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Modelling the supercritical CO_2 extraction kinetics of soybean oil

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Summary

Different empirical models were used to describe the supercritical CO_2 extraction of soybean oil obtained at series of operational parameters namely pressure, temperature, solvent flow rate and characteristic particle size. Process yields obtained by supercritical CO_2 were up to 19.33%. Several kinetic models: Brunner, Kandiah and Spiro, Tan and Liou, Martinez et al. and Esquivel et al. were used to test the experimental yield data. All models were analysed using nonlinear regression method. Also a new model, modified Esquivel et al., was proposed and analysed using nonlinear regression method as well. According to the obtained results for extraction yield of soybean oil, the modified Esquivel et al. model show the best agreement between experimental and model calculated data.

Keywords: soybean oil, supercritical CO_2 extraction, modelling, kinetics

Introduction

Supercritical fluid extraction has attracted considerable attention in recent years as a promising alternative to the conventional solvent extraction and mechanical pressing in food processing as it offers a number of advantages, including the absence of solvent residue and better retention of aromatic compounds. In the last few decades this powerful separation process has drawn an increasing interest in commercial application, particularly due to its technical and environmental advantages compared to the current classical extraction methods by organic solvents. Carbon dioxide (CO_2) is mainly used as the extraction agent in this extraction process because extracts obtained using CO_2 are solvent-free/without any trace of toxic extraction solvents, and are thereby highly valued (Jokić et al., 2014; Cvjetko Bubalo et al., 2015).

Use of supercritical CO_2 as a replacement of organic solvents in soybean oil extraction during the two decades is being considered by Brühl and Matthäus (1999), Nodar et al. (2002), Artz et al. (2005), Jokić et al. (2010), Jokić et al. (2012), Jokić et al. (2013). The oil extracted from soybeans with supercritical CO_2 is much higher quality than the hexane-extracted oil. It does not contain any phospholipids, thus eliminating the degumming step. The great advantage of the extraction of soybean oil with CO_2 compared to the conventional extraction is that the refinement stages are simplified significantly and the solvent distillation stage is completely removed (the two most costly steps in terms of energy consumption). Unfortunately, supercritical CO_2 extraction is still relatively new technique and is not widely used on the commercial scale for the extraction of edible oils mainly due to very high investment costs of equipment. But nowadays, according to global trends, "green" products and technologies are needed to replace conventional ones. When considering industrial application, it is essential to provide research on the fundamentals of the supercritical processes and to test the applicability of the appropriate model used for the scale-up of laboratory data to industrial design purposes (Jokić et al., 2011).

Mathematical modelling of complex phenomena is important from economic point of view. Brunner (1984) explored the basic variables that influenced the mass transfer of solutes and provided the basis for several other modelling studies involving oilseed. Among the first in modelling of soybean oil extraction with supercritical CO_2 were Hong et al. (1990) in which work the mass transfer calculations were used. In our previous work (Zeković et al., 2014) we investigate three empirical models (Brunner 1984; Kandiah and Spiro, 1990; Esquivel et al., 1999) to describe the extraction kinetic curves of *Ocimum basilicum* L. and they show to be useful for mathematical modelling.

The aim of this study was to describe the supercritical CO_2 extraction process of soybean oil using different empirical models and to find the model which shows the best agreement between experimental data and model calculated data.

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Material and methods

Material

Supercritical CO_2 extraction was performed on the soybean cultivar “Ika” created at the Agricultural Institute Osijek in Croatia. Reagent-grade n-hexane was used for laboratory Soxhlet-extraction. Commercial CO_2 (Messer, Novi Sad, Serbia) purity of 99.9% was used for laboratory supercritical CO_2 extraction.

Determination of the initial oil content

The initial oil content (x_0) was measured by automatic extraction systems Soxterm by Gerdhart with n-hexane (Aladić et al., 2014). The measurement was done in triplicate.

