Pilot Scale Extraction of Rice Bran Oil with Dense 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

The purpose of this study was to measure the effects of temperature, pressure, and flow rate of dense CO_2 on its ability to extract, refine, and fractionate rice bran oil. Column beds (300 g) of rice bran were extracted with dense CO_2 at a flow rate of ~2.5 kg/h, temperatures of 0−60 °C, and pressures of 17−31 MPa over a period of 6 h. The extracted total oil; the free fatty acid, α-tocopherol, sterols (campesterol, stigmasterol, β-sitosterol), and oryzanol components; together with moisture were measured at intervals. Extraction was almost complete in 6 h, and rates of extraction were consistent with saturation of the CO_2 with rice bran oil throughout most of the process. Extraction of the oil components was described by apparent partition coefficients between the oil and CO_2 phases. The observed differences in partition coefficients provide a basis for refining and fractionation of rice bran oil.

Keywords: *Dense carbon dioxide; extraction; rice bran oil*

INTRODUCTION

Rice bran is a byproduct of rice milling which contains 15−20% oil by weight. The potential for extracting high value products from rice bran for the food and pharmaceutical industries is well recognized (Hargrove et al., 1994). The composition of hexane-extracted rice bran oil has been reported previously (Nicolosi et al., 1994). These investigators showed that the triglyceride fraction of the oil is rich in oleic (C18:1) and linoleic (C18:2) acids, with an overall fatty acid profile similar to that of olive oil. The major components of the unsaponifiable fraction of the oil are sterols (42%), higher alcohols (24%), and ferulic acid esters (oryzanol, 20%), some of which are reported to have antioxidant properties. The amount of α-tocopherol present in rice bran oil is relatively large (0.1% of the total oil) compared with other vegetable oils. The free fatty acid (FFA) content of crude rice bran oil is also relatively high, due to the high level of lipase activity in the bran (Nicolosi et al., 1994). Organic solvents, such as hexane, are commonly used to extract rice bran oil, but the resultant solvent residues, as well as partial degradation of some heat-labile components in traditional extraction processes, are becoming of concern to some consumers, health authorities, and food manufacturers. As an alternative solvent, dense carbon dioxide (CO_2) offers the advantages of being nontoxic and easily removed from the extracted oil, being commonly used at temperatures that do not cause appreciable degradation of heat-labile components, and possibly offering a superior product compared with that obtained by hexane extraction (Ramsay et al., 1991; Palmer and Ting, 1995).

Several studies have reported the use of supercritical carbon dioxide (SC-CO_2) to extract high value products from rice bran. Taniguchi et al. (1987) used a laboratory scale SC-CO_2 extraction plant to investigate the effects of pressure, temperature, and time of extraction of 20 g batches of three kinds of rice bran on the recovery of oil, oryzanol, phosphorus, and color. Zhao et al. (1987) also used a small scale SC-CO_2 plant to extract oil from 20 g of rice bran and obtained a product low in FFA. They suggested that SC-CO_2 extraction offered a new method of producing edible oils with lower acid values than those produced by solvent extraction or cold pressing. Ramsay et al. (1991) used a larger SC-CO_2 plant than that used by Zhao et al. (1987) to extract 150 g of rice bran. Under optimum extraction conditions of 30 MPa and 35 °C and an extraction time of 5 h, they were able to obtain comparable yields of oil and sterols to those obtained with hexane. Saito et al. (1991) performed fractional extractions of rice bran oil and its esters with SC-CO_2, with entrainers or a column packed with silica gel−$AgNO_3$ at 40−100 °C and 8.2−19.8 MPa. These workers found that the use of a column packed with silica gel−$AgNO_3$ was extremely effective for fractionating fatty acid esters in the rice bran oil.

Knowledge of the solubilities of the various oil constituents in SC-CO_2 is essential for the design and development of such extraction processes. Solubilities of some pure FFAs and triglycerides and their synthetic mixtures in SC-CO_2 have been determined and modeled by a number of investigators (Chrastil, 1982; Bamberger et al., 1988; Ikushima et al., 1988; Brunetti et al., 1989; Nilsson et al., 1991; Maheshwari et al., 1992). Other researchers have reported the solubilities of various vegetable oils including canola, soybean, and wheat germ oils in CO_2 (Friedrich and List, 1982; Bulley et al., 1984; Taniguchi et al., 1985; del Valle and Aguilera, 1988; Fattori et al., 1988; Temelli, 1992; Maheshwari et al., 1992). A detailed, pilot-scale study of the recovery of oil, FFA, α-tocopherol, sterols, and oryzanol of rice bran in CO_2 with varying temperatures and pressures, and the extraction trends of oil and individual components with time has not been reported to date.

