

Ultrasound induced green solvent extraction of oil from oleaginous seeds

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A B S T R A C T

Ultrasound-assisted extraction of rapeseed oil was investigated and compared with conventional extraction for energy efficiency, throughput time, extraction yield, cleanness, processing cost and product quality. A multivariate study enabled us to define optimal parameters (7.7 W/cm² for ultrasonic power intensity, 40 °C for processing temperature, and a solid/liquid ratio of 1/15) for ultrasound-assisted extraction of oil from oilseeds to maximize lipid yield while reducing solvent consumption and extraction time using response surface methodology (RSM) with a three-variable central composite design (CCD). A significant difference in oil quality was noted under the conditions of the initial ultrasound extraction, which was later avoided using ultrasound in the absence of oxygen. Three concepts of multistage cross-current extraction were investigated and compared: conventional multistage maceration, ultrasound-assisted maceration and a combination, to assess the positive impact of using ultrasound on the seed oil extraction process. The study concludes that ultrasound-assisted extraction of oil is likely to reduce both economic and ecological impacts of the process in the fat and oil industry.

Keywords:

Ultrasound
 Extraction
 Oilseed
 Green impact
 Degradation
 Unit operation

1. Introduction

Rapeseed oil is the third most widely consumed vegetable oil worldwide after palm and soybean, and ranks first in Europe for frying oil, margarine and salad dressings [1,2]. The rapeseed oil production process involves several steps including preparation of seeds, mechanical pressing and solvent extraction of the press cake (Fig. 1) [2].

The oldest method for oil recovery from seeds is pressing to squeeze the oil out of the solid residue [3]. However, matrices containing more than 30% oil, such as rapeseed, which contains nearly 50%, require more than simple pressing to recover all the oil available in the seed. Conventional processing begins by a conditioning step to increase seed plasticity by warming to 50–60 °C. Seeds are then flaked between smooth rollers to increase the surface area and help release oil. The flakes undergo a cooking step lasting 20–60 min, which brings the temperature into the range 90–120 °C. This step produces significant changes in the cell, especially by destroying oil bodies and causing oil droplets to merge and migrate across cell walls. As a result, the mechanical extraction

by pressing that follows the cooking step removes 65–70% of the oil contained in seeds. It permits to continue the cell wall disruption needed to obtain a high rate of oil recovery in press cake [4,5]. The press cake then undergoes solvent extraction. This step is performed in countercurrent extractors using hydrocarbon solvents, with 40–60% *n*-hexane, sourced from fossil resources and registered under the REACH Regulation as a category 2 reprotoxic and a category 2 aquatic chronic toxic substance [6]. Reducing the amount of hexane used in oil processing while keeping the same extraction performance has become desirable and is a key issue for industries for economic and ecological reasons.

Over the past few years, much interest has been paid to the applications of ultrasound (US) in food science and technology [7–10]. Applications of US generally involve processes that can enhance rates, improve quality and/or safety, and reduce processing time. A growing trend is the possible application of US for the extraction and promotion of natural compounds of interest [11] for industry [12,13]. The benefits of US are attributed to acoustic cavitation: micro-bubbles created in a liquid phase when subjecting a mixture to US will grow and oscillate quickly before collapsing due to pressure changes [14,15]. These violent implosions will fragment or disrupt the surface of the solid matrix, enhancing mass transfer and accelerating diffusion. Several studies suggest that

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Nomenclature

A	ultrasonic intensity (W/cm ²)	V	overflow phase (V = E + S)
B	temperature (°C)	L	underflow phase (L = E + I + S)
C	solid/liquid ratio	F	feed (rapeseed press cake)
CV	conventional extraction	M	ternary mixture point (M = F + S)
E	solute (assumed as oil)	SFA	saturated fatty acids
I	inert phase (solid)	MUFAs	mono unsaturated fatty acids
S	solvent phase (hexane)	PUFAs	poly unsaturated fatty acids

ultrasonic technology is an effective tool for vegetable oil extraction from seeds [16–19].

This paper describes an investigation on the influence of US for the extraction of rapeseed oil. Rapeseed oil is rather difficult to extract compared with sunflower oil, for example [20]. This is attested by the levels of residual oil in rapeseed meal, with residual oil contents in the range 1.8–4.1% [21] against 1.0–2.5% in sunflower meal [22]. These results are obtained at the cost of significant constraints on the preparation step (cooking), which could be reduced by an intensification treatment. The ultrasonic extraction parameters such as ultrasonic power intensity, extraction temperature and solid/liquid ratio for rapeseed oil extraction were optimized with the response surface methodology (RSM) using a three-variable central composite design (CCD). Extracts were qualitatively and quantitatively analyzed by GC-FID to investigate the

influence of US on yield and oil quality. Three concepts of multi-stage cross-current extraction were then investigated and compared: conventional multistage maceration, US-assisted maceration, and a combination thereof [23] to highlight the impact of using US. The study was extended by a preliminary assessment on economic, energy and ecological impacts comparing conventional and US-assisted extraction.

2. Materials and methods

2.1. Chemicals

Rapeseed, of the Astrid breeding line (Euralis Semences), was provided by the Technical Institute for Oilseeds (Terres Inovia,



Fig. 1. Conventional processing procedures for rapeseed oil extraction towards greener extraction.

Pessac, France). Hexane of technical grade was sourced from VWR International (Darmstadt, Germany). Methanol, sulfuric acid, sodium chloride, acetic acid, chloroform, potassium iodide, sodium thiosulfate, starch, potassium hydroxide, isopropanol, toluene, phenolphthalein and *n*-hexane were of analytical grade and were sourced from VWR International (Darmstadt, Germany).

2.2. Experimental procedure

2.2.1. Extraction procedure

The experimental setup for the extraction of oil from rapeseed cake is depicted in Fig. 2.

Extractions, with and without US, were performed on rapeseed previously pressed using a Komet press CA59G3 (IBG Monforts Oekotec, Germany) as shown in Fig. 3. The seeds had not undergone a cooking step, as pressing with the Komet is significantly more intense than the industrial combination of steps of preparation and pre-pressing to take into account ratios of seed size to equipment. This study is exploratory, and will need to be confirmed on an industrial scale.

Press cake was placed inside a cellulose cartridge (Legallais, Montferrier-sur-Lez) inserted in a double-jacketed reactor that allowed water to circulate using a cooling/heating system to control and regulate the medium temperature. All the experiments were conducted in the same reactor and under agitation in 100 g hexane for 15 min.