Supercritical CO_2 extraction

The experiments were performed on the laboratory-scale high pressure extraction plant (HPEP, NOVA-Swiss, Effertikon, Switzerland) explained in detail elsewhere (Jokić et al., 2011). 130 g of ground soybean sample was placed into the extractor basket. The extracts were collected in glass tubes weighed previously and placed in the separator at ambient temperature and pressure. The amount of extract obtained at regular intervals of time was established by weighing (balance precision ± 0.00001 g). Separator conditions were 15 bar and 25 °C. Duplicate experiments were conducted and the means of the total yield determinations with standard deviation and the applied experimental conditions are given in Table 1. These results were published in our previously published manuscript (Jokić et al., 2012) and in this work will be used for modelling the kinetic extraction curves using different empirical models.

Modelling the extraction curves

The extraction curves of soybean oil were adjusted using few models presented in the literature.

Brunner (1984) gave the global model expressed as:

$$Y_E = x_0\left(1-e^{-kt}\right) \tag{1}$$

where Y_E is extraction yield; k is the constant rate and t is the time at which the extraction from the particle core starts.

The second model considered was proposed by Kandiah and Spiro (1990):

$$Y_E = x_0\{1-[f_1\exp(-k_1t)+f_2\exp(-k_2t)]\} \tag{2}$$

where Y_E is extraction yield; f_1 and f_2 are the fractions of solute extracted with rate constant of k_1 and k_2,respectively.

The third model considered was proposed by Tan and Liou (1989):

$$Y_E = x_0\frac{\dot{m}_f\rho_s}{m_s\rho_f}\frac{1-\varepsilon}{\varepsilon}\frac{1}{k_d}\left(1-\exp\left(k_d\frac{\varepsilon\cdot h_E}{u_s}\right)\right)\left(\exp\left(-k_dt\right)-1\right) \tag{3}$$

where the Y_E is extraction yield; x_0 is initial oil concentration in the solid phase; $\dot{m}_f$ is mass flow of the fluid; ρ_s is density of the solid phase; h_E is height of the extractor basket; ε is void fraction in bed; u_s is supercritical velocity and k_d is desorption constant.

The extraction curves of soybean oil were adjusted with the model of Martinez et al. (2003) represented by the following equation:

$$Y_E = x_0\frac{1}{\exp\left(B_2t_m\right)}\left\{\frac{1+\exp\left(B_2t_m\right)}{1+\exp\left(B_2\left(t_m-t\right)\right)}-1\right\} \tag{4}$$

where Y_E is extraction yield; t is the extraction time, B_2 and t_m are the adjustable parameters expressed in (h^{-1}) and (h), respectively.

Esquivel et al. (1999) empirical model is represented by the following equation:

$$m_{ext} = x_0F\left(\frac{t}{b+t}\right) \tag{5}$$

where m_{ext} is mass of the extract; F is the mass of solid material; t is the extraction time; x_0 is the initial solute mass ratio in the solid phase; and b is an adjustable parameter.

In order to obtain better agreement of experimental and model calculated parameters, the next step in this study was to make the correction in the model given by Esquivel et al. (1999). The following form of model was obtained:

$$m_{eks} = x_0m_t\left(\frac{t^2}{b+t^2}\right) \tag{6}$$

New improved equation Eq. (6) was used also to correlate the kinetic study of soybean oil in supercritical CO_2.

The parameters of all models were calculated by non-linear regression method using software *Mathcad 14* (Svilović et al., 2009).

Statistical analysis

The concordance between the extraction yield experimental data and calculated value obtained using different mathematical models was established by the average absolute relative deviation (AARD) as follows:

$$\mathrm{AARD} = \frac{1}{n} \cdot \sum_{i=1}^{n} \left| \frac{y_{\exp} - y_{cal}}{y_{\exp}} \right| \quad (7)$$

Results and discussion

The mathematical models used to describe the process of supercritical fluid extraction usually have one, two or more parameters, which are necessary to calculate or adjust their values to experimental data. As a result of mathematical modeling in this study the parameters of different applied models were obtained by minimizing the deviation value of the calculated yield by model and experimental data and the average absolute relative deviation (AARD) were calculated for each experiment.