The aims of this experimental study were (i) to investigate effects of pressure, temperature and time on the extraction yields of oil and other components in rice bran with sub- and supercritical CO_2; (ii) to determine the recoveries of oil, FFA, α-tocopherol, sterols and oryzanol from rice bran under different extraction conditions, with a pilot scale extraction plant; and (iii) to gather data for a feasibility study of suitable conditions for refining and fractionation of rice bran oil.

* Author to whom correspondence should be addressed (telephone 61-03 9216 8288; fax 61-3-9216-8284).

[†] Victoria University of Technology.

[‡] Australian Food Industry Science Centre.

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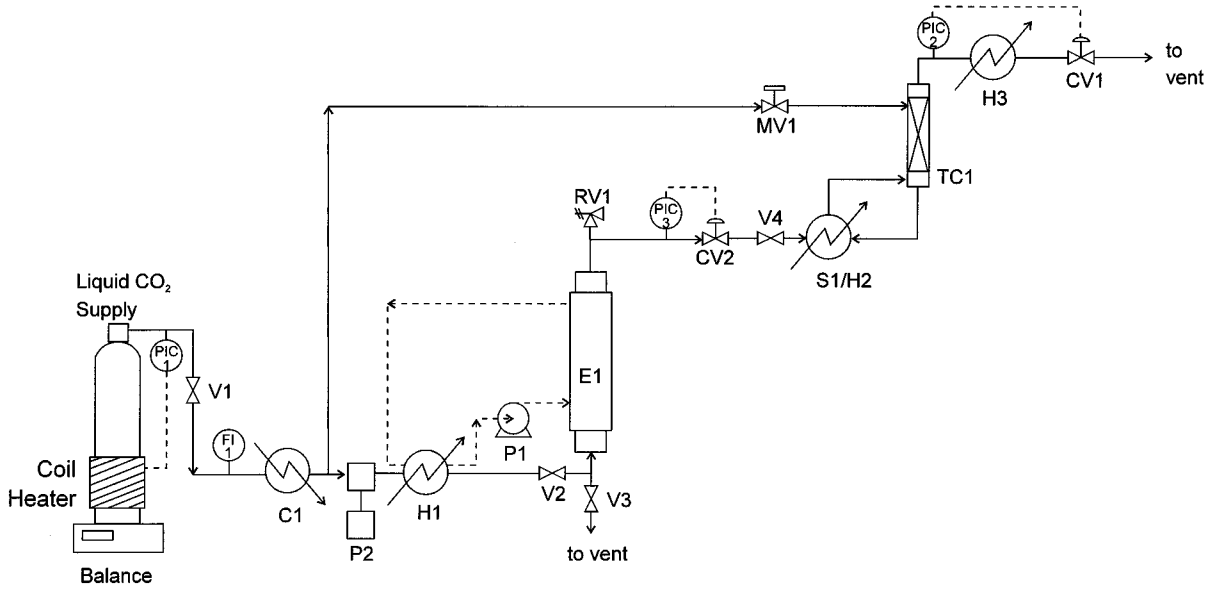

Figure 1. Schematic diagram of the pilot scale CO_2 extraction plant used in this study: variable pressure indicator controllers (PIC), heaters (H), coolers (C), piston pumps (P), separation vessel (S), tailing column (TC), valves (V), and control valves (CV).

MATERIALS AND METHODS

Materials. Medium-grain rice bran was provided by the Ricegrowers' Co-operative Limited, Leeton, Australia. The moisture content and total hexane extractable oil in the bran were 10.1 and 18.7%, respectively. The size distribution of the material, as determined by sieving, was as follows: >600 μm, 15.6% (by weight); 600−500 μm, 5.7%; 500−300 μm, 21.2%; 300−250 μm, 10.9%; 250−180 μm, 40.0%; and <180 μm, 6.6%.

Extraction Methods. The term "dense" rather than "supercritical" CO_2 has been used in the general description of this study, because two of the six extraction conditions used CO_2 below its critical temperature of 31.1 °C. A schematic diagram of the pilot plant extraction unit (Distillers MG Ltd., UK) is shown in Figure 1. Food grade liquid CO_2 (99.8% purity; CIG, Melbourne, Australia) was cooled and pressurized to 17, 24, or 31 MPa, by a piston pump which was regulated and checked by a variable pressure indicator controller. The pressurized CO_2 passed through a heater to adjust the temperature to 0, 20, 40, or 60 °C, and was allowed to flow up through the vertically mounted extraction cell equipped with a water jacket to maintain the extraction temperature. The extraction cell (internal diameter, 38 mm; total length, 1428 mm; loading length, 747 mm) was loaded with 300 g of rice bran and each end was plugged with stainless steel mesh. The oil-laden CO_2 from the extractor passed through a separation vessel with a glass window where it was depressurized and vented through a packed tailing column and vaporizer, leaving the extracted oil in the separation vessel. The CO_2 flow rate was manually adjusted by changing the pump stroke length to an average of 2.5 kg/h. Extractions were continued for 6 h. After each hour, the CO_2 flow was stopped and the rice bran oil sample was collected. Extractions were performed in duplicate. For comparison and standardization purposes, rice bran samples were extracted with hexane (95% purity, Ajax Chemicals, Australia) by Soxhlet extraction for 7 h at 70 °C (water bath temperature).