US-assisted extraction experiments were performed with a Hielscher (Teltow, Germany) Industrial Ultrasonic Processor UIP-1000hd (frequency 20 kHz, variable amplitude 25 μ m), Generator 230 volts, transducer IP65 grade with titanium horn and O-ring flange RFCA100 (stainless steel, diameter 100 mm) sealing to tita-



Fig. 3. Rapeseed meal produced with Komet press.

niun sonotrode BS2d22 (length 125 mm, diameter 22 mm). The experiments were conducted with an aluminum sheet covering the top of the reactor to prevent solvent losses during US treatment. After the extraction, miscella was transferred into a distillation flask and the solvent was evaporated under reduced pressure. All the experiments were carried out in triplicate.

Considering the input, power from the device was converted to heat, which was dissipated in the medium. Calorimetric measurements were made to assess actual US power P (W), calculated by Eq. (1) [24]:

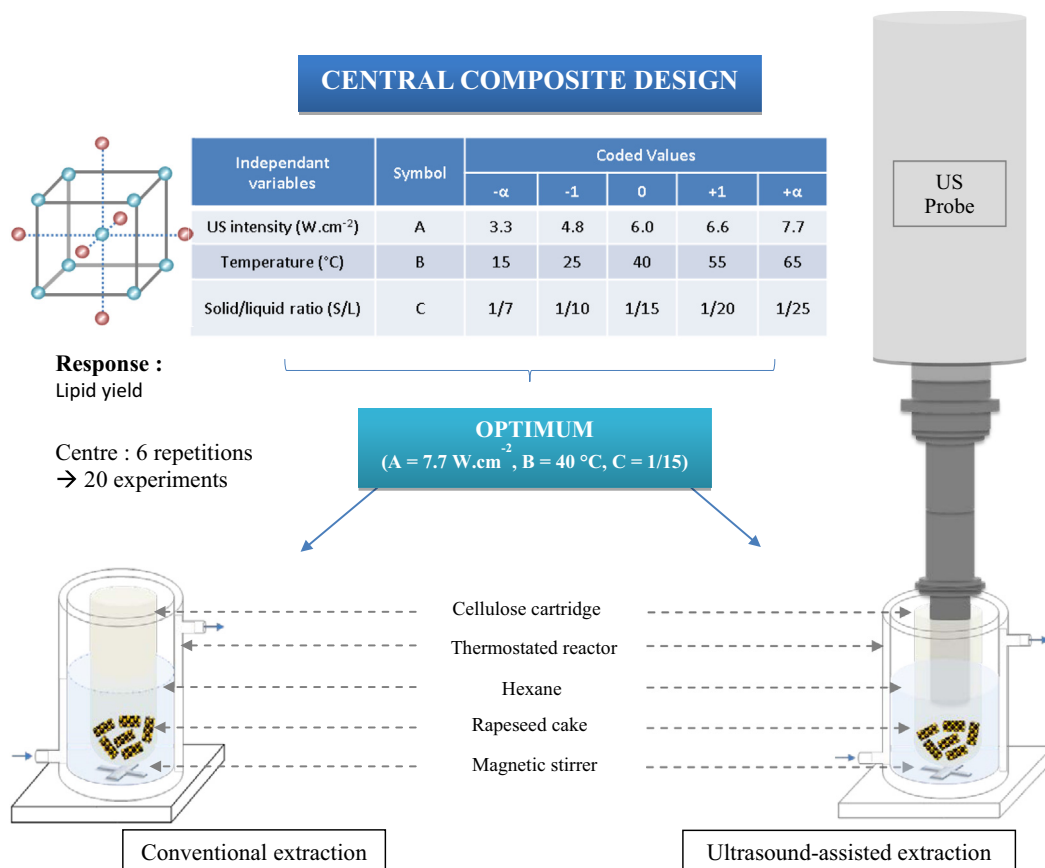


Fig. 2. Experimental procedure.

$$P = mC_p \frac{dT}{dt} \quad (1)$$

where C_p is the heat capacity of the solvent at constant pressure ($J g^{-1} ^\circ C^{-1}$), m is the mass of solvent (g) and dT/dt is temperature rise per second ($^\circ C s^{-1}$). The applied ultrasonic power intensity (UI) was then determined using the calculated power as given in the Eq. (2)[24]:

$$UI = \frac{4P}{\pi D^2} \quad (2)$$

where UI is the ultrasonic power intensity ($W cm^{-2}$), P is the ultrasound power (W) as calculated by Eq. (1) and D is the diameter (cm) at the probe tip.

2.2.2. Experimental design

To investigate the influence and relevance of the US-assisted processing variables on rapeseed oil extraction, a response surface methodology was used. Three independent factors, namely the ultrasonic power intensity (A), the temperature (B) and the solid/liquid ratio (C) were studied with the lipid yield as response. The relationships between the response and process variables were established according to a central composite design (CCD), along with the optimal conditions of the process. The independent variables, given in Fig. 2, were coded according to Eq. (3):

$$x_i = \frac{X_i - X_{i0}}{\Delta X_i} \quad (3)$$

where x_i and X_i are respectively the dimensionless and the actual values of the independent variable i , X_{i0} is the actual value of the independent variable i at the central point, and ΔX_i is the step change of X_i corresponding to a unit variation of the dimensionless value. For the three variables, the design yielded 20 randomized experiments (to avoid effects of extraneous factors) with eight (2^3) factorial points, six axial points ($-\alpha$ and $+\alpha$) to form a central composite design, and six center points for replications and estimation of the experimental error and to prove the suitability of the model. For the developed CDD the axial distance $\alpha = \sqrt[3]{N}$, with N the number of experiments in the orthogonal design, i.e. the factorial design (in our case 1.68). Coded values of the independent variables are listed in Fig. 2.

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i x_i + \sum_{i=1}^3 \beta_{ii} x_i^2 + \sum_{i < j}^3 \sum_j^3 \beta_{ij} x_i x_j + \sum_{i < j}^3 \sum_{j < k}^3 \sum_k^3 \beta_{ijk} x_i x_j x_k \quad (4)$$

The complete description of the process requires a cubic model. The lipid yield is related to the coded independent variables x_i , x_j , x_k according to the third order polynomial expressed in Eq. (4) with β_0 the interception coefficient, β_i the linear terms, β_{ii} the quadratic

terms, β_{ij} the interaction terms and β_{ijk} the cubic terms. To best describe the model, cubic terms β_{111} , β_{112} , β_{113} , β_{122} , β_{222} and β_{333} were excluded. Fisher's test for analysis of variance (ANOVA) performed on experimental data was used to assess the statistical significance of the proposed model. Response surfaces as represented in Fig. 4 were drawn using the analysis design procedure of Statgraphics (StatPoint Technologies, Inc., USA) for Windows.

