Modelling and Simulation of Supercritical CO₂ Oil Extraction from Biomass

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Abstract

The aim of this work is to model the kinetics of the supercritical CO₂ extraction of oils from biomass, namely from industrial grape seeds and chia seeds. A model introduced by Sovova and Stateva (2015) is used and solved using gPROMS ModelBuilder. The supercritical extraction experiments performed at different temperature, pressure and flow rate conditions, provide the data to the modelling studies and for model parameter estimation, using gPROMS parameter estimation.

The partition coefficient and the maximum oil content corresponding to monolayer adsorption was estimated and the absolute average relative deviation between the experimentally measured and simulated extraction curves for the cases examined is within the range (1-9) %, which may be considered as a good agreement taking into consideration the very complex nature of the systems under study.

Keywords: Grape seeds, chia seeds, supercritical CO₂ extraction, extraction kinetics, mathematical modelling.

1. Introduction

Increasing attention is being drawn to the effective use of waste biomass and vegetal material as renewable resources of high added value compounds with applications in food, cosmetics, pharmaceutical industries, biodiesel production, etc. Grape (*Vitis vinifera* L.) seed biomass contains typically (8-15) % (w/w) of oil rich in long chain polyunsaturated fatty acids (PUFAs) and antioxidants (Bail et al., 2008; Fernandes et al., 2013). Although representing about (20-25) % of the biomass generated by the wine industry, it is still considered a disposable material and rarely valorised. Chia (*Salvia hispanica* L.) seeds are attracting great attention due to its health beneficial properties and are being studied as a source of protein and dietary fiber. Furthermore, they have a high

oil content (20-35 % w/w), rich in PUFAs, mainly the omega-3 α -linolenic acid which represents (60-65) % of total fatty acids (Porrás-Loaiza, 2014).

Supercritical CO₂ extraction (SCE) is known to prevent or minimize the degradation of bioactive compounds due to the comparatively low temperatures applied and oxygen free atmospheres. It also allows obtaining solvent-free products. Unsurprisingly, it is currently establishing itself as the viable and eco-friendly alternative to the use of organic solvents. Yet, kinetic data are not abundant, and, particularly for chia seeds oil extraction they are scarce and superficial.

In view of the above, the aim of our work is to model the kinetics of the SCE of oils from industrial grape seeds, obtained directly from a Portuguese wine industry (Coelho et al., 2018), and from two sets of chia seeds - high oil content (HOCS), and underutilized low oil content (LOCS) seeds, by applying an efficient solution method to a recently introduced kinetics model (Sovova and Stateva, 2015).

2. Methodology

The seeds were prepared prior to extraction. Grape seeds, which were supplied crushed, have been dried for 48 h at 343 K while the chia seeds were cleaned from straws and other extraneous material prior to being grounded and sieved. No other pretreatment was applied. The average particle diameter (d_p) was calculated to be 0.62 mm for the grape seeds and 0.37 mm for the chia seeds.

The SCE of the grape seeds was performed at temperatures of (313 and 333) K, pressures of (20, 30 and 40) MPa and flow rates of (1.8, 2.3 and 2.8) $\times 10^{-3}$ kg $\cdot$ min $^{-1}$ of CO₂. Regarding the chia seeds, SCEs from LOCS were carried out at (25 and 45) MPa, (313 and 333) K and a CO₂ flow rate of 40 $\times 10^{-3}$ kg $\cdot$ min $^{-1}$. The extractions of HOCS were performed at 45 MPa, 313 K and several CO₂ flow rates, namely (27, 40 and 54) $\times 10^{-3}$ kg $\cdot$ min $^{-1}$. The amount of sample used for the experiments was 17 g (grape seeds) and 130 g (chia seeds). A detailed description of the units employed for the extraction of grape and chia seeds can be found, respectively, in the studies reported by Coelho et al. (2018) and Villanueva-Bermejo et al. (2017).

