Food Engineering Reviews (2021) 13:148–160
https://doi.org/10.1007/s12393-020-09274-5

Entrained Oil Loss Reduction and Gum Yield Enhancement by Megasonic-Assisted Degumming

Mohamed A. Fouad M. Gaber[1,2] · Pablo Juliano[2] · Maged Peter Mansour[2] · Francisco J. Tujillo[1]

Received: 10 January 2020 / Accepted: 10 December 2020 / Published online: 25 January 2021

Abstract

The degumming step in seed oil refining is essential to avoid deleterious oxidative reactions caused by the presence of gums, which may impact on the refined oil stability and shelf life. However, conventional degumming techniques produce gums with significant amounts of entrained oil that is not recovered. The present work evaluated the application of megasonic waves during acid degumming of canola, soybean, and sunflower oils to recover entrained oil in the gums and increase the gum yield. Oil-acid mixing options were explored at selected temperatures and times, with and without a megasonic treatment (2 MHz, 340 W, 81.6 kJ/kg, 20 min). Megasonics best enhanced the acid degumming of canola oil after a one-pass ultra-turrax shearing for 3 min at 40 °C. Such megasonic-assisted acid degumming conditions were effective in reducing residual phosphorus content in both canola and soybean oil by 54.3% and 67.0%, respectively, but less effective in sunflower oil (39%, relative to the non-megasonic degumming). The megasonic treatment also reduced the loss of gum-entrained canola, soybean, and sunflower oil by 50.0%, 35.0%, and 28.4%, respectively. Furthermore, the gum yield (% w/w oil, dry basis) obtained from canola, soybean, and sunflower oil degumming was also enhanced by 22.7%, 18.7%, and 16.0%, respectively, compared with the control. The three megasonic-assisted degummed oils met industry standard specifications for refined seed oil, including free fatty acids, chlorophyll, peroxide, and phosphorus content. Income from additional oil and gum recovery, resulting from megasonics, was initially indicative of the economic viability of the process. Further cost benefit analysis is required, from pilot to industrial scale process data, to validate economic viability.

Keywords Acid degumming · Megasonic · Phospholipids · Gum recovery · Entrained oil recovery

Introduction

Refined seed oil is the largest segment in the edible oil sector. The major oilseed crops grown worldwide are canola, sunflower, and soybean [1, 2]. The global demand for refined canola, soybean, and sunflower oil has been estimated to be 160, 130, and 150 million tonnes, respectively, in 2019/2020. The degumming process in oil refining produces large amounts of gums [3]. Crude gums are complex mixtures comprising phospholipids (mainly lecithin), oil, and minor amounts of other constituents such as phyto-glycolipids, phytosterols, tocopherols, and fatty acids [4, 5]. During oil refining, gums separated during degumming retain significant amounts of oil, making refining inefficient due to oil losses. Generally, crude gums containing residual oil are blended with the hexane de-oiled seed meal to sell it as an animal feed ingredient. The retained oil in gums is considered to add calorific value to the meal. Another option is to de-oil and purify the gum for lecithin production. Lecithin, typically a major co-product of soybean degumming, is used in many ingredient applications as emulsifier, lubricant, antioxidant, and/or flavour protector [4, 6–9]. However, lecithin obtained from refining processes of canola and sunflower oil is rarely value-captured and transformed as an ingredient for food applications. Therefore, there are economic benefits from recovering both oil and gums during refining. Furthermore, improving seed oil degumming efficiencies can open opportunities to (a) reduce oil losses, (b) reduce the de-oiling requirements for soybean lecithin production, and/or (c) potentially produce canola and sunflower lecithin.

✉ Pablo Juliano
Pablo.Juliano@csiro.au

[1] School of Chemical Engineering, The University of New South Wales, Sydney, NSW, Australia

[2] CSIRO Agriculture and Food, Melbourne, VIC, Australia

The industrial process for extraction of seed oils involves mechanical pressing, often followed by solvent extraction using hexane. The details of the seed oil extraction are discussed elsewhere [10–16]. The oils obtained after both mechanical pressing and hexane extraction, generally termed "crude oil," which are degummed to remove phospholipids and impurities. Degumming is achieved by high shear mixing of the crude oil with different aqueous reagents, depending on the type of phospholipids. Water degumming removes hydratable phospholipids, but it does not remove non-hydratable phospholipids. Therefore, if there are high amounts of non-hydratable phospholipids present in the crude oil, degumming using phosphoric or citric acid is needed to facilitate their removal by converting the non-hydratable phospholipids into hydratable phospholipids [13, 17].