2.3. Analysis

2.3.1. Lipid yield and profile by GC analysis

Fatty acid methyl esters (FAMES) were separated, identified and quantified by gas chromatography coupled with a flame ionization detector (GC-FID). Samples were prepared from extracted oils using acid-catalyzed trans-methylation [25]. 1 mL methanolic sulfuric acid (5% v/v) was added to a specific amount of extracted oils and internal standard. The mixture was then heated at 85 $^\circ C$ for 90 min and then taken off the heater. 1.5 mL of sodium chloride (0.9%) solution and 1 mL of *n*-hexane were then added. The flask was stoppered, shaken vigorously for 30 s, and centrifuged at 4000 rpm for 2 min. A small amount of the organic layer was removed, transferred into a vial, and injected directly into a gas chromatography.

Analyses were performed on a 7820A GC system (Agilent Technologies, USA) equipped with a FID detector and auto-sampler. Gas chromatography was performed on a BD-EN14103 capillary column (30 m \times 0.32 mm \times 0.25 μm) using helium as carrier gas at a velocity of 33 cm/s. 2 μL of various samples were injected in split mode (split ratio: 1:20) at 250 $^\circ C$. The oven temperature program was operated as follows: initial temperature 50 $^\circ C$ for one minute, increasing at 20 $^\circ C/min$ to 180 $^\circ C$ and at 2 $^\circ C/min$ from 180 $^\circ C$ to 230 $^\circ C$, held isothermally at 230 $^\circ C$ for 10 min. Data were collected with Agilent EZChrom Elite software. FAMES were identified by comparison with purified FAME standards (Sigma Co., USA). Quantification was performed using internal calibration. The internal standard was glyceryl triheptanecanoate (Sigma Co., USA).

2.3.2. Oil quality

Acid value was determined by the AOCS Method Cd 3d-63 [26], Peroxide value was determined by the AOCS Method Cd 8-53 [27] and conjugated dienes by the AOCS Method Ti 1a-64 [28].

3. Results and discussion

3.1. Experimental design and statistical analysis

Three variables that could potentially affect extraction efficiency of oil when assisted by US were studied in a central

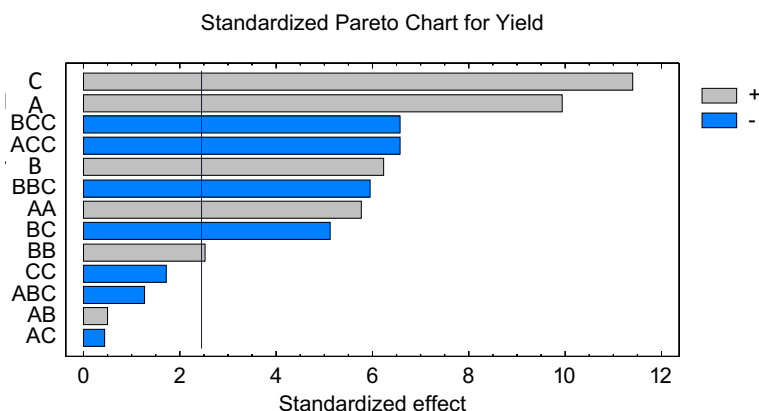


Fig. 4. Standardized Pareto chart for % Yield. A: ultrasonic intensity; B: temperature; C: solid/liquid ratio. Combination of these factors are indicated by coupled letters. +: positive effect; -: negative effect.

Table 1

Central composite design (CCD) with experimental values of fatty acid composition of extracts (A: ultrasonic intensity; B: temperature; C: solid/liquid ratio).

N°	A	B	C	C16	C16:1n9	C18	C18:1n9	C18:2n6	C18:3n3	C20	C20:1	C22:1n9
1	0	0	−α	4.99	0.34	1.43	59.63	21.74	10.06	0.49	1.09	0.23
2	−1	+1	+1	5.08	0.36	1.46	59.42	21.87	9.93	0.51	1.08	0.28
3	+1	+1	+1	5.08	0.35	1.48	59.45	21.85	9.90	0.51	1.10	0.27
4	−1	−1	−1	4.91	0.32	1.46	59.91	21.53	10.00	0.49	1.11	0.28
5	−1	+1	−1	4.96	0.33	1.46	59.78	21.61	9.94	0.50	1.15	0.27
6	0	0	+α	4.93	0.33	1.46	59.87	21.57	9.97	0.49	1.10	0.28
7	+α	0	0	4.95	0.35	1.46	59.67	21.69	10.05	0.48	1.07	0.28
8	−α	0	0	4.99	0.34	1.46	59.70	21.66	9.98	0.49	1.10	0.28
9	+1	+1	−1	5.01	0.33	1.46	59.73	21.67	9.98	0.49	1.08	0.26
10	−1	−1	+1	4.92	0.33	1.50	59.61	21.64	9.95	0.66	1.13	0.27
11	+1	−1	+1	4.97	0.35	1.45	59.55	21.51	9.88	0.63	1.40	0.27
12	0	−α	0	5.02	0.36	1.47	59.67	21.69	9.89	0.51	1.13	0.27
13	0	+α	0	5.02	0.35	1.48	59.73	21.62	9.89	0.51	1.12	0.28
14	+1	−1	−1	4.99	0.33	1.45	59.67	21.76	9.96	0.49	1.07	0.28
Centre 1	0	0	0	5.14	0.39	1.47	59.32	21.93	9.91	0.50	1.08	0.26
Centre 2	0	0	0	5.04	0.35	1.49	59.64	21.63	9.94	0.50	1.13	0.28
Centre 3	0	0	0	5.05	0.35	1.46	59.21	21.95	10.17	0.48	1.08	0.26
Centre 4	0	0	0	5.00	0.34	1.46	59.72	21.63	9.91	0.51	1.15	0.28
Centre 5	0	0	0	4.99	0.34	1.48	59.73	21.59	9.97	0.50	1.13	0.27
Centre 6	0	0	0	5.02	0.35	1.45	59.56	21.73	10.04	0.49	1.10	0.26

Table 2

p-Values and variance inflation factor (VIF) for the effects (A: ultrasonic intensity; B: temperature; C: solid/liquid ratio).