Analytical Methods. Water was separated from crude extracts of rice bran by centrifugation with a Sorvall Superspeed Centrifuge (SS-3 Automatic) at 16 000 rpm for 30 min. The amounts of total extract and oil were determined gravimetrically. The total amount of FFA in each sample was determined by titration, according to AOAC Method 940.28 (1990). Oryzanol content of the extracts was determined by ultraviolet spectroscopy (UVS) at 315 nm, according to the method of Seetharamaiah and Prabhakar (1986). The analytical reference standard of oryzanol was obtained from Tokyo Chemical Industry Company Ltd., Tokyo, Japan.

Tocopherols were analyzed by high-performance liquid chromatography (HPLC) according to the method of Speek et al. (1985), using the modified solvent system of hexane:2-propanol (99.5:0.5%, v/v) as recommended by Pocklington and Dieffenbacher (1988). The tocopherols were separated with a Merck Lichrosorb Si 60 (5 μm) column (250 × 4 mm) and a solvent flow rate of 1.5 mL/min. Tocopherols were identified by fluorescence detection at 296 nm (excitation) and 320 nm (emission). Standard compounds were obtained from the Sigma, St. Louis, MO. The purity of these reference standards was checked by UVS by the procedure outlined by Pocklington and Dieffenbacher (1988).

The unsaponifiables were extracted with hexane after an internal standard, 5α-cholestane (98% purity, Sigma, St. Louis, MO) was added to a saponified solution of rice bran oil. The unsaponifiables were analysed as free sterols (Ramsay et al., 1991). A Varian GC 3400 was used for the analysis of sterols. Chromatographic separations were performed with a J&W Scientific. DB-17HT-coated, 15 m × 0.25 mm capillary column, with a temperature variation program from 220 to 270 °C and a split injection system. The gas chromatography was directly coupled to the input of a Varian Saturn GC-MS and mass spectra were produced by electron impact ionization. Reference factors with 5α-cholestane as the internal standard were used to quantify campesterol, stigmasterol, and β-sitosterol. These sterols were identified by the GC-MS spectrum library (NIST90) and by comparing their retention times with authentic standards of campesterol (65% purity), stigmasterol (96% purity), and β-sitosterol (98.3% purity). All of these sterols were obtained from Sigma, St Louis, MO.

RESULTS AND DISCUSSION

Oil Extraction Conditions. The effect of temperature and pressure on oil yield is shown in Figure 2 as a function of the amount of CO_2 used. Oil yield is reported as a percentage of the amount extractable by hexane. Oil was extracted linearly up to 80% of the hexane-extractable amount at 24 MPa/20 °C and 40 °C and 31 MPa/40 °C, or remained linear throughout the whole extraction experiment at 24 MPa/0 °C and 60 °C and 17 MPa/40 °C. The extractions at 31 MPa/40 °C gave the highest oil yield, which was 96.8% of hexane-extractable oil. There are several possible explanations for the extraction trends shown in Figure 2. First, the flattening of the extraction profiles could be due to the heterogenous nature of the rice bran with respect to

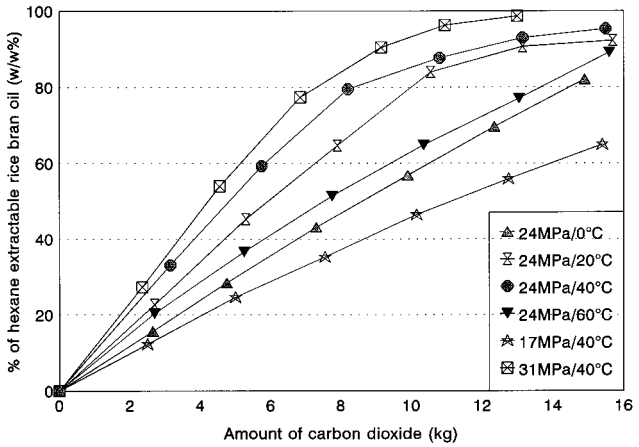

Figure 2. Extraction of oil from rice bran by dense CO_2 at different pressures and temperatures (CO_2 flow rate, average of 2.5 kg/h). Single points represent the mean values of data from duplicate or triplicate experiments.