In industry, the phospholipids removal in the crude oil is followed by measuring the elemental phosphorus content (mg/kg) in the oil, which is used as an indicator of degumming efficiency. Currently, the gum separation process is inefficient, retaining up to 1% of the expeller oil in the separated gums after degumming and centrifugation. Recovery of the gum entrained oil represents a significant oil yield increase for the refining process [18]. For example, a typical refinery processing 50,000–100,000 tonnes per year of crude oil may lose between USD 200,000–300,000 worth of oil entrained in gums. At present, the reduction of oil entrained in gums has received little attention in the literature. The application of physical methods for oil recovery has been mainly focused on crude oil extraction processes [19, 20] rather than in refining processes. Among the physical methods employed for oil recovery, the application of high frequency ultrasound, or megasonics, is attracting interest in various industries as a safe and gentle separation method for crude oil recovery [21].

Megasonic separations make use of two physical mechanisms: (i) microstreaming, which is induced by the formation of stable cavitation bubbles and promotes the mass transfer of substances between phases, and (ii) the trapping of particles or droplets in the nodal or anti-nodal planes of acoustic standing waves [22]. These mechanisms promote oil droplet coalescence and solid material agglomeration at the high pressure and low pressure antinodal nodal planes, respectively [23]. Therefore, the technology described by the present work may be incorporated into industrial degumming processes to enhance not only the separation and recovery of refined oil but also semi-solid gums following solid material agglomeration.

The megasonic-assisted oil recovery of oil-bearing biomass including avocado, canola, coconut, olive, and palm has been demonstrated in several water-based oil extraction processes [15, 21, 22, 24–26]. The authors have previously demonstrated that a megasonic aqueous-based intervention up to 45% increased the recovery of canola oil from canola cake by applying a treatment of 2 MHz and 80 °C for 30 min to the canola cake dispersed in water [15]. However, studies addressing gum recovery are unprecedented in the literature, and therefore worthy of exploration when a degumming process is incorporated with a megasonic intervention.

The application of megasonics during acid degumming has also shown to have a significant impact in removing phospholipids from canola oil [27]. Among various conditions studied, a megasonic treatment of 2 MHz at 40 °C for 20 min in the pre-sheared oil-acid mixture has shown to double the reduction of phosphorus in canola oil during phosphoric acid degumming. However, further investigations are required to demonstrate the benefits of megasonics during soybean and sunflower oil refining. Furthermore, little is understood about the effect of applying various oil-acid mixing techniques followed by a megasonic intervention on phospholipid removal.

The aim of this study was to explore the application of megasonic treatments during degumming in view of its potential to increase (a) the removal of phospholipids in canola oil when using various degumming acid-oil mixing techniques, (b) the removal of phospholipids in soybean and sunflower oil, (c) the recovery of entrained oil from the gums in all tested oils, and (d) the amount of crude gums separated from each refined oil, when compared with a non-megasonic degumming process.

Materials and Methods

Materials

Crude expeller soybean and sunflower oils were obtained from GrainCorp Foods (Victoria, Australia). The other two crude canola oils were obtained from the expeller pressing of canola seeds and from the hexane extraction from the canola cake after pressing (Cargill Company, Victoria, Australia). The phosphorus and free fatty acids (FFA) content of the crude soybean, canola and sunflower oils were quantified by the respective suppliers and are shown in Table 1.