Effect	<i>p</i> -value	VIF
A	0.0001	2.41421
B	0.0008	2.41421
C	0.0000	2.41421
AA	0.0012	1.01827
AB	0.6306	1.0
AC	0.6732	1.0
BB	0.0453	1.01827
BC	0.0022	1.0
CC	0.1357	1.01827
ABC	0.2506	1.0
ACC	0.0006	2.41421
BBC	0.0010	2.41421
BCC	0.0006	2.41421

composite design, namely ultrasonic power intensity (A), temperature (B) and solid/liquid ratio (C). A range from 3.3 to 7.7 W/cm² was chosen to fit the limits of the ultrasonic device. The choice of the B variation domain was selected considering the boiling point of hexane, which is 69 °C, and also considering the temperature commonly used during industrial processing, i.e. 55 °C. Moderate temperatures were then chosen in the range 15–65 °C. C was chosen to range from 1/7 solid/liquid to 1/25 considering the cartridge size and the experimental setup. The controlled variables were studied in a multivariate study with 20 experiments as shown in Fig. 2 and Table 1.

3.1.1. Extraction results from the experimental design

Responses varied greatly as a function of the combination of parameter settings. The oil content of rapeseed cake is 23.18 ± 0.88 g oil/100 g, and represents 100% of total oil. Extraction yield ranged from 60.5% to 97% of total oil. Significance and suitability of the design were studied using an analysis of variance (ANOVA). The statistical significance of each effect (including interaction terms, linear, quadratic and cubic effects) was determined using the Fisher test (*F*-value), and the probability *p* (*p*-value) given in Table 2. By considering a confidence level of 95%, the linear effects of the three key variables (A, B, C) as well as the cubic effects (*B* · *C*², *A* · *C*², *T*² · *R* and *A* · *B* · *C*) and all quadratic effects (*A*², *B*² and *C*²) were significant. For these effects, the *p*-value was below 0.05. The results also show that interactions between variables A · B,

A · C and B · C were significant, with a *p*-value lower than 0.05 (Fig. 4). The experimental data obtained from the central composite design allowed the determination of an empirical relationship linking response studied (yield) and key variables involved in the model (in coded units). Thus a third-order polynomial equation was obtained (Eq. (5)) where only the significant effects are shown (*p* < 0.05):

$$Y = 141.5180 - 1.2819 \cdot A - 2.4705 \cdot B - 14.2459 \cdot C + 0.0029 \cdot A^2 + 0.0029 \cdot A \cdot B + 0.1291 \cdot A \cdot C + 0.0198 \cdot B^2 + 0.2231 \cdot B \cdot C + 0.4233 \cdot C^2 - 0.0014 \cdot A \cdot B \cdot C - 0.0041 \cdot A \cdot C^2 + 0.0 \cdot B^2 \cdot C - 0.0041 \cdot B \cdot C^2, \quad (5)$$

with *Y* = extraction yield, *A* = applied ultrasonic power intensity, *B* = temperature, and *C* = solid/liquid ratio.

The quality of the model was evaluated by the correlation coefficient *R*² and also the lack-of-fit value. From ANOVA, *R*² was determined to be about 98.4% and *p*-value of lack-of-fit was greater than 0.05 (non-significant), suggesting that the model was adequate for the observed data at the 95.0% confidence level within the limits of the experimental ranges of the variables. Moreover, the variance inflation factors (VIF) given in Table 2 are relatively low (<4), and suggest that the model prediction capabilities were not degraded.

As shown in Table 1, there was no significant difference in fatty acid profile, which means there was no disruption of C—C bonding, and so no negative influence of the use of US for intensification of rapeseed oil extraction from cake.

3.1.2. Optimization of extraction conditions

Three-dimensional profiles of a multiple non-linear regression model (Fig. 5) illustrate the linear, quadratic and cubic effects together with the interaction effects on the extraction yield given in Table 2. Fig. 5 highlights the behavior of the yield as a function of two variables. In each plot, the third variable is fixed at the central value ("0"). The most influential effects are the linear terms of ultrasonic intensity (A) and solid/liquid ratio (C) as can be seen in Table 2, with a *p*-value very close to zero. As expected, the model confirms that extraction yield clearly increases with temperature (B) and ratio (C) but the ultrasonic power intensity (A) also exerted a very significant positive effect. Influence of cubic terms given in Table 2 is clearly illustrated in Fig. 5a and b by observation of the surface curvatures of the plots. Optimal settings for the maximization of the extraction yield were 7.7 W/cm² for ultrasonic power

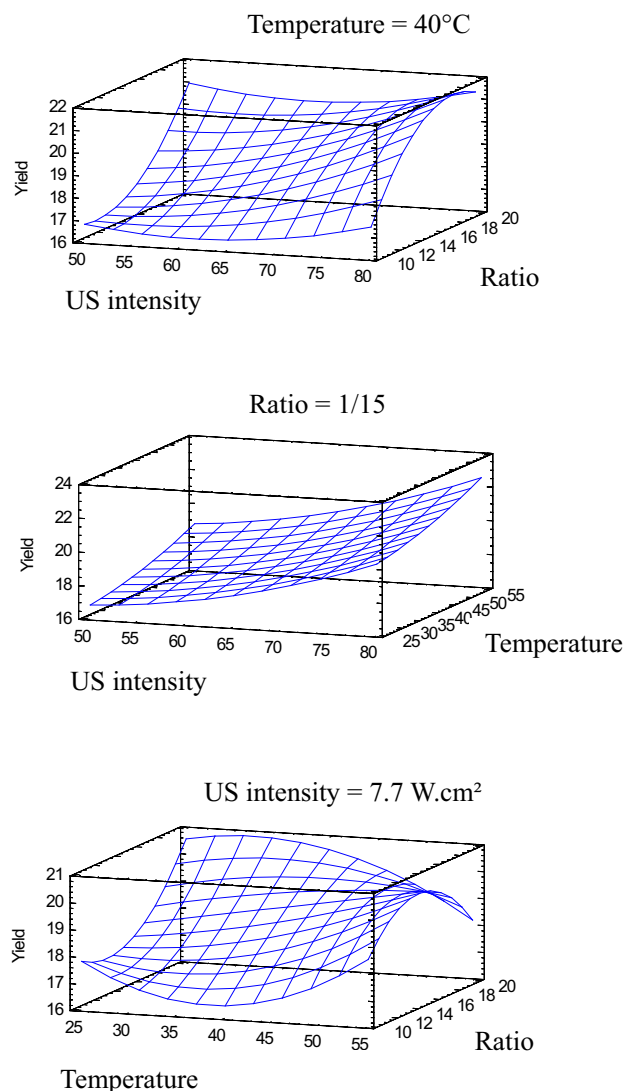


Fig. 5. 3D response area obtained for extraction Yield investigation in the multivariate study. (a) Yield as a function of ultrasonic intensity and sonication time. Temperature is set to 40 °C. (b) Yield as a function of ultrasonic intensity and temperature. Solid/liquid ratio is set to 1/15. (c) Yield as a function of temperature and solid/liquid ratio. Ultrasonic intensity is set to 7.7 W cm².

