independent variable is therefore recommended for studies of isotherms in supercritical fluids.

Partition Coefficients and Solubilities. Any data on total solubility of a relatively homogeneous mixture carry the assumption that the measured solute is present in the oil phase at 1000 g/kg. Thus, if solubility data are expressed in grams per kilogram of CO_2 , they can be converted to partition coefficients for comparison with the present results by dividing by 1000. A similar treatment of the connection between measured solubilities and partition coefficients was described by Bamberger et al. (1988), who used partition coefficients based on mole fractions. Table 4 compares the present results with those from the literature on vegetable oil solubilities. The partition coefficients for triglycerides measured in this study and our previous study (Shen et al., 1996) can thus be directly related to the extensive literature on the solubility of vegetable oils (mixtures of triglycerides) in dense CO_2 (Brunetti et al., 1989; Eggers et al., 1985; Lee et al., 1986; Stahl et al., 1980).

ACKNOWLEDGMENT

We gratefully acknowledge the Ricegrowers' Co-operative Ltd., Leeton, Australia, for a generous supply of rice bran and the State Chemistry Laboratory, Victoria, for part of the chemical analyses.

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Received for review April 8, 1997. Revised manuscript received August 11, 1997. Accepted August 12, 1997.*

JF970292W

* Abstract published in *Advance ACS Abstracts*, September 15, 1997.