Experimental Design

To study the effect of non-megasonic and megasonic treatments on the acid degumming of crude canola, soybean, and sunflower oils, a set of five experiments were designed as shown in Table 2. Experiment 1 evaluated the effect of three phosphoric acid degumming mixing techniques on the degummed canola oil residual phosphorus content, without and with a megasonic treatment, at 40 °C and 80 °C (details in "Three Mixing Techniques"). Experiment 2 studied the effect of three high shear mixing times (3 min, 6 min, and 10 min) using the ultra-turrax one-pass method on the

Table 1 Phosphorus and free fatty acid composition in the seed crude oils as provided by the suppliers

Composition parameter	Canola oil I[1]	Canola oil II[2]	Soybean oil[1]	Sunflower[1]
Phosphorus content (mg/kg crude oil)	400 ± 15	550 ± 20	750 ± 40	300 ± 20
FFA (g oleic acid, % crude oil basis)	1.4 ± 0.2	1.7 ± 0.3	2.8 ± 0.4	2.0 ± 0.3
Peroxide value (meq O_2/kg)	14.2 ± 1.8	——	15.4 ± 2.4	15.9 ± 1.8
Chlorophyll (mg/kg)	12.5 ± 1.4	——-	11.5 ± 0.9	12.0 ± 1.2

[1]Crude oils obtained from expeller pressing

[2]Crude canola oil obtained from hexane extraction from the canola cake after pressing

degummed canola oil residual phosphorus content. After Experiment 1 and 2 on canola oil, the most efficient mixing technique and mixing time were selected for subsequent experiments that also included soybean and sunflower oil. Experiment 3 studied the effect of non-megasonic and megasonic-assisted degumming on the residual phosphorus content of canola, soybean, and sunflower degummed oils. Experiment 4 investigated the effect of non-megasonic and megasonic-assisted degumming on oil and gum recoveries in the three oils. The quality parameters of the control and megasonic degummed oils were studied in Experiment 5. All experiments were performed in triplicate.

Methods

Each crude oil was mixed intensively with a motor driven impeller (500 r.p.m.) inside an oil tank to obtain a homogenous sample, and a 600-g portion was taken for further mixing . The crude oil samples destined for control and megasonic-assisted degumming were equally divided into 6 tubes (100 g each). The phosphorus content in each tube was verified in triplicate prior to degumming with and without megasonic treatment ("Acid Degumming with Phosphoric Acid" and "Three Mixing Techniques"), corroborating the original supplier crude oil values (Table 1).

Acid Degumming with Phosphoric Acid

Acid degumming of 100 g of crude oil was carried out by heating to 80 °C, followed by the addition of water at 2% (w/w crude oil) and phosphoric acid (concentration 14%, v/v) at 10% (v/w crude oil). The crude oil and reagents were then subjected to the selected mixing methods (see "Three Mixing Techniques"). The non-megasonic (control) and megasonic treated samples were then heated to a selected temperature depending on the experiment (see Table 2) and subjected to megasonic or non-megasonic control treatments as described in section ("Megasonic Treatment Process"). Non-sonicated and sonicated samples were centrifuged (Centrifuge J6-MI, Beckman Coulter, Pasadena, United States of America) at a speed of 4000 × *g* force for 20 min at 20 °C to separate the aqueous phase and gums from the degummed oil phase.

Three Mixing Techniques

After the water and phosphoric acid addition into the crude oil, three mixing techniques were tested to determine which mixing method achieved the highest phospholipid removal. The first mixing technique involved *shaking* by hand (gentle mixing) for 3 min, and subsequent phospholipid evaluation without and with megasonic treatment. The second mixing technique involved a one-pass high shear mixing with an Ultra-Turrax probe (Ultra-Turrax-T25, Janke & Kunkel, Germany) for 3 min at 9100 r.p.m (henceforth ultra-turrax one-pass), and subsequent phospholipid evaluation without and with megasonic treatment. The third technique involved repeating the second mixing technique, treating the emulsion with or without megasonics, and applying another high shear mixing treatment of 3 min followed by another non-megasonic or megasonic treatment and subsequent phospholipid evaluation. Henceforth, the third technique is referred to as ultra-turrax two-passes. Table 2 shows the conditions used for two experiments where the three techniques are compared (Experiment 1) and the more adequate technique was compared at 3 mixing times (Experiment 2) without and with megasonics.