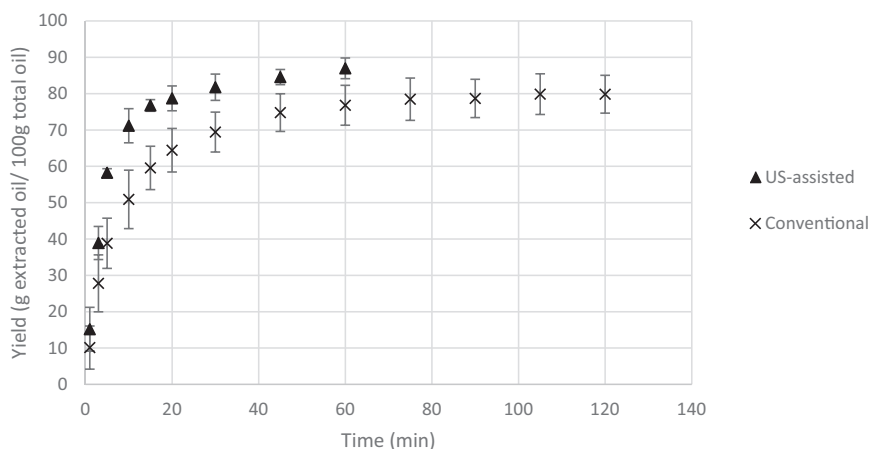


Fig. 6. Extraction kinetics of rapeseed oil from press-cake in optimal conditions, with and without US.

intensity, 40 °C for processing temperature and a solid/liquid ratio of 1/15.

Extraction kinetics in optimum conditions are presented in Fig. 6. We see the influence of the ultrasound treatment on the oil extraction speed; nearly 80% of total oil is extracted in 60 min in conventional conditions, whereas this took only 15 min with US-assisted extraction. The extraction processing time was thus reduced by a factor of 4. The kinetics of extraction were clearly improved, which may be explained by ultrasonic cavitation, since this was the only variable that changed between the two experiments. The use of US is therefore an efficient intensification tool for the extraction of rapeseed oil from press cake.

Table 3 presents the results of the analysis of extracts obtained by conventional and US-assisted extraction in optimal conditions. It can be seen that fatty acid profiles are similar. Concerning oil quality, the acid value is the same, but a slight increase in peroxide value and percentage of conjugated dienes can be observed. The Codex Alimentarius [29] standard for the quality of oils stating a maximum acid value of 4.0 mg KOH/g oil and a maximum peroxide value of 15 meq O₂/kg oil, both extracts are below the limit despite the increase observed for the US-assisted extraction. As illustrated by these results, the use of US on food products can lead to degradation [30] and especially to lipid oxidation [31]. Effects and causes of degradation by US cavitation are presented in Fig. 7. One of the main effects of oxidation is the formation of hydroperoxide owing to the presence of O₂ and the metallic probe [32]. An additional US-assisted extraction was thus performed under a flow of argon to exclude O₂. The peroxide value of the extract was 0.53 meq O₂/kg oil. Working in the absence of O₂ is thus an efficient way to limit and avoid the degradation of the oil during the US-assisted extraction process.

3.2. Multistage cross-current simulation

3.2.1. Experimental results

Three concepts of multistage cross-current extraction (Fig. 8) were implemented. Three stages of conventional extraction (CV) were compared with three stages of ultrasound-assisted extraction (US) and a third mixed configuration with a first stage US followed by two conventional extractions. The experiments were performed in the same extraction conditions: B = 40 °C, C = 1/15, constant stirring, solvent: 100 g hexane (renewed at each stage) and A = 90% for US. Each stage lasted 10 min. This duration is related to the conditions observed at industrial scale. Fig. 9 presents the extraction yields obtained for the three concepts. It can be concluded that a

large part of the total amount of oil was extracted during the first extraction stage, but the US stages significantly extracted more than the CV stage. It can be also observed in Fig. 9 that extraction of cake with only two stages of US-assisted extraction produced a similar yield to that obtained for three CV stages. Concerning the mixed concept, the 2 CV stages were not significantly different from the last two conventional stages, so only one US-assisted extraction stage is insufficient.

In the light of these observations, as only two US stages are sufficient to reach the same extraction performance as three CV stages, the total amount of solvent is likely to be reduced by one third. On the other hand, for the same number of stages, an increase of 6% of oil is obtained. This might allow a simplification of the preparation steps, and also, given that the oil is more valuable than the meal, this result is particularly interesting from an

Table 3

Analyses of extracts obtained in optimal extraction conditions for conventional (CV) and US-assisted (US) extractions.

Fatty acids	CV	US
C16	4.93 ± 0.23	5.00 ± 0.02
C16: 1 n-7	0.36 ± 0.01	0.35 ± 0.00
C18	1.44 ± 0.00	1.46 ± 0.02
C18: 1 n-7	59.70 ± 0.17	59.58 ± 0.19
C18: 2 n-6	21.65 ± 0.13	21.64 ± 0.03
C18: 3 n-3	10.08 ± 0.01	10.01 ± 0.13
C20	0.50 ± 0.01	0.50 ± 0.02
C20: 1 n-9	1.11 ± 0.01	1.09 ± 0.01
C22: 1 n-9	0.26 ± 0.00	0.28 ± 0.00
ΣSFAs	6.87	6.96
ΣMUFAs	61.43	61.30
ΣPUFAs	31.73	31.65
Acid value (mg KOH/g)	3.18 ± 0.06	2.98 ± 0.14
Peroxyde value (meq O ₂ /kg)	8.58 ± 0.76	11.93 ± 1.23
Conjugated dienoic acids (%)	0.12 ± 0.01	0.15 ± 0.02
Extraction yield (g/100 g)	16.6 ± 1.9	21.2 ± 0.7

SFAs: saturated fatty acids, MUFAs: mono unsaturated fatty acids, PUFAs: poly unsaturated fatty acids.

