CHEMICAL ENGINEERING TRANSACTIONS Volume 24, 2011
Editor Sauro Pierucci
 ISBN 978-88-95608-15-0 ISSN 1974-9791
DOI: 10.3303/CET1124136

Ethanolic Extraction of Soybean Oil: Oil Solubility Equilibria and Kinetic Studies

Christianne E. C. Rodrigues*, Natália M. Longo, Cibele C. Silva, Keila K.. Aracava, Bruna R. Garavazo

Separation Engineering Laboratory (LES), Department of Food Engineering (ZEA / FZEA), University of Sao Paulo (USP)
PO Box: 23, Zip Code: 13635-900 – Pirassununga – SP – Brazil.
chrisrodrigues@usp.br

The main goal of this work was to evaluate the ethanol performance on the extraction process of soybean oil. The influence of process variables, solvent hydration and temperature was evaluated using the response surface methodology. In addition, the kinetics of extractable substances from soybean flakes with ethanol as solvent was studied and the results were modeled considering the model of So and Macdonald. It can be noted that oil solubility in ethanol was highly affected by the water content while increasing temperature only promotes the increased level of soluble solids extraction for conditions where solvents with low contents of moisture are used. The free fatty acids extraction is improved by increasing the moisture content in the solvent while the retention index is only dependent on solvent moisture content. The values for this dependent variable increase as the solvent hydration levels increases. It was also observed that the moisture transfer process, from the soybean flakes to the extracted phase, is not temperature dependent. In general, the non-linear multiple regression allowed us to obtain models with good predictive capability. In the kinetic study, the results produced by the model of So and Macdonald were found to be in good agreement with the experimental data ($0.89 \leq R^2 \leq 0.99$).

1. Introduction

The search for alternative solvents to extract edible oil from oilseeds has regained attention mainly due to growing environmental concerns related to the use of hexane, the most common solvent used around the world. This fossil solvent is chosen due its high stability and high capability of dissolving oil. Furthermore, this solvent allows one to obtain a defatted meal of good quality that can be used in food formulations for human consumption. A variety of solvents have been proposed to replace hexane as extractant of vegetable oils: water with or without enzymes, aldehydes, ketones, short-chain alcohols, among others (Johnson and Lusas, 1983). Replacing hexane with a biorenewable solvent may be interesting, especially if the substitute is largely available, it presents low cost and similar extracting efficiency for neutral lipids and nutraceutical compounds (Rodrigues and Oliveira, 2010). In Brazil, the high volume of ethanol production allows one to purchase this material at low prices, encouraging research on

Please cite this article as: Rodrigues C.E.C., Longo N.M., Silva C.C., Aracava K.K. and Garavazo B.R., 2011, Ethanolic extraction of soybean oil: oil solubility equilibria and kinetic studies, Chemical Engineering Transactions, 24, 811-816
DOI: 10.3303/CET1124136

the substitution of hexane by ethanol (Rittner, 1992). The main goal of this work was to evaluate the ethanol performance on the extraction process of soybean oil.

2. Materials and Methods

2.1 Materials

The solvents used in this work were absolute ethanol, from Merck (Germany), with purity greater than 99.5 %, and aqueous solvents with varying moisture contents, in the range of 2.97 to 20.01 %, on mass basis, prepared by diluting deionized water into absolute ethanol. Soybeans, previously cracked, dehulled and flaked, were kindly supplied by Cargill (Brazil) and were used as received, without further pretreatment. Soybean flakes were characterized in terms of oil content, protein content, and moisture content according to official methods (AOCS, 1998). All measurements were performed in quintuplicates. The raw material was also characterized in terms of free fatty acids (FFA) by titration (IUPAC 1979).

