EFFECT OF HIGH-INTENSITY ULTRASOUND ON THE PARTICULATE ALMONDS OIL EXTRACTION KINETICS USING SUPERCRITICAL CO_2

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The influence of high-intensity ultrasound on supercritical CO_2 extraction of oil from particulate almonds was studied. An ultrasonic transducer was installed inside a high pressure 5 L extractor and a power of 50W was applied during the extraction. All experiments were performed at 280 bar and 55ºC with and without ultrasound in order to examine the effects of the acoustic waves. The experimental results showed that the kinetic parameter, considering the process as a second order reaction, was improved about 30% due to ultrasonic radiation and the oil extraction yield was enhanced in about 20% at the end of the process (8.5 h). For design purposes, the experimental data were described applying two empirical models (Naik and Weibull) as well as the model proposed by Sovovà.

INTRODUCTION

Due to the increasingly stringent environmental regulations, supercritical fluid extraction (SFE) using CO_2 has gained wide acceptance in recent years as an alternative to conventional solvent extraction in many analytical and industrial processes. SFE presents important advantages (non-toxic, recyclable, cheap, relatively inert and non-flammable) over traditional techniques [1]. However, one of the main difficulties when applying a supercritical fluid as solvent for extraction is the usually slow kinetics of the process. The solubilities of many substances in supercritical fluids are usually less than in fluids used for conventional extraction processes; therefore the mass transfer rate is smaller [2]. A classical way to accelerate separation or extraction processes is the application of a mechanical agitation system. Another possibility is the use of high-intensity ultrasounds.

High-intensity ultrasounds are elastic waves with frequencies higher than 20 kHz and intensities over 1 W/cm^2. Ultrasonic radiation represents an efficient way of producing deep agitation, enhancing mass transfer processes, because of some mechanisms (microstreaming, compressions and descompressions in the material, heating and cavitation) [3, 4]. In the case of SFE, the characteristics of the equipment do not easily allow the use of mechanical stirrers; therefore, ultrasonic waves could be an interesting alternative for this purpose. The study of the influence of high-intensity ultrasounds on the supercritical extraction kinetics was the aim of this work. Almond oil extraction curves were obtained and several mathematical models were applied in order to evaluate the results.

MATERIALS AND METHODS

Raw material

Almonds (*Prunus amygdalus*) from a variety known as “Marcona comuna” were used in this investigation. The raw almonds were blanded, pealed, dried and finally grounded before the extraction process. The particle size was measured using different sieves and was estimated in a range of 3-4 mm.

Equipment description

The experiments were carried out in a pilot plant of SFE (AINIA, Valencia). The supercritical pilot equipment mainly included a high pressure vessel (5L), two separation units (a cyclone and a decanter), a diaphragm pump and different sensors for temperature, pressure and flow rate.

The ultrasonic equipment consists of a power ultrasound generator, an impedance adapter, a transducer and a control computer. In order to study the effect of the acoustic waves in supercritical fluid extraction, an experimental system based on the integration of a power ultrasonic transducer inside the extractor, inserted on the upper lid of the vessel, was designed and developed [5]. A scheme of the equipment is shown in figure 1.

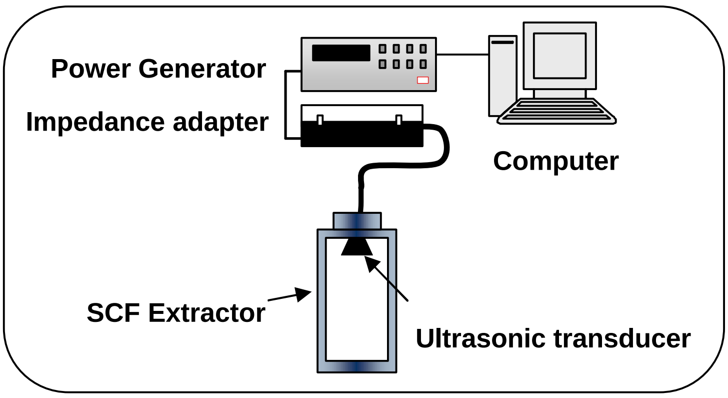

Figure 1: Ultrasonic device used for the SFE assisted by acoustic waves

The transducer is the part of the equipment that generates acoustic waves. The resonant frequency of the traducer used was 20 kHz and the power applied 50 W. A software developed in Labview was used to monitor the behaviour of ultrasonic parameters (impedance, frequency and power) during the extraction.