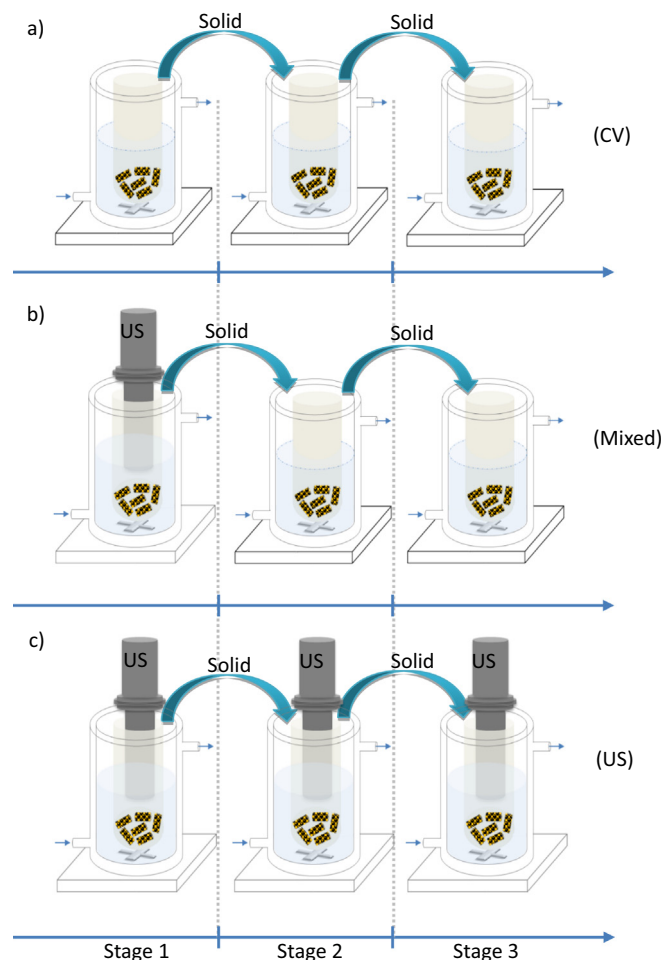


Fig. 8. Multistage cross-current extraction; (a) multistage conventional maceration (CV), (b) multistage extraction combination of (a) and (c) (mixed), (c) multistage maceration, ultrasound-assisted (US).

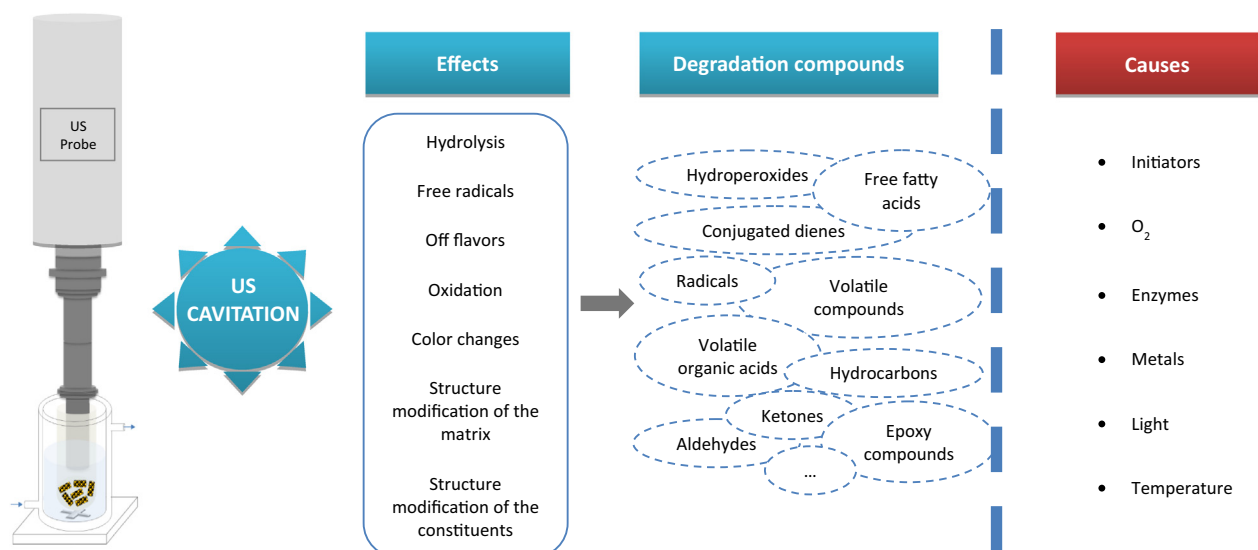


Fig. 7. Effects and causes of oil degradation generated by ultrasound cavitation.

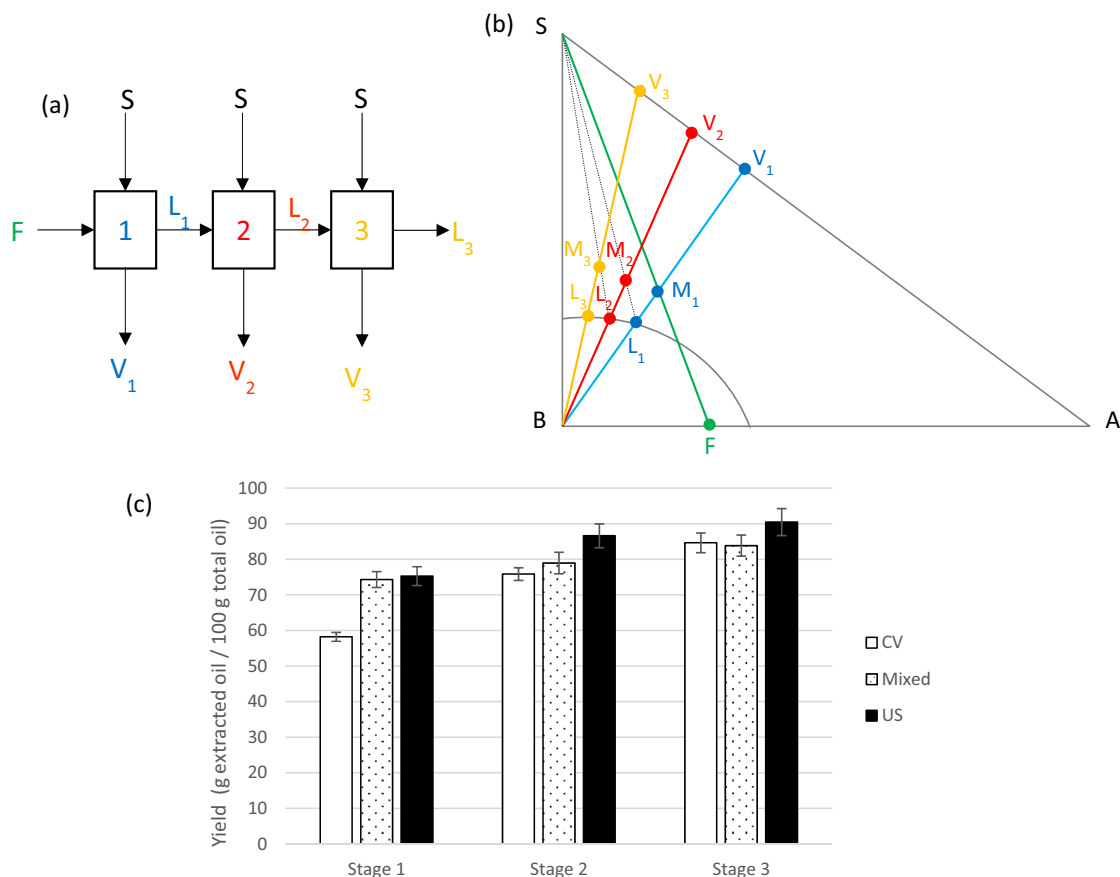


Fig. 9. (a) Multistage extraction, (b) phase diagram of solid/liquid extraction; A: Solute, B: Inert, S: Solvent, (c) cumulated extraction yields in multi-stage cross-current extraction; conventional (CV), under ultrasound (US) and mixed.

industrial point of view, since the use of US can provide a significant gain under the same extraction conditions.