2.2 Methods: equilibria and kinetic studies

Batch extractions were carried out in 50 mL isothermal cylindrical cells built in pyrex glass, according to procedure developed by Rodrigues and Oliveira (2010). The cells were sealed to avoid solvent losses and the system temperature was controlled in a pre-set value (40 to 60) ± 0.1 °C using a thermostatic bath (Tecnal, Brazil). The solid-liquid systems were obtained by adding known masses of soybean flakes and solvent in the mass ratio of 1:4.5 (solid: solvent). The pre-set quantities of flakes and solvent were weighed in analytical balance with readability of 0.0001 g (Adam, UK). For experiments related to the phase equilibria study, a magnetic stirrer was used (Ika, Germany) to agitate the mixture for at least 24 hours. In the case of kinetic study, samples of raffinate and extracted phases were obtained every 5, 10, 15, 20, 30, 50, 60, 180, 300 and 1440 minutes. The stirring velocity was kept constant at 800 rpm for all the extraction experiments. For both kinds of experiments, the raffinate phase mass was weighed on an analytical balance and the extracted phase composition was measured according to the following methods: FFA concentration was determined by titration (IUPAC, 1979). The total solvent concentration was determined by evaporation at 60 °C. The water concentration was determined by Karl Fischer titration (AOCS, 1998). The soluble substances composition was determined by difference. In this work, all measurements were performed, at least, five times.

2.3 Response surface methodology

The response surface methodology (RSM) was used to investigate the effect of some process variables (temperature and water content in the solvent) on the soluble substances, and FFA transfers, during an equilibrium stage of the solid–liquid extraction process. The fatty compounds and water transfers were calculated by eq 1 (Rodrigues and Oliveira, 2010).

$$T_i(\%) = 100\frac{m^{EP}w_i^{EP}}{m^{solid}w_i^{solid}} \quad (1)$$

where m is the mass, w is the mass fraction, EP is extracted phase, solid refers to soybean flakes at the beginning of the extraction process, i is soluble substances or FFA. In this case, the extracted phase mass was determined by mass balance (Rodrigues

and Oliveira, 2010). A factorial design was planned to obtain quadratic models for the responses of interest. The complete set comprised 2^2 trials plus a star configuration (or axial points) with three replicates in the central point (11 trials) (Box et al., 1978). Contour curves were then sketched using the quadratic model for the statistically significant variables. The Statistica® software (Statsoft, v. 9.0) was used to analyze the results following the central composite design. To test the predictive capacity of the statistical models obtained in this investigation, the average relative deviations (ARD) were calculated according to eq 2.

$$ARD(\%) = \left[\sum_{i=1}^{n} \left(\left| y_i^{ex} - y_i^{calc} \right| / y_i^{ex} \right) \right] \times \frac{100}{n} \quad (2)$$

where y_i is the response transfer, n is the number of trials, ex and calc are related to the experimental data and those estimated using the RSM models, respectively.

2.4 Kinetic model

The mathematical model proposed by So and Macdonald (Meziane and Kadi, 2008) was used to correlate the kinetic data. This model considers that this extraction occurs according to two simultaneous processes: (a) oil occurring on the seed surface is quickly removed by simple washing with the solvent; and (b) the extraction of any remaining oil in the broken or unbroken cells is governed by a diffusion process in two steps occurring inside the seed: slow (diffusion 1), and a very slow (diffusion 2). The concentration (C) at any time (t) of oil in the solvent is given by the following equation:

$$\begin{aligned} C &= C_e^w\left(1-\exp\left(-k_w t\right)\right) + C_e^{d1}\left(1-\exp\left(-k_{d1} t\right)\right) + C_e^{d2}\left(1-\exp\left(-k_{d2} t\right)\right) \\ C_e &= C_e^w + C_e^{d1} + C_e^{d2} \end{aligned} \quad (3)$$

where C_e is the oil concentration at equilibrium; C_e^w is the washing step; C_e^{d1} and C_e^{d2} are the diffusion constants related to steps 1 and 2; k_w, k_{d1} and k_{d2} represent the mass transfer coefficients of the washing and diffusion steps (min^{-1}), and the numbers 1 and 2 represent the relative indexes to the first and the second diffusion. Values of the mass transfer coefficients k_w, k_{d1} and k_{d2} as well as the oil yields at equilibrium C_e^w, C_e^{d1} and C_e^{d2} have been calculated numerically with a non-linear least squares fitting method using the program Origin® 8.0.

