Fractionation and Refinement of Crude Rice Bran Oil with Supercritical CO_2

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Rice bran is a by-product of rice industries which contains 15-20% oil (w/w), being usually treated as a waste. The high potential for extracting high value-added products from rice bran for the pharmaceutical and food industries is well known. In despite of that, the aim of this study was to investigate the effect of experimental conditions on the high-pressurized CO_2 ability to extract and refine crude rice bran oil (RBO). It is well known that rice bran batch extractions can be perfectly coupled with countercurrent (CC) extraction of RBO. The first step corresponded to crude RBO batch extractions. These experiments were carried out between 100 and 400 bar and at 50 and 60 °C. The evaluation and the modelling of the fractionation of the key-components profile – such as free fatty acids (FFA), triglycerides (TG), sterols and oryzanols – obtained through batch extractions was investigated. In order to perform the CC experiments, the crude RBO was extracted at 300 bar and 60 °C. Based on previous experiments, the CC experimental conditions investigated were 200 and 250 bar and 60 and 80 °C. The main goal was to isolate the undesired FFA fraction from the refined oil, mainly composed by TG. The results obtained indicated that the deacidification of the crude RBO was successfully achieved: extract fractions were enriched up to approximately 98 % (w/w) FFA and the concentration in the raffinate fractions was < 1% FFA.

Keywords: Supercritical fluid extraction, modelling, rice bran oil, free fatty acids, triglycerides.

INTRODUCTION

Rice bran oil (RBO) is a high valuable oil, being extensively consumed in Asian countries such as China, Korea, Japan and Thailand. Nowadays, the western countries are increasing the RBO consumption, specially due to its potential as edible oil/food supplement. RBO has received some attention due to its unique health benefits, it is considered an excellent source of nutraceutical substances, like γ-oryzanol, tocotrienols and phytosterols, which ones present hypocholesterolemic- and antioxidant activities [1,2]. The exploitation of agricultural by-products could increase the value of processing industries, which ones usually manage with difficulties the disposal of their high volume wastes: rice bran, for instance, is commonly used as animal feed. One of the biggest problems when dealing with rice bran consists on the fact that it presents a high level of active lipase, which promotes hydrolysis of important components of the oil, like triglycerides (TG), to free fatty acids (FFA). In spite of that, the FFA content of crude RBO is higher than that of other vegetable oils: palm oil, for instance contains approximately 4.6% FFA (w/w) and crude RBO may contain between 7–12.0 % (w/w) FFA [3,4].

Organic solvents, such as hexane, are usually employed in the extraction and deacidification of RBO. The main disadvantages of the traditional techniques are related to the resultant solvent residues in the extracts, as well as the partial degradation of some thermolabile components. It has been reported that refining of RBO can result in up to 22 % oil losses during the conventional oil processing [2]. In the last years, these aspects are becoming of concern to consumers, food manufacturers and health authorities. As an alternative tool, supercritical carbon dioxide (SC-CO_2) processes offer some important advantages, since CO_2 is non-toxic, non-flammable, being used normally at mild temperature levels, i. e., avoiding an appreciable degradation of heatlabile components. It can also be easily removed from the final product, which present possibly superior quality compared to the ones obtained by the traditional methods.

The optimization of operational conditions used in supercritical processes is very important in order to make this technique economically viable. The main objective of the mathematical modelling consists on the determination of process design parameters, such as particle size, solvent flow rates and equipment dimensions. By modelling overall and fractionation extraction curves, it is possible to predict the viability of the supercritical processes on an industrial scale. Such models are already extensively presented in the literature [5-7].

Several studies have reported the use of SC-CO_2 in the extraction of high added value components from rice bran and the deacidification of RBO [3,8-11]. Most of the studies related to the deacidification process dealt with the enrichment of phytosterols in the raffinate fractions [3,10,11]. These experiments were carried out in the semi-continuous mode, i. e., the feed was provided in a batch mode [3,10], or in a continuous mode [11]. In both cases, CO_2 was provided in a continuous mode, but no extract reflux was employed.

A previous paper [1] dealt with the proposal of a process line for the production of raffinated rice oil from rice bran. Batch extraction experiments were performed from 100 to 400 bar and the overall extraction curves were adjusted to the experimental points by using the model presented by Brunner [5]. Deacidification experiments were also performed with a countercurrent (CC) column at 250 bar and 67 °C and the results have shown that the FFA concentration in the extract was 12 times higher than the one presented in the feed stream.

In this paper the work was divided in two parts. The first one was related to the modelling of the fractionation of four different classes of compounds present in crude RBO (FFA, TG, sterols and oryzanols) through batch extractions. For the batch extraction experiments the pressures varied from 100 to 400 bar at 50 and 60 °C. The RBO deacidification was then performed in a CC column, with the experimental conditions ranging from 200 to 250 bar and at 60 and 80 °C. The results have shown that the deacidification and consequent enrichment of TG, oryzanol and sterols in the raffinate fractions were successfully achieved.

I – MATERIALS AND METHODS

Rice bran was supplied by Müllers Mühle and Euryza (Germany). Carbon dioxide (99.95% purity) was supplied by Yara Deutschland, Germany.