3.2.2. Theoretical considerations on solid-liquid multistage cross-current extraction

Solid/liquid extraction is the separation of a solute (solute, E) from a mixture of insoluble solids (inert, I) by dissolving it in a liquid phase (solvent, S), as can be seen in Fig. 9 [33]. The extraction process can be described by four major steps: (i) solvent diffusion within the solid matrix, (ii) internal solute dissolution in the solvent, (iii) solute diffusion in the solvent within the solid and its migration towards the surface, and (iv) external transfer (by diffusion, but more generally by convection or stirring, etc.) of the solute from the surface of the solid to the external environment [34]. Most of the time, the extraction rate is controlled by the intra-particle diffusion of soluble compounds [35]. The transfer of compounds of interest to the surrounding solvent is accomplished by solvent diffusion into the solid, which results in a concentration gradient of solute between the inner solution near the solid phase (more concentrated) and the liquid phase (less concentrated). At the end of the operation, the system reaches equilibrium and the diffusion is near-nil. In the case of a multistage cross-current extraction performed in this study (Fig. 8), at the end of each stage, the liquid phase constituting the extract (E + S) is recovered and the solvent (S) is renewed. The diffusion therefore continues until complete exhaustion of the solid phase. At the end of this process, the exhausted solid, called inert (I) contains a very limited amount of solute [36], the system reaches equilibrium and the diffusion is near-nil. In the case of a multistage cross-current extraction, the liquid phase making up the extract (E + S) is recovered, and the

solvent (S) is renewed at the end of each stage; the diffusion of the solute continues until almost complete exhaustion of the solid phase. The phase diagram presented in Fig. 10 was constructed for CV and US stages in order to understand the extraction process. Each cross-current extraction stands for one stage (both phases are in thermodynamic equilibrium). The overflow ($V = E + S$) was recovered and then quantified and the underflow ($L = E + I + S$) composed of exhausted inert solid and the solvent adsorbed was recovered to undergo a further stage of extraction with renewed solvent. Equilibrium of extraction is represented by a right-angled triangle (Fig. 10), where each corner represents a pure substance, S (100% of solvent), E (100% of solute) and I (100% of inert). Each side of the triangle stands for a binary mixture, and each point inside the triangle is a ternary mixture. The material balance of the first stage is expressed as $F + S = L_1 + V_1 = M$. The quantity of feed ($F = E + I$) and solvent (S) were fixed, so point M can be placed on the phase triangle according to Eq. (6)[37]:

$$F \cdot \overline{FM} = S \cdot \overline{SM} \rightarrow \overline{FM} = F + S \cdot \frac{\overline{SM}}{\overline{FS}} \quad (6)$$

The equilibrium (I, L_1, M_1, V_1) is then displaced and replaced by the equilibrium (I, L_2, M_2, V_2) for stage 2 and then by the equilibrium (I, L_3, M_3, V_3) for stage 3.

3.3. Influence of US on the extraction and on rapeseed cake structure

As the extraction is carried out on cake, i.e. previously pressed seeds, the matrix is not homogeneous, and its surface is very rough. Fig. 11 shows the appearance of the cake after conventional (Fig. 10a) and US-assisted (Fig. 10c) solvent extractions. It can be

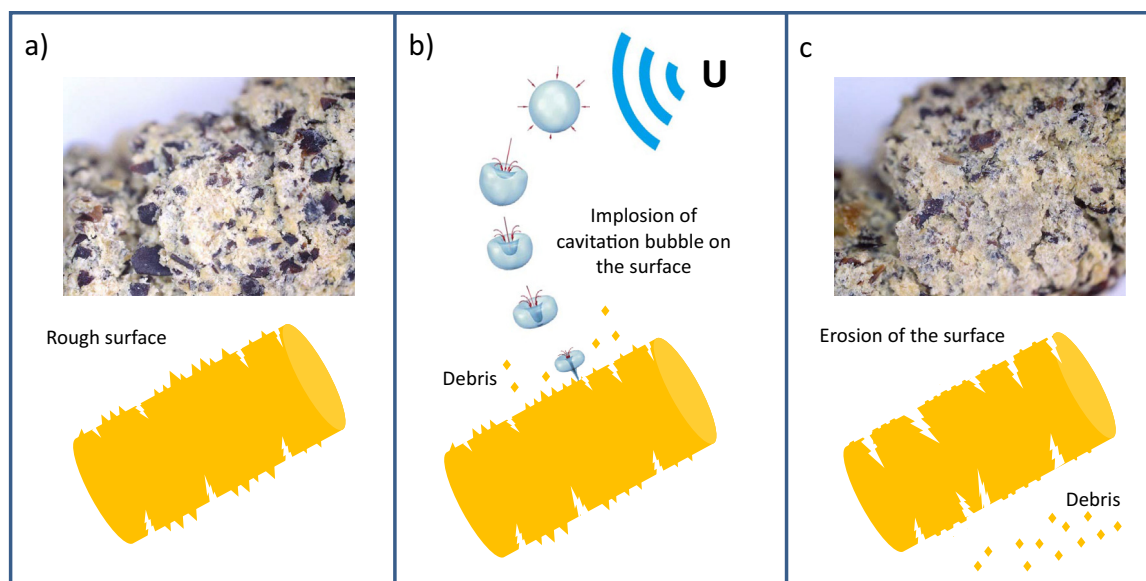


Fig. 10. Impact of US on press-cake ((a) Cake after conventional solvent extraction. (b) Hypothesis of the degradation phenomenon of the press-cake by the implosion of cavitation bubble generated by US in the solvent. (c) Cake after US-assisted solvent extraction).