3. Results and Discussion

Density of the soybean flakes used in this work was 335 ± 18 kg m^{-3}, based on ten replicates. The results obtained for the different characterizations of the solid material were: moisture, (6.63 ± 0.09) %; Oil (dry basis) (21.83 ± 0.13) %; Free fatty acids (dry basis) (0.42 ± 0.01) %; Protein (dry basis) (38.83 ± 0.55) %.

To verify the effect of the process variables, temperature (T) and water content in the solvent (W), on the extraction process, a factorial design was implemented. Table 1 presents all combinations of the studied variables in the statistical analysis and the corresponding responses for the factorial design. The statistical analysis yielded the following models, eqs 4 to 7, representing the responses, as a function of statistically significant variables, where W*, and T* are coded variables.

$$T_{sol}\,(\%) = 50.32 - 16.74W^{*} + 9.56W^{*2} + 10.70T^{*} - 5.76T^{*2} \quad (4)$$

$$T_{FFA}\,(\%) = 32.75 - 1.54W^{*} + 3.56W^{*2} + 1.73T^{*} + 1.77T^{*2} + 3.43T^{*2} - 2.96W^{*}T^{*} \quad (5)$$

$$RI(kg/kg) = 1.49 + 0.12W^{*} \quad (6)$$

$$Water_{EP}\,(\%) = 10.16 + 6.15W^{*} - 0.35T^{*} + 0.47T^{*2} \quad (7)$$

Table 1: Factorial design: 2^2 + star configuration + central points

Coded Variables		Actual Variables		Responses			
W*	T*	W[a] (mass %)	T (°C)	T_{sol}[b] (%)	T_{FFA}[b] (%)	RI[c] (kg/kg)	$Water_{EP}$[d] (%)
-1	-1	2.97	42.4	61.40	33.39	1.40	4.65
+1	-1	17.45	42.4	38.78	41.24	1.62	17.97
-1	+1	2.97	57.1	97.18	43.16	1.28	4.46
+1	+1	17.45	57.1	51.52	39.16	1.61	16.54
-1.41	0	0.04	50.0	90.09	46.05	1.27	1.55
+1.41	0	20.01	50.0	43.83	34.61	1.56	18.33
0	-1.41	10.02	40.0	36.88	37.89	1.62	11.23
0	+1.41	10.02	60.0	62.98	42.22	1.55	10.43
0	0	10.02	50.0	49.02	33.80	1.52	9.94
0	0	10.02	50.0	47.66	33.18	1.48	10.23
0	0	10.02	50.0	50.38	31.26	1.45	10.23

[a] Content of water in the solvent (% in mass); [b] Transfer (%); [c] Retention index (mass of adhered solution/mass of inert solid); [d] Water content in extracted phase (% in mass).

Table 2 shows the analysis of variance (ANOVA) for these responses at 95.0% confidence. As it can be seen in Table 2, the vast majority of responses presented high correlation coefficients and acceptable ARD values.

Table 2: Analysis of Variance (ANOVA)

Source of variation	T_{sol} (%) SS[a]	T_{FFA} (%) SS[a]	RI SS[a]	$Water_{EP}$ SS[a]
Regression	3840.06	214.51	0.1166	304.24
Residual	59.50	55.98	0.04418	1.33
Total	3899.56	239.69	0.1607	305.56
F value (F list)	96.81 (4.53)	6.13 (3.69)	23.80 (5.12)	533.75 (4.35)
CC[b]	0.99	0.88	0.85	0.99
ARD (%)[c]	11.12	5.01	3.42	3.02

[a] Sum of Squares; [b] Correlation coefficient; [c] Average relative deviation (eq 2).