Experimental procedure

SFE was performed in all cases with 1500 g of grounded almonds. The solvent used was CO_2 at 99.9% purity (Abelló Linde, Valencia, Spain). The pressure, the temperature and the flow rate of the process were 280 bar, 55º C and 20 kg/h, respectively. To examine the effect of the acoustic waves all experiments were carried out with and without ultrasound application and replicated twice. The extraction curves were fitted to several mathematical models in order to identify the parameters of interest.

MATHEMATICAL MODELLING

Two empirical models have been used to describe the experimental data: the equation proposed by Naik et al. [6] and the Weibull model [7]. The Naik equation (1) is a simple empirical model that represents the extraction yield, Y (kg extract/100 kg raw material), as a function of time (t):

$$Y = \frac{Y_\infty t}{b + t} \qquad (1)$$

The parameters of the model are Y_∞?and b. Y_∞ is the yield after infinite extraction time and b the time needed to reach the half of the extraction at infinite time ($Y_\infty/2$). $Y_\infty/b = R_0$ could be an approximation of the initial extraction rate [8].

The Weibull model (2) considers three parameters: the extraction yield at infinite time (Y_∞); the parameter behaviour index or shape parameter (α); and the scale parameter (β) as the time needed to achieve a fractional extraction of $1\text{-}e^{-1}$ (approximately 0.63). This model could be interesting for predicting delay times in some extraction processes.

$$Y = \left[1 - e - ^{-\left(\frac{t}{b}\right)^{a}}\right] \cdot Y_\infty \qquad (2)$$

The fit of the experimental data was carried out using two different approaches for the value of Y_∞. First, a fixed value for Y_∞ equal to the total oil content in the almonds (55.03%) was used. The second approach considered Y_∞ as a parameter to be indentified.

A theoretical model developed by Sovovà et al. [9, 10] was also applied in this work. The equations of the model are listed below:

$$Y = \begin{cases} q y_r \left[1 - \exp(-Z)\right] & q < q_m \quad (3) \\ y_r \left[q - q_m \exp(z_w - Z)\right] & q_m \le q < q_n \quad (4) \\ x_0 - \frac{y_r}{W} \ln\left\{1 + \left[\exp\left(\frac{W x_0}{y_r}\right) - 1\right] \exp\left[W(q_m - q)\right] \frac{x_k}{x_0}\right\} & q \ge q_n \quad (5) \end{cases}$$

where q is the specific amount of solvent passed through the extractor (kg solvent/kg solute-free feed); y_r represents the apparent solubility of the solute in the solvent (kg solute/kg solvent); x_0 and x_k represent total initial solute content and the initial concentration of the difficult accessible solute in the solid (kg solute/kg solute-free feed); Z, the dimensionless mass transfer parameter in the fluid phase; W, the dimensionless mass transfer parameter in the solid phase; z_w, the dimensionless axial co-ordinate between fast an slow extraction; q_m, the q value when extraction begins inside the particles; and q_n, the q value when the easily accessible part of solute is all extracted. The equations (3), (4) and (5) describe respectively the linear part of the extraction curve (oil easily accessible), the intermediate stage of the extraction and the stage controlled by diffusion.

RESULTS AND DISCUSSION

The extraction curves and the main mathematical models applied are plotted in figures 2 and 3. The results show that for noticying the effect of ultrasound some time is needed. As a consequence, at the end of the extraction time (8.5 h), the yield was significantly higher when the process was acoustically assisted (25.80% ± 0.93% compared to 21.36% ± 1.05% without ultrasound application). This increase involves an improvement of the extraction yield of 20.8%.

On the other hand, the data was described adequately by a second order reaction (R^2>0.97). From the linear form of this equation [11] the kinetic parameter was identified and differences were found with or without ultrasound application. This parameter was $4.23 \cdot 10^{-5}$ s^{-1} (kg extract/kg raw material)$^{-1}$ without ultrasound while the value of $5.60 \cdot 10^{-5}$ s^{-1} (kg extract/kg raw material)$^{-1}$ was found when acoustic field was applied.