The batch experiments were carried out in a single-stage extraction apparatus, Spe-ed® SFE manufactured by Applied Separations, Inc., PA, USA. The set-up consisted of an oven, where the extraction column was placed. 19 g of rice bran were used. The bottom of the column was connected to the solvent inlet valve, while the upper part of the column was connected to the outlet valve where the solvent flow rate was measured and the extract was collected. In order to perform the CC experiments, RBO was extracted at 300 bar and 60 °C. These extractions

were carried out by using a batch extractor (15.8 l volume) and one separator. CO_2 was recycled.
The CC column employed in this study was the same one previously described by Jungfer [12]. The column presented an effective separation height of 6 m equipped with a Sulzer EX gauze packing. 0.5 m at each end of the column were left packing free areas, in order to allow the phase separations. The inner diameter of the column was 17.5 mm and the feed was introduced at the middle of the column and part of the extract was reintroduced (reflux) at the top of the column to ensure countercurrent flow. CO_2 was recycled. The feed sample, which was very viscous at room temperature, was heated at 50-60 °C before pumping into the column. The feed lines were also heated to avoid sample solidification.
The standard analytical method employed for the analysis of FFA, sterols and TG was gas chromatography. The gas chromatograph used for the analysis (HP5890A) was equipped with an autosampler and FID. For the analysis of FFA and sterols, a capillary DB-5 fused silica column (Stabilwax: 30 m, 0.1 μm, ID 0.25 mm) was employed. The temperature program started at 150 °C and stopped at 350 °C. For the TG analysis a capillary HT5 column (SGE: 6 m, 0.1 μm, ID 0.53 mm) was used. The temperature program started at 100 °C and stopped at 370 °C. Oryzanol analysis were performed as described by Shen et al. [8].
The logistic model (LM) [6] used for modelling the RBO fractionation were implemented in MATLAB (version 6.5, The MathWorks, Inc.). The VTII model proposed by Brunner [5] was also used. The description of these models can be found elsewhere [5,6] and will not be presented in this paper.

II – RESULTS AND DISCUSSIONS

The characterization of the rice bran particles and the fixed bed formed inside the extractor are presented in Table 1.

Table 1: Particle and bed characteristics.

Solid density (kg/m^3)	Diameter (mm)	Porosity	Bed height (m)	ID (mm)
460.60	0.72	0.65	0.20	13.60

The modelling of the batch extractions was performed by using the logistic model (LM) and the obtained results are presented in Figure 1. The results obtained indicate that the model can be used with good accuracy for the simulation of the overall extraction curves in the extraction of RBO.
For the simulation of the fractionation of RBO, four different classes of compounds were chosen: FFA (composed mainly by oleic-, palmitic- and myristic acids), TG (composed by triolein, trimyristin and tripalmitin), sterols (composed by sitosterol, campesterol and stigmasterol) and oryzanols.
The fractionation of RBO was performed at 60 °C with a solvent flow rate of 4.16 g CO_2/h and the results are presented in Figures 2 (a) and (b). The curves were adjusted by using the LM and VTII models. It can be observed that, at the lowest solvent density (250 bar) the FFA extraction rate in the initial 20 minutes was slightly higher than the extraction rate of TG. This can be explained by the higher solubility as well as selectivity for FFA in SC-CO_2 under this condition. After 20 minutes of extraction, the FFA profile did not changed with the time, considering that these components were completely extracted. It can also be seen that TG were not completely extracted. At 400 bar (highest solvent density), it is possible to observe that the extraction for all components studied achieved a maximum yield in less than 1 hour.

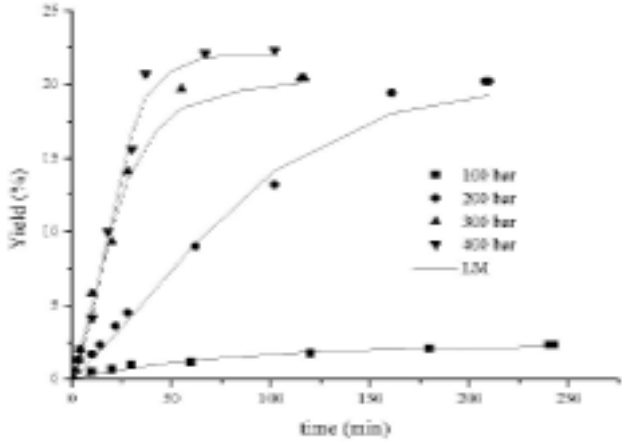
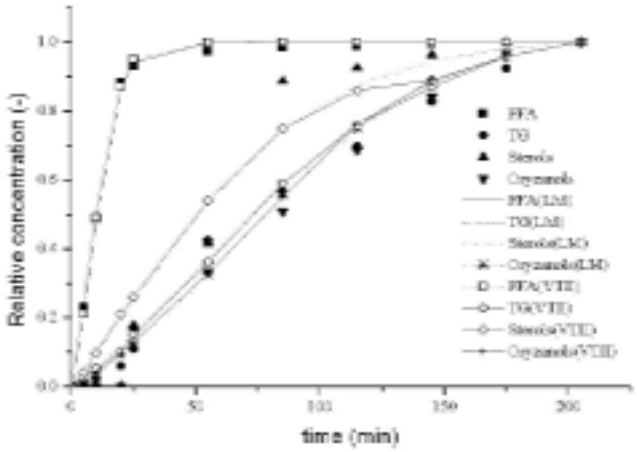
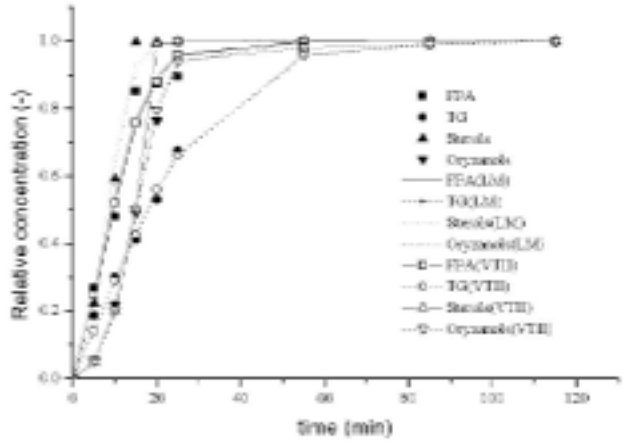