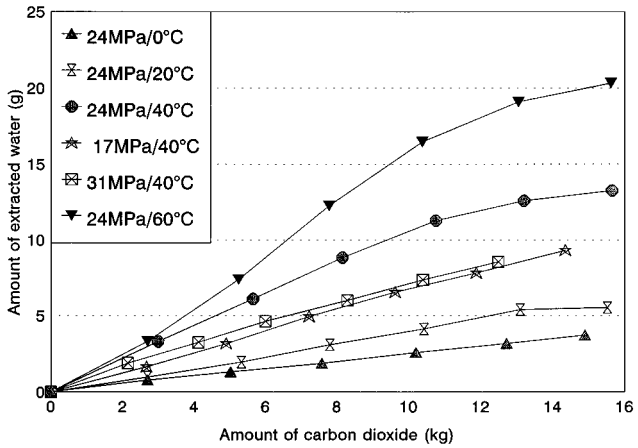

Figure 3. Extraction of water from rice bran by dense CO_2 at different temperatures and pressures (CO_2 flow rate; average of 2.5 kg/h). Single points represent the mean value of data from duplicate or triplicate experiments.

Table 1. Apparent Solubility of Rice Bran and Vegetable Oils in CO_2

				apparent solubility (g of oil/kg of CO_2)	
method	CO2 density (g/mL)	temp (°C)	pressure (MPa)	vegetable oil (published data)	rice bran oil this study)
liquid CO_2	1.0359	0	24	NA[a]	3.16
	0.9587	20	24	4.8[c]	4/58
SC-CO_2	0.8087	40	17	2.2[b]	2.50
	0.8732	40	24	3[b]	5.52
	0.9159	40	31	6.5[b]	6.93
	0.7767	60	24	3.2[b]	3.52

[a] Not available. [b] Maheshwari et al., 1992 (measured from Figure 4). [c] del Valle and Aguilera, 1988 (measured from Figure 3).

particle size and differences in oil accessibility to solvent in various types of particle, which result from brown rice grain polishing and bran milling processes (Zhao et al., 1987; Silvala et al., 1991). Oil contained in intact aleurone cells and within larger bran particles would be extracted more slowly than oil in small particles and free oil contained in and on the surface of broken aleurone cells. Thus, under high solubility conditions (24 MPa/20, 40 °C and 31 MPa/40 °C), it appears that free oil is extracted more quickly and diffusion-controlled extraction is reached, whereas under lower solubility conditions (24 MPa/0, 60 °C and 17 MPa/40 °C) not all of the free oil is extracted even after 6 h (Figure 2). Second, CO_2 passing from the base of the extractor column through the 74.7 cm long bed of rice bran (300.0 g) would extract rice bran oil from the lower part of the bed first, so that toward the end of the run, when the oil mainly existed in the higher part of the bed, the CO_2 may not be in contact with the oil sufficiently long enough for saturation to occur. Third, the slower extraction of components of lower solubility (e.g., higher molecular weight triglycerides, oryzanol, and some sterols) may also account for the extraction profile.

Solubility of Rice Bran Oil in SC-CO_2. It is notable that the apparent solubilities of rice bran oil in CO_2, as determined from the initial linear portions of the extraction profiles, were similar to the modeled solubilities of vegetable oil under similar conditions (del Valle and Aguilera, 1988; Maheshwari et al., 1992; Table 1). Fattori et al. (1988) measured the solubility of canola oil from 7 g of flaked seed in CO_2 at 24 MPa/40 °C with a CO_2 flow rate of 0.7 g/min, and found a value of ~4.4 g oil/kg CO_2. Temelli (1992) measured the solubility of canola oil from 50 g of canola flakes or press cake in CO_2 at 34.5 MPa/40 °C with a CO_2 flow rate of 1.3 g/min, and obtained a value of ~7 g oil/kg CO_2. In the present study we found a value of 5.52 g/kg CO_2 for the apparent solubility for rice bran oil at 24 MPa/40 °C and 6.93 g/kg CO_2 at 31 MPa/40 °C.

A series of experiments was performed to show that the CO_2 flow rate was sufficiently low to ensure saturation of CO_2 with rice bran oil. At 24 MPa and 40 °C, the apparent solubility of rice bran oil was measured at 2.5, 3.25, and 3.65 kg/h of CO_2. The apparent solubilities were 5.52, 5.60, and 5.56 g/kg CO_2.