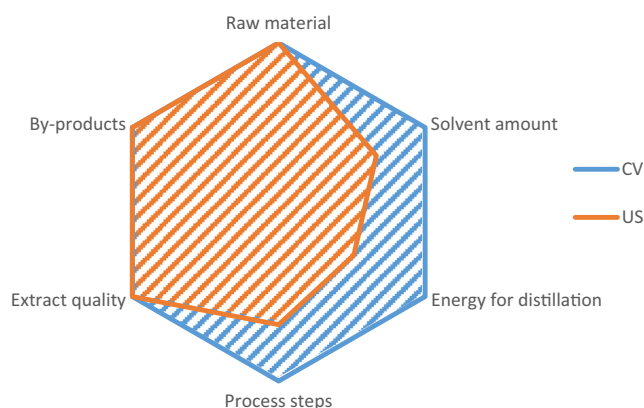


Fig. 11. Eco-footprint: conventional process (CV) vs US-assisted process (US).

observed that after conventional extraction the surface of the cake presents a ruggedness that is no longer visible on the US-treated feed. The formation of debris (Fig. 10c) can also be noted. These changes highlight the physical action of the ultrasound on the matrix. These effects are most probably due to the action of US cavitation at the surface of the cake as shown in Fig. 10b. The cavitation bubbles formed in the solvent by the action of ultrasound implode at the surface of the matrix. As the exchange surface between the solvent and the matrix is increased, this likely accelerates the transfers. It will also possibly increase the solvent retention in the meal.

3.4. Cost, cleanliness and up-scaling

On the model of Leseurre et al. [41], Fig. 11 gives a preliminary assessment of a possible reduction of the global environmental impact of the use of US in the rapeseed oil extraction process. It takes into account the raw material, the amount of by-products, the quality of the extract, the number of extraction stages, the solvent quantity and the energy required for solvent distillation [42,43].

On the basis of what is obtained at lab scale, there is no change of raw material and by-products, and as described previously, no significant degradation of the extract is observed. Nevertheless, the residual oil content can be reduced along with the damage to proteins during the cooking step considering a more efficient extraction. Moreover, the use of ultrasound allows one less stage of extraction compared with conventional processing, which has an impact on the amount of solvent to be used for extraction and then to be evaporated.

Considering all these aspects, we note that the use of US compared with conventional rapeseed oil extraction can allow a reduction of around 30% in the eco-footprint of the process.

Table 4 shows a preliminary estimation of the consumption of the operations occurring during the process using conventional hexane extraction compared with US-assisted extraction considering the results of the lab part and extended to 1 tonne of seeds.

The conventional rapeseed crushing process (covering both preparation and extraction steps) requires an overall heat consumption of around 580 MJ per tonne of crushed seeds. This energy, provided by heated steam, represents an overall consumption of 270 kg of steam per tonne of crushed seeds [38]. The assessment of the theoretical heat required at the different stages of crushing must take into account the specific heats of hexane, seeds, oilcake, meal and oil as well as all processing temperatures. The data required for the calculations are described by Sicaire et al. [39].

As can be seen in Table 4, there was no difference between conventional and US-assisted extraction in energy consumption for the preparation step, as no solvent was used, and the US treatment was applied during the extraction step.

Regarding the solvent extraction step, considering results presented previously, a reduction of one third of total hexane used for conventional extraction is taken for the calculation of the energy consumption of the US-assisted process.

The total amount of energy assessed for the distillation step is assessed around 70 MJ/t for US-assisted extraction instead of 139 MJ/t with conventional extraction, which represents a reduction of nearly 50%. As less energy was recovered from the desolventizer, the overall energy consumption of the whole process (preparation + extraction) was 563 MJ/t for the US-assisted process

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Table 4

Energy consumption in total extraction process for 1 tonne of seeds: conventional (CV) vs US-treated (US).

Step	Material	Change	Heat required (MJ/t)		Steam consumption (kg/t)	
			CV	US	CV	US
Conditionning	Seeds	T°: 15 → 60 °C	78	78	36.6	36.6
Cooking	Flakes	T°: 55 → 105 °C	110	110	53.4	53.4
		Vaporization of 30 kg of water	66	66	32.2	32.2
	Air (dry) for drying	T°: 20 → 100 °C	15	15	7.2	7.2
Total preparation			270.0	270	129	129
Desolventization	Meal	T°: 55 → 105 °C	52	52	26.1	26.1
	Solvent	T°: 55 → 69 °C	8	8	3.9	3.9
		Vaporization	75	75	37.6	37.6
	Steam	Sparged	77	77	27.5	27.5
		Condensed	38	38	13.5	13.5
Distillation	Miscella	T°: 55 → 69 °C	8	5	2.7	2
	Oil	T°: 69 °C → 110 °C	10	10	3.6	3.6
	Solvent	Vaporization	122	56	58.9	27.1
Total distillation			139.0	71.3	65.2	32.6
Heat recovered from the gas from the DT			−104.3	−53.5	−48.9	−24.5
Total extraction			284	267	125	117
Losses (5%)			28	27	12.7	12.3
Total preparation + extraction			581	563	267	258

instead of 581 MJ/t for the conventional process. This represents 258 kg steam/t instead of 267 kg steam/t for the conventional process. However, the use of US in the extraction process gave rise to a slight reduction of the energy consumption which could lead to a reduction of the costs implied in energy production.

Considering the oil yields obtained during the three stages with and without US, the total gain in additional oil is evaluated at around 6%, which represents around 13.5 kg of oil per ton of seeds. This additional oil generates an equivalent loss in the amount of cake. As the price of oil is around 900 EUR/t [40] and the price of cake around 350 EUR/t [40], a gain of 7.4 EUR/t seeds can be made.

In this study, the positive impact of US on extraction has been studied at lab scale on a matrix suspended inside the solvent which is different from what happens in industry. Moreover, as the solid/liquid ratio is quite different from what commonly occurs in counter current industrial extractors, the impact in industrial conditions needs to be further investigated, as it might clearly be beneficial to the industry.

4. Conclusion

This work shows the high potential of US-assisted extraction for the vegetable oil industry. A multivariate study allowed the definition of optimal parameters for US-assisted extraction in order to maximize lipid yield while reducing solvent consumption and extraction time. In comparison with conventional extraction, the multistage cross-current US-assisted extraction showed that the use of US was very efficient in intensifying the process by reducing the number of stages (two stages with US equivalent to three stages with conventional processing), thereby reducing the amount of solvent and the extraction time, as well as allowing a gain in extracted oil. It also shows that it is likely to have a positive impact on the energy consumption, economical model and eco-footprint of the global process. These are preliminary results on the use of US that need to be further investigated under the conditions of a countercurrent extractor with a liquid-to-solid ratio of around 1.5.

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