The grape and chia seed oils are very complex mixtures of mainly triacylglycerols (TAGs) with minor amounts of other compounds. Due to this complexity, and in order to reduce the size of the kinetics modelling task, the oils composition is usually being represented by model TAGs. Following the results of the composition analyses, the grape seed oil was represented by triolein (Coelho et al., 2018), while chia seed oil should be represented by trilinolenin. However, considering the lack of any experimental information on the VLE of trilinolenin+scCO₂ and the total lack of data (both experimental and estimated) on the thermophysical properties of trilinolenin, triolein was selected as the model TAG to exemplify the chia seed oil.

To calculate the solubility of the representative TAG in the scCO₂, the VLE of the two-component system (triolein+CO₂) was modelled applying the predictive Soave-Redlich-Kwong (PSRK) cubic EoS (Holderbaum and Gmehling, 1991).

To simulate the extraction curves in terms of yield and composition of the oil extracts for both the grape and chia seeds, the novel model of Sovova and Stateva (2015), which reflects the complex relationship between kinetics and phase equilibria (solubility), was

applied. Although the model was originally developed for multicomponent systems extraction, it remains valid for single component systems too.

This model considers homogeneous concentration in the extractor at both solid and fluid phases and assumes that the extracts are located on the surface of the solid particles. This assumption allows neglecting internal diffusion, which is compatible with finely ground substrates where the diffusion path in the particles is short and the extract is easily accessible, resulting in negligible internal mass transfer resistance. Further details on the model can be found elsewhere (Sovova and Stateva, 2015)

The model was deployed, validated and executed using gPROMS ModelBuilder (Process Systems Enterprise, Ltd.), an equation-oriented modelling and optimisation platform for steady-state and dynamic systems. gPROMS offers an integrated framework where all the tasks can be performed within the same environment, with embedded solvers that can usually complete the simulations without further user input provided that a complete and well formulated model, with the adequate initial conditions, is available.

gPROMS Modelbuilder parameter estimation was used to estimate the partition coefficient (K) for all the cases studied. The maximum oil content corresponding to monolayer adsorption (w_i) was also estimated for the chia seeds cases. gPROMS uses a maximum likelihood parameter estimation problem and attempts to determine values for the uncertain physical and variance model parameters that maximize the probability that the mathematical model will adequately predict the values obtained from the experiments.

In order to compare the fitting accuracy, a standard deviation measure, the absolute average relative deviation, $AARD$, was also calculated after the parameter estimation using Eq. (1), where N is the total number of experimental points, and e_i^{exp} and e_i^{est} - the i -th experimental and estimated point, respectively.

$$AARD = \frac{100}{N} \sum_{j=1}^N \frac{|e_i^{exp} - e_i^{est}|}{e_i^{exp}} \quad (1)$$

3. Results and discussion

Figure 1 shows the experimental and simulated cumulative extraction curves and Figure 2 - the simulated composition profiles for the solid and fluid phases of the SCE of grape seeds oil. The positive effect of the pressure increase on the extraction rate is clearly demonstrated on the yield, while the effect of temperature is not so well-defined. The simulated profiles for solid and fluid phases depicted in Figure 2, where the increase in pressure results in higher extraction rates, are compatible with the behaviour depicted in Figure 1.

For LOCS (Figure 3) analogous effect of the pressure is observed, while the temperature effect on the rate of extraction and on the total amount of extracted oil is more significant. Figure 4 depicts the profiles for HOCS at different scCO₂ flows, with the yield increasing faster for higher flows.

From the analysis of Figure 1, 3 and 4, a steepest ascent in cumulative mass fraction may be observed for chia seeds, indicating that the oil is more readily available than in the in the grape seeds.

The parameter K was estimated for all systems studied, while w_i - only for the chia seeds cases. The values obtained are presented in Table 1. The AARD values obtained ranged

Figure 1. Experimental (symbols) and simulated (lines) extraction curves for grape seeds at different temperatures, $p = 30$ MPa (dashed lines) and $p = 40$ MPa (solid lines) and scCO_2 flow rate of $1.8 \times 10^{-3} \text{ kg} \cdot \text{min}^{-1}$.