The oil content in soybeans was determined to be 20.08 ± 0.14% using Soxhlet method and n-hexane as a solvent. Experimental conditions for supercritical CO_2 extraction are given in Table 1 and the obtained extraction yield applying different process parameters (extraction pressure, temperature, solvent flow rate and particle size) are given. From Table 1 it can be seen that the highest extraction yield (19.33 ± 0.34) was obtained applying pressure 400 bar, temperature 40 °C and the smallest particle size of 0.238 mm.

In our previous study (Jokić et al., 2012) we used Sovová's model to describe the extraction curves. For the Sovová's model (Sovová, 1994) supercritical fluid extraction can be related to the time of extraction through the overall extraction curves, clearly divided in three sections: the constant extraction rate period, controlled by the convection transport, where the mass transfer resistance lays in the solvent phase; the falling extraction rate period, where both mass transport mechanism are important, convection and diffusion; and the diffusion period, controlled by the solid phase mass transfer resistance. The model assumes that the extractible oil content is divided in accessible oil, or free oil from the broken solid particles, and inaccessible oil, oil content trapped inside the un-ruptured solid structure. The mass transfer of the easily accessible solute is characterized by the fluid-phase mass transfer coefficient, while the solid-phase mass transfer coefficient is related to the solute diffusion inside the particles. Applying Sovová's model a lot of additional parameters are needed to be measured and calculated. So, in this study we applied much simpler and the most used empirical models in the literature for modelling the extraction kinetics just to show is it possible to get a good results applying much simpler models. Also, we proposed modified empirical model which show good agreement between experimental and model obtained results. To describe the kinetics of supercritical CO_2 extraction of soybean oil several empirical models were used (Eqs. 1-6). The success of the approximation of applied mathematical model was analyzed based on AARD (%) which is considered to be acceptable up to 5% and above 10% indicates poor approximation of experimental and model predicted values of data. Using software *Mathcad 14*, the AARD values and the adjustable parameters of the each applied models were calculated and given in Table 2 and Table 3.

Table 1. Experimental conditions and the yields of the extraction experiments. These results were used in another published manuscript (Jokić et al., 2012)

Extraction conditions	P (bar)	T (°C)	$\dot{m}_f$ (kg/h)	d_0 (mm)	Total yield* (%)
Run 1	500	40	0.194	0.383	18.05 ± 2.04
Run 2	400	40	0.194	0.383	17.61 ± 1.12
Run 3	400	50	0.194	0.383	18.51 ± 2.57
Run 4	400	60	0.194	0.383	19.01 ± 3.23
Run 5	400	40	0.194	1.06	13.49 ± 1.38
Run 6	400	40	0.436	0.383	18.29 ± 3.11
Run 7	300	40	0.194	0.383	18.52 ± 0.54
Run 8	400	40	0.194	0.238	19.33 ± 0.34

P = pressure; T = temperature; m_f = solvent flow rate; d_0 = particle size

*Mean ± standard deviation (n=2)

Table 2. AARD (%) for all applied models

Extraction runs	Brunner	Kandiah and Spiro	Tan and Liou	Martinez et al.	Esquivel et al.	Modified Esquivel
1	10.939	7.680	14.036	10.602	23.6942	6.1700
2	11.090	6.235	14.734	11.086	24.5035	7.0164
3	10.808	6.430	15.013	10.807	24.7123	6.2330
4	9.681	6.085	13.845	9.082	23.1220	5.7259
5	5.434	4.946	3.175	5.438	5.5376	2.6655
6	6.657	5.911	7.867	6.643	16.1739	3.6812
7	16.792	10.514	20.934	16.784	31.2822	10.9632
8	10.853	7.113	15.055	10.858	24.6979	5.5505

Table 3. Calculated parameters of the applied empirical models for soybean oil extraction