<u>Empirical models</u>

As can be seen in figures 2 a) and 2 b) the empirical models were useful to describe the extraction kinetics, being the percentage of explained variance always higher than 98%.

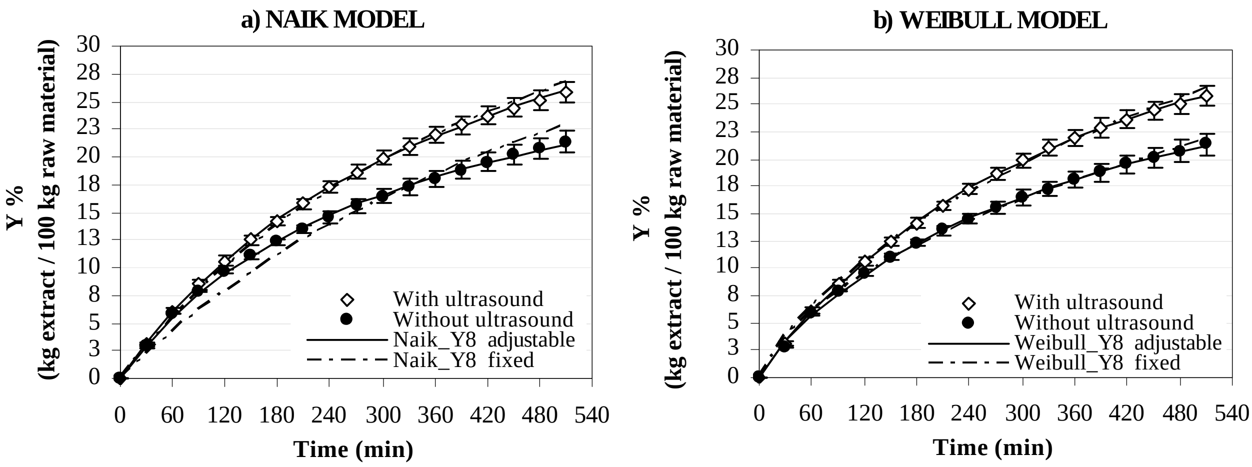

Figure 2: Effect of ultrasound on the yield of extracted oil from particulate almonds. Predicted results (lines) obtained with a) Naik Equation and b) Weibull Model.

In table 1 are reported the values for the constants of the Naik equation and Weibull model, as well as the goodness of the fittings. As can be observed, the best fit was achieved, in both models, when Y_∞ was adjusted. In this case, the models revealed that the extraction yield at infinite time (Y_∞) was higher with ultrasound.

As the kinetic parameter (b and β) of theses two models are dependent on Y_∞ value, in order to analyze the influence of ultrasound on the extraction time, this value was fixed to the maxim extraction yield (55.03%). In this way, the results obtained from the Naik model showed that the time needed to reach the half of the extraction at infinitive time (b) was significantly lower with ultrasound than without them. The same conclusion was obtained from the β parameter of Weibull model.

Table 1: Modelling results from Naik equation and Weibull model

Model				$Y_¥$	b (min)	R_0	% var
NAIK	$Y_¥$	Adj.	Without US	34.17 ± 2.97	316.88 ± 30.45	0.180 ± 0.001	99.9
			With US	46.59 ± 1.62	407.00 ± 0.19	0.191 ± 0.004	99.9
		Fixed	Without US	55.03 ± 0.01	716.95 ± 42.82	0.128 ± 0.005	98.4
			With US	55.03 ± 0.01	541.32 ± 30.49	0.169 ± 0.006	99.8
				$Y_¥$	b (min)	a	% var
WEIBULL	$Y_¥$	Adj.	Without US	28.85 ± 1.40	363.41 ± 4.34	0.84 ± 0.03	99.9
			With US	33.13 ± 1.62	330.31 ± 30.63	0.95 ± 0.03	99.9
		Fixed	Without US	55.03 ± 0.01	1424.55 ± 191.11	0.68 ± 0.03	99.7
			With US	55.03 ± 0.01	883.957 ± 56.13	0.77 ± 0.00	99.7

* US: Ultrasound application

Theorical model of Sovovà

The results obtained from empirical models could be explained theoretically using the Sovovà model. This model takes into account the interactions between the solute and the solid matrix; therefore, it provides a more real description of the results. Five parameters are used by the model (y_r, x_0, x_k, W and Z), two of them were previously established (y_r was obtained from the Del Valle and Aguilera correlation [12] and x_0 was determinate analytically). Figure 3 presents the agreement between the experimental data and those obtained with the model.