With these statistical models, eqs 4–7, it is possible to sketch contour curves that represent the influence of temperature and water content in the solvent on the responses (Fig 1). In Fig. 1(a) it can be observed that the soluble substances transfer (T_{Sol}) is strongly influenced by the water content in the solvent. In fact, the increase of water content in ethanol strongly suppresses the soluble substances extraction while increasing temperature only promotes the increased level of soluble solids extraction for conditions where solvents with low contents of moisture are used. Figure 1(b) shows

that the FFA extraction increases with increasing temperature. This effect is more significant when the moisture content in the solvent is low. In Fig. 1(c) we can observe that the retention index is only dependent on solvent moisture content. The values for this dependent variable increase as the solvent hydration levels increases. In Fig. 1(d), it can be seen that the moisture transfer process, from the soybean flake to the extracted phase, is not temperature dependent.

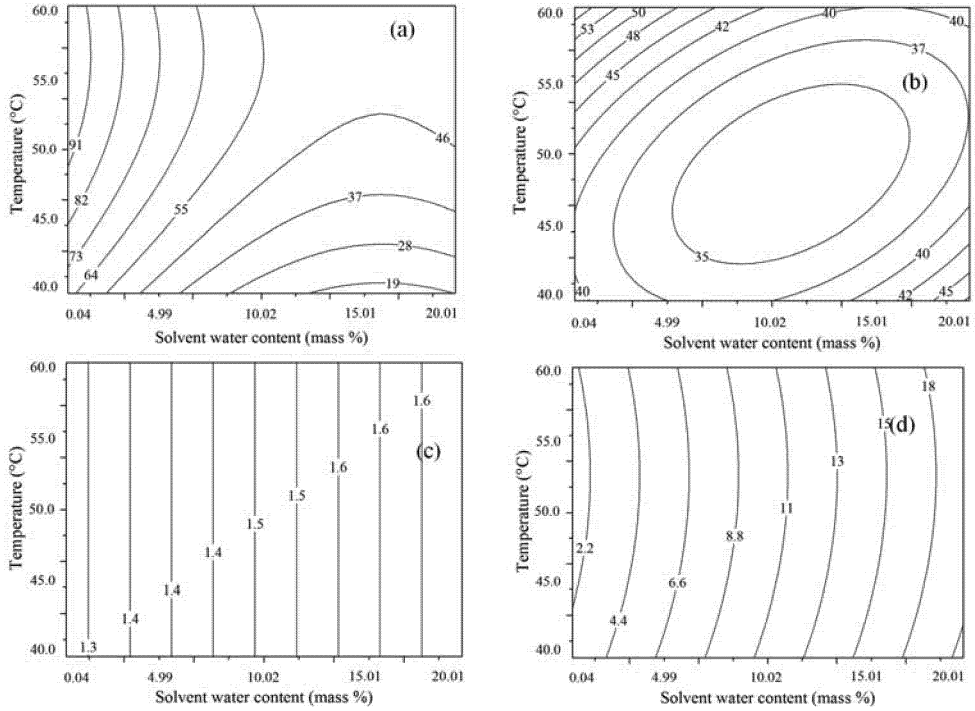

Figure 1: Contour curves of responses expressed as a function of water content in the solvent (mass %) and temperature (° C). (a) T_{Sol}; (b) T_{FFA}; (c) RI; (d) $Water_{EP}$.

Experimental data of kinetic of extraction, given in Fig. 2, were fitted with the mathematical model of So and Macdonald. Very good fits are observed as shown by the high values of the coefficients of determination ($0.89 \leq R^2 \leq 0.99$).

As expected, the increase in temperature results in an increase in oil yield in the extract phase. The change in yield can be explained by the fact that the rise in temperature increases the solubility and the facility of diffusion of the oil while decreasing viscosity.