As expected, the apparent solubility of oil in CO_2 increased with pressure at 40 °C because of an increase in CO_2 density that increases its solvent power. At 24 MPa, solubility increased with temperature up to 40 °C because of an increase in the tendency of oil molecules to leave the oil phase, as reflected in the increase of oil vapor pressure with temperature (Fattori, 1988). A further increase in temperature resulted in a decrease in CO_2 density that sufficiently reduced its solvent power to overcome the increasing tendency of oil molecules to leave the oil phase, as discussed by Fattori (1988) in relation to canola oil. Similar behavior has been reported for other vegetable oils (Friedrich, 1982).

Extraction of Water. The amount of water extracted from the rice bran matrix with CO_2 increased with extraction temperature at 24 MPa (Figure 3), because of an increase in the vapor pressure of water. At 60 °C , ~65% of the water in the feed material was extracted. At 50 °C and pressures from 20 to 60 MPa, the solubility of pure water in CO_2 is ~0.3 wt% (Evelein et al., 1976). The relatively small effect of pressure (at 40 °C) is consistent with the finding of Evelein et al. (1976) that the solubility of pure water in CO_2 is almost independent of pressure over 20 MPa. Taniguchi et al. (1987) reported that the water solubility in CO_2 from rice bran was 0.17 wt% at 40 °C and 30 MPa with a CO_2 flow rate of 8.5 kg/h. The difference between Taniguchi's value of 0.17% and the value of 0.08% determined in this experiment at 40 °C and 24 MPa may have arisen from the different type of rice bran used, different initial moisture contents, and/or different methods used to measure the water content. Taniguchi et al. (1987) measured water content by drying the

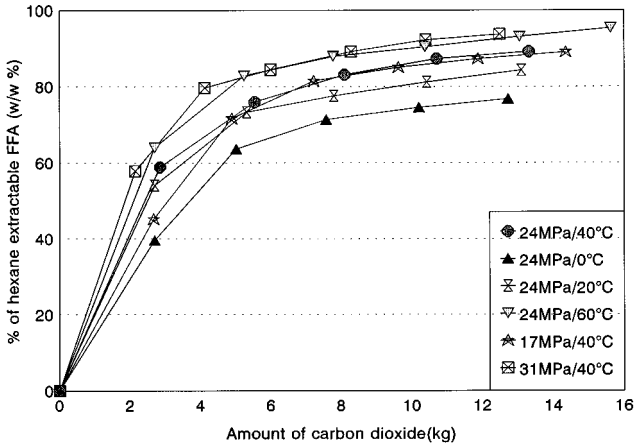

Figure 4. Extraction of total FFAs from rice bran by dense CO_2 at different temperatures and pressures (CO_2 flow rate, average of 2.5 kg/h). Single points represent the mean value of data from duplicate or triplicate experiments.

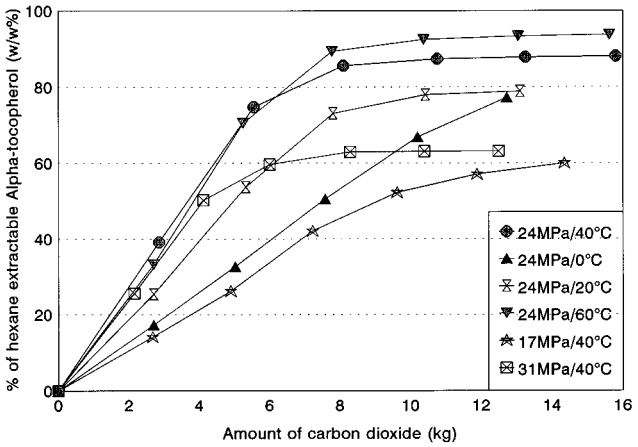

Figure 5. Extraction of α-tocopherol from rice bran by dense CO_2 at different temperatures and pressures (CO_2 flow rate; average of 2.5 kg/h). Single points represent the mean value of data from duplicate or triplicate experiments.

Table 2. Main Fatty Acid Profile of Rice Bran Oil

extraction conditions	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	$C_{20:0}$	$C_{20:1}$
hexane extractable	16.7	1.3	40.6	367.4	1.5	0.5	0.6
24 MPa/0 °C	17.3	1.1	38.8	40.4	1.7	0.3	0.4
24 MPa/20 °C	17.2	1.4	41.1	37.8	1.5	0.5	0.5
24 MPa/60 °C	17.9	1.4	40.4	37.9	1.5	0.4	0.5
17 MPa/40 °C	17.7	1.2	40.1	38.6	1.5	0.4	0.5
31 MPa/40 °C	16.5	1.4	41.4	38	1.5	0.6	0.6

extract at 135 °C for 3 h, whereas centrifugation of the crude extract was used to separate water in present study. Addition of a second separator to the extraction unit to collect water separately from the lipid extract would be beneficial in any future studies.