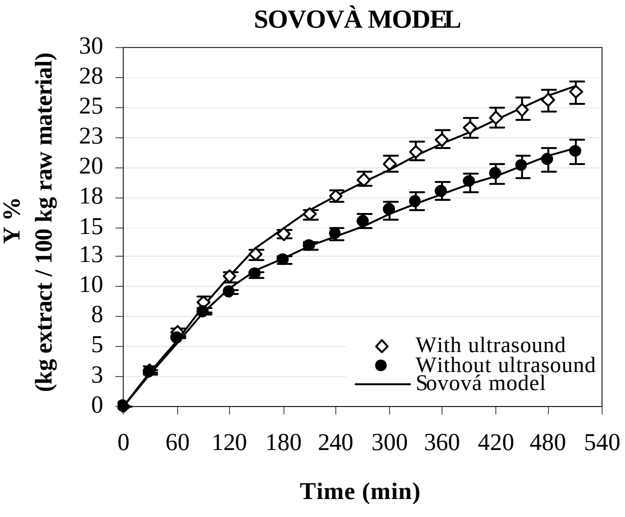

Figure 3: Effect of ultrasound on the yield of extracted oil from particulate almonds. Predicted results (lines) obtained with the Sovovà model.

Table 2: Parameters from Sovovà model

Parameters	Without US	With US
x_k	0.99 ± 0.01	0.93 ± 0.02
$x_0 - x_k$	0.23 ± 0.01	0.29 ± 0.02
$W_q \cdot 10^5$ (s^{-1})	1.38 ± 0.14	1.97 ± 0.20
$Z_q \cdot 10^3$ (s^{-1})	9.11 ± 0.44	9.97 ± 1.64
$W \cdot 10^3$	1.70 ± 0.16	2.40 ± 0.26
Z	1.12 ± 0.07	1.22 ± 0.21
% var	99.9%	99.9%

Independient parameters: y_r = 0,0059 g/g. x_0 = 1.224

* US: Ultrasound application.

Figure 3 shows that the linear part of the extraction curve was identical in experiments carried out with or without ultrasound: this was the stage controlled by the solubility of solute in the solvent. However, diffusion problems appeared sooner when the extractions were performed without ultrasound. The parameters of the Sovovà model illustrate this fact (table 2). Differences in x_k and Wq were found. The fraction of difficult accessible solute in the solid, x_k, was less with ultrasound. This could mean that ultrasound may access not only to the free oil but also to tied oil located near the particle surface. On the other hand, Wq, that represents the ease with which the solute is transferred in the solid phase, was significantly higher when acoustic field was applied. This result indicates that ultrasound increase the internal mass transfer coefficient. The mechanism that could explain this effect is that ultrasound could penetrate into the almond and cause compressions and decompressions on the solid material improving the extraction (sponge effect).

Other results: ultrasonic equipment behaviour

Transducers operated satisfactorily under high pressure along all the extraction time, although instabilities appeared during the pressurisation stage due to the changeable properties of the medium in this part of the process. Moreover, some relationships between acoustical and process parameters were found. For instance, frequency and pressure presented a similar evolution, such as impedance and density. Therefore, ultrasound could be useful not only for the improvement of the extraction but also for monitoring operating conditions of supercritical process.

CONCLUSIONS

In this study the influence of high-intensity ultrasound on the SFE has been examined. The results show that ultrasound improve the final extraction yield as well as the kinetic of the process. This enhancement could be linked to an increase in the internal mass transfer coefficient. In addition, transducers work well in supercritical fluids and some acoustic parameters could be used for monitoring the extraction process.

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