	Brunner	Kandiah and Spiro				Tan and Liou	Martinez et al.		Esquivel et al.	Modified Esquivel
Run	k (1/h)	f_1	f_2	k_1 (1/h)	k_2 (1/h)	k_d (1/h)	B_2 (1/h)	t_m (h)	b (1/h)	b (1/h)
1	0.2191	0.5280	0.5277	0.2321	0.2321	0.2662	0.2205	-20.4692	2.6319	10.9175
2	0.1631	0.5299	0.5286	0.1738	0.1738	0.2019	0.1631	-52.0567	3.6709	19.6486
3	0.1859	0.5310	0.5309	0.1980	0.1980	0.2313	0.1859	-55.4845	3.0902	15.3580
4	0.2052	0.5301	0.5305	0.2178	0.2178	0.2564	0.1865	-71.0132	2.7111	12.7350
5	0.0995	0.4910	0.4810	0.0951	0.0951	0.1225	0.0995	-90.1187	6.7661	46.4111
6	0.3857	0.5143	0.5143	0.3968	0.3868	0.4397	0.3852	-36.1482	1.4347	3.5200
7	0.1099	0.5426	0.5430	0.1207	0.1207	0.1372	0.1099	-75.7722	5.6911	43.9076
8	0.2248	0.5345	0.5345	0.2399	0.2399	0.2780	0.2249	-45.005	2.4131	10.7420

Table 2 shows the results of modeling of supercritical CO_2 extraction using a simple model proposed by Brunner (1984). This model assumed that the extraction process takes place in one stage where the diffusion is controlled only by means of the internal heat transfer. AARD values (Table 2) range from 5.434% to 16.792% for all examined experimental extraction conditions extraction given in Table 1.

From Table 3 can be seen that the values of the adjustable parameters of Kandiah and Spiro (1990) model, based on the existence of a chemical reaction, k_1 and k_2 are identical, and that the estimated values for the extracted solute fractions f_1 and f_2 are very similar. The fractions of solute extracted f_1 and f_2 have been estimated as the inflection point of the experimental extraction curves. From these results can be concluded that the models based on the chemical reaction can be applied only in cases where the chemical reactions during the extraction process is very slow and thus controlling factor in the process, while the rate of desorption, dissolution and diffusion of extracted components are too large to could slow down the process. This is not the case in the extraction of oil from oilseeds, which cannot be synthesized in the natural matrix during extraction; they already exist such as in it and are not chemically connected.

The results of modeling of supercritical CO_2 extraction using desorption model proposed by Tan and Liou (1989) are shown in Table 2 and 3. The increase in the desorption coefficient k_d with increasing pressure and temperature of extraction is noticed (Table 3). Similar results were published by Campos et al. (2005) where authors investigate the supercritical extraction of extraction of marigold (*Calendula officinalis*) oleoresin.

Results of modeling of the extraction of oil from soybeans by supercritical CO_2 using logistic model proposed by Martinez et al. (2003) are also shown in Table 2 and 3. As a result of the modeling, the adjustable parameters of the model B_2 and t_m are obtained (Table 3). The best agreement between the experimental and predicted values for oil yield was obtained at the following process conditions: pressure of 400 bar, temperature of 40 °C, CO_2 flow rate 0.194 kg/h and for the particle size of 1.059 mm. Furthermore, it is evident that the value for adjustable model parameter t_m are negative, which means that the rate of the extraction is always decreasing, having its maximum value at the initial instant (Elisa Sousa et al., 2005). Physical meaning of the adjustable parameter B_2 is not already well defined, but from the results in Table 5, it was noted that the value of the parameter B_2 increased by increasing the pressure at the isothermal conditions, which indicates that in the system at a higher pressure the equilibrium were more quickly established. Furthermore, the value of parameter B_2 increased with the increase of extraction temperature, which means that at a constant pressure of 400 bar extraction at higher temperatures the equilibrium were more quickly established. According to AARD for all experimental conditions extraction, desorption model shows worse agreement between experimental and model calculated oil yields compared with logistic model, which is explained by the fact that the logistic model through two adjustable parameters (B_2 and t_m) consider the convection and the diffusion mechanisms, while desorption model have only one adjustable parameter (k_d).