Extraction of Free Fatty Acids. The effects of temperature, pressure and the amount of CO_2 used on the extraction of FFAs from 300 g of rice bran are shown in Figure 4. The results obtained in this study indicated that there was a higher percentage (39.6−64.0%) of hexane extractable FFAs extracted in the first hour compared with the lower percentage (16.0−31.4%) found for the total hexane extractable rice bran oil. Thus, the FFA recovery yields are about twice that of rice bran oil, which is mainly composed of triglycerides. From the fatty acid profile of hexane extractable and CO_2 extracted rice bran oil (Table 2), it is evident that oleic and linoleic acid constituted >75% of the total fatty acid. The relative differences between the recovery yield of FFA and rice bran oil extracted from rice bran may be explained by differences in the solubility between pure oleic acid and triolein, as reported by Brunetti (1989), and the solubility differences between pure oleic acid, linoleic acid, and vegetable oil predicted by Maheshwari (1992). At 20 MPa/40 °C the solubility of oleic acid is 4.1 times that of triolein, and at 30 MPa/40 °C, the solubility of oleic acid is 3.64 times that of triolein (Brunetti, 1989). Maheshwari (1992) predicted a higher solubility of oleic and linoleic acid than that of vegetable oil in CO_2 at 40, 50, and 60 °C for CO_2 densities from 0.5 to 1.0 g/mL. The FFA have lower molecular weights than their respective triglycerides, which explains why in the present work they are selectively extracted in the initial stages of the extraction process. In the present study, the FFA yield increased with increasing pressure at constant temperature and with increasing temperature at constant pressure (Figure 4). At 24 MPa, extracted FFA slightly increased with temperature, although the density of CO_2 decreased with increasing temperature. This result is another illustration of the opposing effects of increased temperature on the distribution of an oil component between the oil phase and the CO_2 phase that was discussed earlier in relation to solubility of the whole oil. Furthermore, because FFA have the lowest molecule weight among all oil compounds, increasing temperature outweights decreasing density of CO_2. Maheshwari (1992) has previously reported that at 20.7 MPa, when the temperature increased from 313 to 323 K, the solubility of oleic acid remained unchanged. Furthermore, at 27.6 MPa, when the temperature increased from 313 to 323 K, the solubility of oleic acid increased by 9.5%, but when the temperature increased from 313 to 333 K, the solubility of oleic acid decreased by 4.8%. Brunetti (1989) reported that when total free acids were extracted at 20 MPa, the solubility decreased when temperature increased at constant pressure. Total FFAs in rice bran oil are in a different chemical environment than are pure fatty acids, so that the same extraction trends may not occur. The data shown in Table 2 indicate that there were no significant differences in fatty acid profile between hexane extractable and CO_2-extracted rice bran oil. Zhao et al. (1987) extracted 20 g of rice bran with SC-CO_2 at pressures from 15 to 35 MPa, a temperature of 40 °C, and a flow rate of 0.7−1.2 kg/h, and obtained results similar to those found in present study because the FFAs were concentrated in the first of four fractions.

Extraction of α-Tocopherol. The effects of temperature, pressure, and the amount of CO_2 used on the extraction yield of α-tocopherol are shown in Figure 5. About 90% (wt%) of total extracted α-tocopherol was recovered after 3 h, with an average CO_2 flow rate of 2.5 kg/h at 40 and 60 °C/24 MPa. The extraction of α-tocopherol occurred almost linearly over 3 to 4 h at 0 °C/24 MPa and at 40 °C/17 MPa. The concentration of α-tocopherol in our CO_2 extracts and hexane extracts were comparable with the findings of Zhao et al. (1987). The reason for the early flattening of the extraction profile at 31 MPa/40 °C and 24 MPa/20 °C is not clear.

Extraction of Oryzanol. The effects of pressure, temperature, and the amount of CO_2 used on the amount of oryzanol extracted with SC-CO_2 are shown in Figure 6. Approximately 4.0−14.4% of hexane-extractable oryzanol was extracted in the first hour during all runs. In contrast to the extraction curves

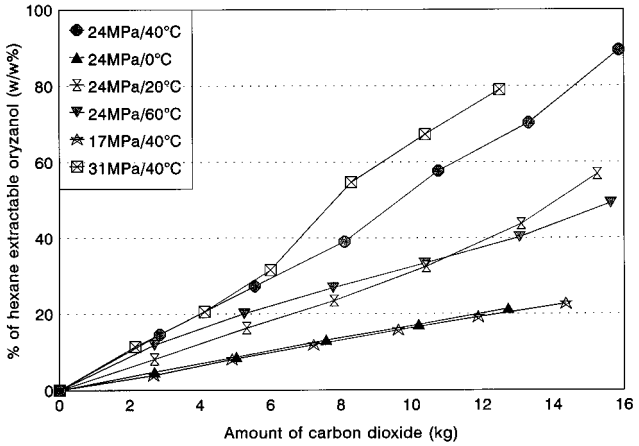

Figure 6. Extraction of oryzanol from rice bran by dense CO_2 at different temperatures and pressures (CO_2 flow rate, average of 2.5 kg/h). Single points represent the mean value of data from duplicate or triplicate experiments.