4. Conclusions

The experimental design allowed us to obtain statistical models using the RSM. The statistical analysis enabled us to select the process conditions, temperature and solvent moisture levels, to maximize T_{Sol} and to minimize RI. In general, the results show that the oil extraction process from soybean using ethanol is possible. In addition, this study showed that the model of So and Macdonald gave excellent fits of the experimental data of oil extraction using ethanol with different hydration levels as solvent.

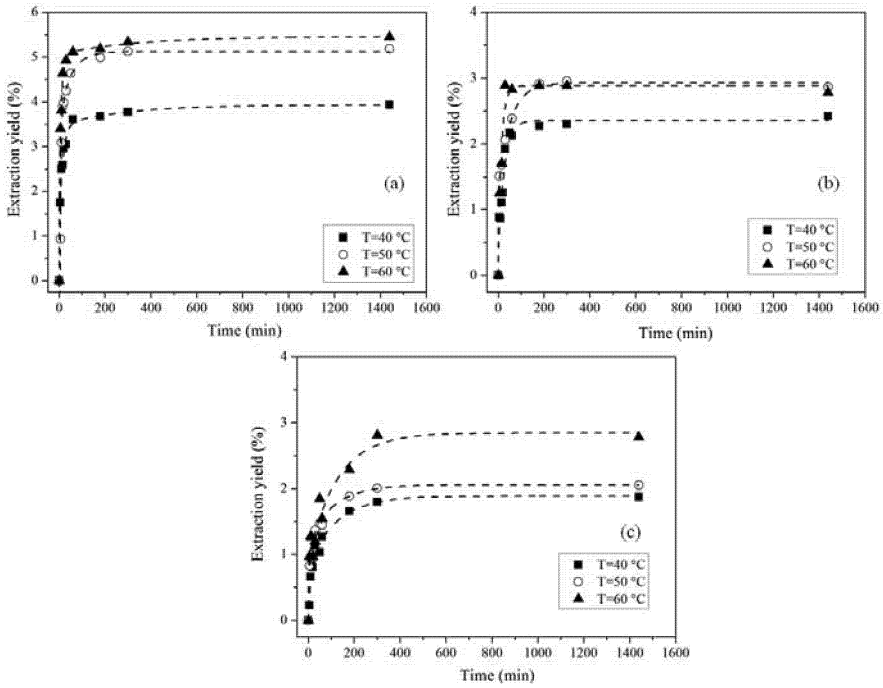

Figure 2: Extraction yield versus contact time showing the effect of temperature (° C) and different water contents in the solvent. (a) (0.06±0.01) mass %; (b) (5.98±0.01) mass %; (c) (15.01±0.07) mass %.( ) So and MacDonald model.

Acknowledgements

The authors wish to acknowledge FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo - 2009/17855-3 and 2008/56258-8) and CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico).

References

AOCS, 1998, Official Methods and Recommended Practices of the American Oil Chemists' Society. AOCS Press, Champaign.

Box G.E.P., Hunter, W.G. and Hunter J.S., 1978, Statistic for Experimenters – an Introduction to Design, Data Analysis and Model Building. John Wiley & Sons, New York.

IUPAC, 1979, Standard Methods for the Analysis of Oils, Fats and Derivatives. Pergamon Press, New York.

Johnson L.A. and Lusas E.W., 1983, Comparison of alternative solvents for oils extraction. Journal of the American Oil Chemists' Society, 60, 229–242.

Meziane S. and Kadi H., 2008, Kinetics and Thermodynamics of Oil Extraction from Olive Cake. Journal of the American Oil Chemists' Society, 85, 391-396.

Rodrigues C.E.C. and Oliveira R., 2010, Response surface methodology applied to the analysis of rice bran oil extraction process with ethanol. International Journal of Food Science and Technology, 45, 813–820.