The kinetics of the supercritical CO_2 extraction of soybean oil was investigated also by modelling the extraction curves using the model described by Esquivel et al. (1999) who used that model for the modelling the extraction of olive oil by supercritical CO_2. The values for the adjustable model parameter b and AARD values for all the experiments are presented in Table 3. It can be observed that the best adjustments of the experimental results were obtained for experiment number 5 where the bigger particle size of material was used. In Eq. 6 we proposed modified Esquivel model which show better agreement between experimental and model calculated extraction yields (the lowest AARD values, Table 2). Compared to Sovová's model, for application of modified Esquivel model the only required data is the raw material extraction rate (kg/kg) value and the raw material mass used, for this reason it is a model of easy implementation. Because of the fact that this model presents only one adjustable parameter, b, it does not give information about the different types of mass transfer mechanisms. In Fig. 1 we summarized the kinetic study of soybean oil supercritical CO_2 extraction using different process parameters. In our previous study (Jokić et al., 2012) it was explained in detail how different process parameters influence the extraction process of soybean oil so this will not be the subject of this work. Fig. 1 just shows the experimental results and results obtained by the model given in Eq. 6 (modified Esquivel model). This model is chosen because it gives the best results according to calculated AARD values.

According to the results of all applied models it can be also noticed that the increase in the CO_2 flow rate reduced the AARD between the experimentally measured and model calculated values of oil yield. This fact can be explained by the reduction of external resistance to mass transfer with the increase of solvent flow, while the internal mass transfer resistance remains constant.

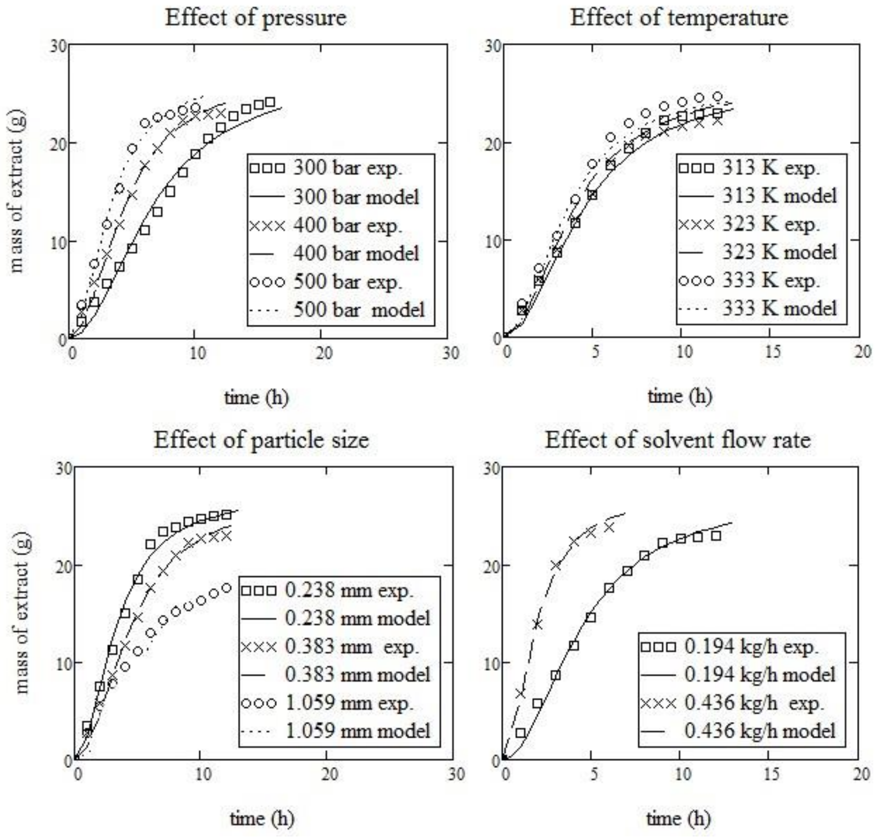

Fig. 1. Kinetic study of soybean oil supercritical CO_2 extraction using different process parameters; experimental results and results obtained by the model which gave the best results

Conclusions

The extraction yield of soybean oil obtained by supercritical CO_2 extraction was correlated using different empirical models. As a result of mathematical modelling in this study the parameters of different applied models were obtained by minimizing the deviation value of the calculated yield by model and experimental data for each experiment. According to the obtained results for extraction yield of soybean oil, the modified Esquivel et al. model best agreed with the obtained experimental data.

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