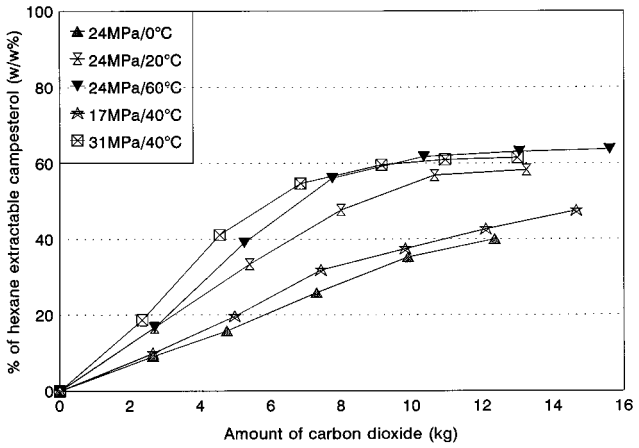

Figure 7. Extraction of campesterol from rice bran by dense CO_2 at different temperatures and pressures (CO_2 flow rate, average of 2.5 kg/h). Single points represent the mean value of data from duplicate or triplicate experiments.

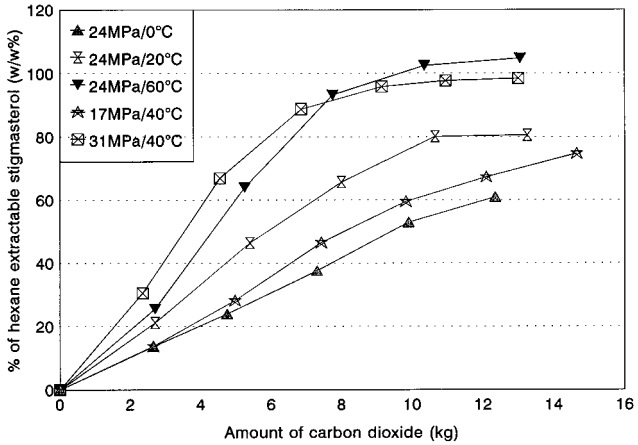

Figure 8. Extraction of stigmasterol from rice bran by dense CO_2 at different temperatures and pressures (CO_2 flow rate, average of 2.5 kg/h). Single points represent the mean value of data from duplicate or triplicate experiments.

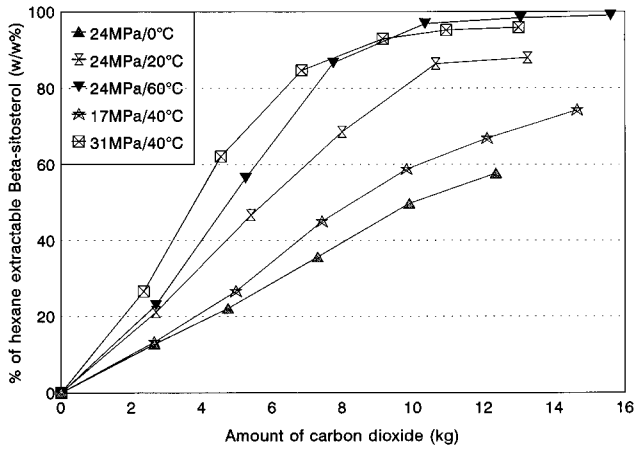

Figure 9. Extraction of β-sitosterol from rice bran by dense CO_2 at different temperatures and pressures (CO_2 flow rate, average of 2.5 kg/h). Single points represent the mean value of data from duplicate or triplicate experiments.

found for FFA and α-tocopherol, those of oryzanol either became steeper as extraction progressed (at 40 °C/24 and 31MPa), or remained almost constant for all other treatments. In contrast with the extraction profile of α-tocopherol, FFAs, and the triglycerides, oryzanol was more difficult to extract from rice bran. The molecular weight of oryzanol is ~270 Da lower than triolein; however, its recovery yield was much lower than that of total rice bran oil, which could be attributed to its more rigid and voluminous polycyclic structure or linkage with other components of the rice bran matrix. The oryzanol concentration of the rice bran oil extracted at 40 °C and 24 MPa was 1.5%, which is close to the value of 1.1% reported by Zhao et al.(1987).