Figure 1: Modelled and experimental overall extraction curves obtained at 50°C.



(a)



(b)

Figure 2 : Fractionation of RBO at 250 bar/60 °C (a) and 400 bar/60 °C (b) and modelled curves.

For the CC experiments, the composition of the feed oil used is presented in Table 2.

Table 2 : Composition of the crude RBO used in the CC experiments.

Component	Mass (%)
FFA	10.00
Oryzanols	1.30
Sterols	0.48
TG	84.66
Others	3.56

CC experiments were conducted at different conditions and the results are presented in Table 3. For these experiments the amount of CO_2 consumed was 2.0 kg/h, the extract reflux employed was represented by an average value of 5.0 g/h and the solvent-to-feed ratio was calculated as 16.67 kg CO_2/kg feed.

Table 3 : Results obtained for the CC-SFE of RBO.

	P (bar) / T (°C)							
	200 / 60		200 / 80		250 / 60		250 / 80	
	E [a]	R [b]	E	R	E	R	E	R
Component	Mass (%)		Mass (%)		Mass (%)		Mass (%)	
FFA	96.68	n.d.	97.82	0.80	92.04	0.63	94.21	0.52
Oryzanols	0.19	1.90	0.25	1.75	0.21	1.70	0.19	1.45
Sterols	0.26	0.91	n.d.	1.04	0.15	0.76	n.d.	0.89
TG	n.d.	91.22	0.72	92.25	n.d.	93.12	0.56	92.89
Non-identified	2.87	5.97	1.21	4.16	7.60	3.79	5.04	4.25

[a] – Extract ; [b] – Raffinat ; n.d. – not detected

By analyzing Table 3, it was possible to observe that the RBO deacidification was successfully achieved, starting from a feed FFA concentration of 10.0 % (Table 2). As expected, the enrichment of FFA in the extract fractions and the consequent separation from the other RBO components achieved the highest concentration (app. 98 % - 9.8 fold) at 200 bar and 80 °C. FFA present a higher solubility and selectivity in SC-CO_2 at lower solvent densities. Because of that, TG are usually presented at very low concentrations under these conditions. The results obtained are in good agreement with literature data [3].

The TG concentrations in the extract fractions were only detected at 80 °C. By changing the operational conditions, the TG concentrations in the raffinate samples were very similar. This can be probably explained due to the small amount of extract collected (10-20 g/h) during the experiments. The TG concentrations in the raffinate samples were slightly higher than that of the feed material at all experimental conditions studied.

The sterol contents were higher at lower CO_2 densities in the raffinate fractions. Starting from 0.48 % (w/w) in the feed sample, it was possible to achieve one enrichment up to 2 fold at 200 bar and 80 °C.

The oryzanol content of the raffinate samples was significantly higher (7 to 10 fold) than the presented by extract samples. RBO refined through conventional processes can present up to 0.6 % oryzanol (w/w) [3].The implication of these results is very important for the application of the supercritical technology to RBO deacidification.

CONCLUSIONS

The fractionation of RBO, as well as its modelling were presented in this paper. At lower solvent densities, it is possible to achieve a higher separation from FFA and TG. The evaluation of the oryzanol and sterol profiles was also presented and the experimental data were modelled with good accuracy. The results obtained from the CC experiments have proved that the refinement of RBO is possible by means of supercritical fluid extraction. Starting from a feed concentration of 10 % (w/w) FFA, it was possible to separate the undesired FFA from the raffinate fractions. Supercritical technology is a true alternative for conventional techniques because of its capability of producing solvent-free products under mild thermal conditions.

ACKNOWLEDGEMENTS

The authors wish to acknowledge CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Brazil) for the financial support.

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