Figure 2. Simulated profile of oil concentration in the grape seeds (w_s) and scCO_2 (w). $T = 333 \text{ K}$ and scCO_2 flow rate of $1.8 \times 10^{-3} \text{ kg} \cdot \text{min}^{-1}$.

Figure 3. Experimental (symbols) and simulated (lines) extraction curves for LOCS at different temperatures, $p = 25$ MPa (dashed lines) and $p = 45$ MPa (solid lines) and scCO_2 flow rate of $1.8 \times 10^{-3} \text{ kg} \cdot \text{min}^{-1}$.

Figure 4. Experimental (symbols) and simulated (lines) extraction curves for HOCS at different at different flow rates. $T = 333 \text{ K}$ and $p = 45 \text{ MPa}$.

approximately from (2 to 9) % for the grape seeds and LOCS, and from (1 to 7) % for HOCS, which should be considered as a good agreement taking into consideration the very complex nature of the systems under study.

The new modelling approach applied incorporates in a rigorous way the interplay between phase equilibria (solubility) and kinetics, and the results obtained demonstrate that albeit the simplifications introduced in representing the grape and chia seed oils, there is a good qualitative and quantitative agreement between the experimental and calculated extraction yields at the SCEs operating conditions examined. It should be emphasized that although the internal diffusion is neglected, the model can still deliver adequate results, providing that the particle size is small, as is the case for the matrix used in this work.

Table 1. Estimated values for parameters K and w_t .

System	P (MPa)	T (K)	F (10^{-3} kg·min $^{-1}$)	K (kg plant · kg $^{-1}$ CO $_2$)	w_t	AARD (%)
Grape	30	313	1.8	2.24E-1	-	4.51
Grape	30	333	1.8	2.22E-1	-	8.84
Grape	40	313	1.8	3.65E-1	-	6.73
Grape	40	333	1.8	4.33E-1	-	8.64
Grape	40	333	2.3	5.58E-1	-	6.68
Grape	40	333	2.8	3.46E-1	-	2.16
LOCS	25	313	40	3.22E-3	8.04E-2	4.82
LOCS	25	333	40	1.36E-2	8.04E-2	9.49
LOCS	45	313	40	4.27E-3	5.76E-2	5.64
LOCS	45	333	40	2.47E-2	5.20E-2	2.13
HOCS	45	313	27	2.00E-2	6.01E-2	1.22
HOCS	45	313	40	1.69E-2	8.25E-2	2.47
HOCS	45	313	54	9.28E-3	8.07E-2	6.65

The values of K are directly related with the extraction rate and the values presented in Table 1 follow generically the same trend observed in Figures 1, 3 and 4, namely K increases with the increase of pressure and temperature. Regarding the scCO $_2$ flow, the trend variation of K is not clear and shows to be system dependent. This behaviour is compatible with the results previously reported by other authors (Honarvar et al., 2013).

4. Conclusions

This work presents the results of the SCE of biomass from industrial grape seeds, obtained directly from a Portuguese industry without preliminary treatment, and from two sets of chia seeds. The influence of the operating conditions on the extraction yield were analysed in detail and reported.

To simulate the extraction process, a kinetic model assuming that the extracts are located on the surface of the solid particles, thus neglecting internal diffusion, was applied. The solubility in scCO $_2$ of the oil, represented as triolein, at the temperatures and pressures of interest to both experiments were obtained applying a rigorous thermodynamic framework, which allowed to interweave the respective solubility functions in the mass balance equations.

The model equations were then integrated using gPROMS ModelBuilder. The qualitative and quantitative agreement between the experimental and simulated extraction curves in terms of yields for both the grape and chia seeds oil was good taking into consideration the complex nature of the systems examined. We can also conclude that the model applied can be successfully used in finely ground matrix where the internal diffusion contribution to the extraction phenomena is very small and, thus, negligible.

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