Extraction of Sterols. The effects of temperature and pressure on the extraction of the three sterols, campesterol, stigmasterol, and β-sitosterol, are shown in Figures 7, 8, and 9, respectively. Overall, these extraction curves are similar to that of the rice bran oil itself, which is composed mainly of triglycerides. The reason for the incomplete recovery of hexane-extractable campesterol from rice bran (Figure 7) compared with the other sterols, stigmasterol (Figure 8) and β-sitosterol (Figure 9), is difficult to explain because these sterols have similar molecular weights. On the basis of all the sterol results it seems that sterol concentration in the remaining rice bran oil (oil bodies) is relatively constant, and, therefore, the extraction rate would also stay constant until the sterols neared exhaustion. Ramsay et al. (1991) extracted 150 g of rice bran with SC-CO_2 and reported values that are comparable with those found in this study; for example, campesterol (1.85 and 1.65 g/kg oil), β-sitosterol (4.05 and 5.11 g/kg oil), and stigmasterol (1.35 and 1.02 g/kg oil).

Apparent Partition Coefficients of Rice Bran Oil Components. Bamberger et al. (1988) investigated the

Table 3. Apparent Partition Coefficients on a w/w Basis (10^3) for Components of Rice Bran Oil

component	24 MPa/0 °C	24 MPa/20 °C	24 MPa/40 °C	24 MPa/60 °C	17 MPa/40 °C	31 MPa/40 °C
triglycerides	3.16	4.58	5.52	3.52	2.50	6.93
FFA	8.18	11.17	11.51	13.23	9.45	15.01
α-tocopherol	3.58	5.26	7.66	6.87	2.96	6.65
oryzanol	1.00	1.69	2.86	2.46	0.82	2.97
campesterol	1.91	3.45	4.29	4.04	2.20	4.43
stigmasterol	2.87	4.80	6.00	6.71	3.16	7.25
β-sitosterol	2.68	4.82	5.87	6.24	2.98	6.31

solubilities of pure fatty acids, pure triglycerides, and mixtures of triglycerides in SC-CO_2 and suggested that the intermolecular interactions in the liquid phase would affect the solubilities in the supercritical phase. A correlating variable was chosen to be the partition coefficient, K_i, which is defined as ($K_i = Y_i/X_i$), where Y_i is the measured mole fraction of component (i) in the supercritical phase and X_i is the calculated mole fraction of the same component in the liquid phase (the concentration of CO_2 dissolved in the liquid was neglected). Nilsson et al. (1991) followed the usual procedure of defining the partition coefficient to interpret quaternary system (monoolein−diolein−triolein−CO_2) data to understand better the optimum conditions of pressure and temperature for selective removal of the lower acylglycerols from such mixtures. In Nilsson's work, X_i was calculated from material balance considerations and Y_i was measured gravimetrically. Rice bran oil is a mixture of many components; therefore, similar coefficients can be useful in obtaining a better understanding of the optimum pressure and temperature conditions needed to remove FFA and concentrate other high value products like oryzanol, α-tocopherol and sterols from rice bran oil. In the present study, the calculations of apparent partition coefficients of components of rice bran oil over the first hour of CO_2 extraction were based on the saturation of these components in carbon dioxide over this period and the assumptions that the composition of the oil bodies in rice bran at the beginning of each extraction was the same as the composition of the hexane extract of rice bran. The apparent partition coefficients, calculated by dividing the concentrations measured in the CO_2 phase by the concentrations of the components of the hexane extract of rice bran on a w/w basis are presented in Table 3. The concentration of each component of the oil was expressed in units of g/kg oil, and the concentration in CO_2 in units of g/kg CO_2 in our work. The apparent partition coefficients of all the components of rice bran, whether major or trace components, are almost of the same order of magnitude because of the chemical similarities of all the components. The earlier extracting components, FFA and α-tocopherol, have larger apparent partition coefficients, whereas the late-extracting component, oryzanol, has a smaller apparent partition coefficient. If two components have the same partition coefficient under given system conditions they will be extracted by CO_2 in the same ratio as exists in the rice bran oil body; the end result is that no selectivity can be achieved. On the other hand, if the partition coefficients differ greatly, it should be possible to selectively extract the various components. For example, at 17 MPa/40 °C, the partition coefficient of FFA is 3.78 times that of triglycerides, 3.19 times that of α-tocopherol, and 11.52 times that of oryzanol, which are the greatest differences observed among all our extraction conditions. The present calculations are similar to trends observed by Maheshwari et al. (1992) who showed that the lower the density of CO_2, the more efficiently FFAs are separated from triglycerides. Work is continuing on the extraction and fractionation of rice bran oil by connecting a second fractionation column operating at different pressure and temperature, to better exploit the differences of partition coefficients between the components removed and concentrated.

The use of such partition coefficients should assist in the selection of the most suitable conditions for the extraction of high value oils in a commercial plant.

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