Megasonic Treatment Process

Acid degummed samples were subjected to the megasonic treatment of 2 MHz (340 W, 81.6 kJ/kg) for 20 min based on our preliminary study [27], by using the temperature conditions described in Table 2. The degummed oil-reagent mixtures were placed in a 120-mL glass test tube inside the megasonic reactor for treatment as shown in Fig. 1. The megasonic reactor consisted of a rectangular stainless-steel vessel of 40 × 21 × 20 cm containing a transducer plate (16 × 16 × 3.2 cm), (Sonosys, Neuenburg, Germany). Transducer cooling was required for operations beyond 40 °C and achieved by recirculating cooled water through a jacket (H) around the transducer plate (G). The reactor was filled with water, set at test temperatures and controlled within ± 2 °C by a thermocouple controlled electrical heater (B, E).

Table 2 Non-megasonic and megasonic experiments examining various parameters during acid degumming

Experiment	Degumming method	Processing parameters[1]	Variables	Degumming parameters	Statistical design
1 Three mixing techniques for degumming	Acid degumming (phosphoric acid)	Canola oil I[2] *f* (2 MHz) *t* (20 min) mixing time (3 min) *P* = 340 W Es = 81.6 (kJ/kg)	Mixing (shaking, ultra-turrax one-pass, ultra-turrax two-passes), *T* (40 and 80 °C) Megasonics (OFF, ON)	Phospholipids content	Factorial design 3 × 3 × 2 3 replicates (ANOVA)
2 Oil-acid mixing time	Acid degumming (phosphoric acid)	Canola oil I[2] Mixing: ultra-turrax 1 pass *f* (2 MHz) *t* (20 min) *T* (40 °C) *P* = 340 W Es = 81.6 (kJ/kg)	Mixing time (3 min, 6 min, 10 min) Megasonics (OFF, ON)	Phospholipids content	Factorial design 3 × 2 3 replicates (ANOVA)
3 Crude oil comparison	Acid degumming (phosphoric acid)	*f* (2 MHz) Mixing: ultra-turrax 1 pass mixing time (3 min) *t* (20 min) *T* (40 °C) P = 340 W Es = 81.6 (kJ/kg)	Canola I[2], canola II[3], soybean[2] and sunflower[2] oil Megasonics (OFF, ON)	Phospholipids content	Factorial design 4 × 2 3 replicates (ANOVA)
4 Entrained oils and gums recovery	Acid degumming (phosphoric acid)	*f* (2 MHz) Mixing: ultra-turrax 1 pass mixing time (3 min) *t* (20 min) *T* (40 °C) *P* = 340 W Es = 81.6 (kJ/kg)	Canola I[2], canola II[3], soybean[2] and sunflower[2] oil Megasonics (OFF, ON)	Recovered oil, and gum yield	Factorial design 4 × 2 3 replicates (ANOVA)
5 Other oil quality parameters	Acid degumming (phosphoric acid)	*f* (2 MHz) Mixing: ultra-turrax 1 pass mixing time (3 min) *t* (20 min) *T* (40 °C) *P* = 340 W Es = 81.6 (kJ/kg)	Canola I[2], canola II[3], soybean[2] and sunflower[2] oil Megasonics (OFF, ON)	FFA, PV, and chlorophyll content	Factorial design 4 × 2 3 replicates (ANOVA)

FFA free fatty acids, *PV* peroxide value

[1]Where *f* is a frequency (MHz), *T* is a temperature (°C), *t* is time (min), and Es is specific energy

[2]Crude oils obtained from expeller pressing

[3]Crude canola oil obtained from hexane extraction from the residual canola cake after pressing

FFA (free fatty acids), and PV (peroxide value)

Gravimetric Quantification of Gum Yield and Entrained Oil in Gums

A gravimetric procedure was developed to determine the amount of entrained oil that remained within the gums after centrifugation. Firstly, centrifuged gums were separated from the bulk refined oil by vacuum filtration through a filter paper (570 mm). Secondly, the gums remaining in the filter paper were quantified gravimetrically for gum yield determination. Thirdly, the residual entrained oil in the vacuum filtrated gums was determined by the following three methods of extraction (see "Method I: Determination of Retained Oil in Gums Using Hexane Extraction (Wet Gum Basis)", "Method II: Determination of Retained Oil in Gums Using Acetone Extraction (Wet Gum Basis)", and "Method III: Determination of Retained Oil in Gums Using Hexane Extraction (Dry Gum Basis)").

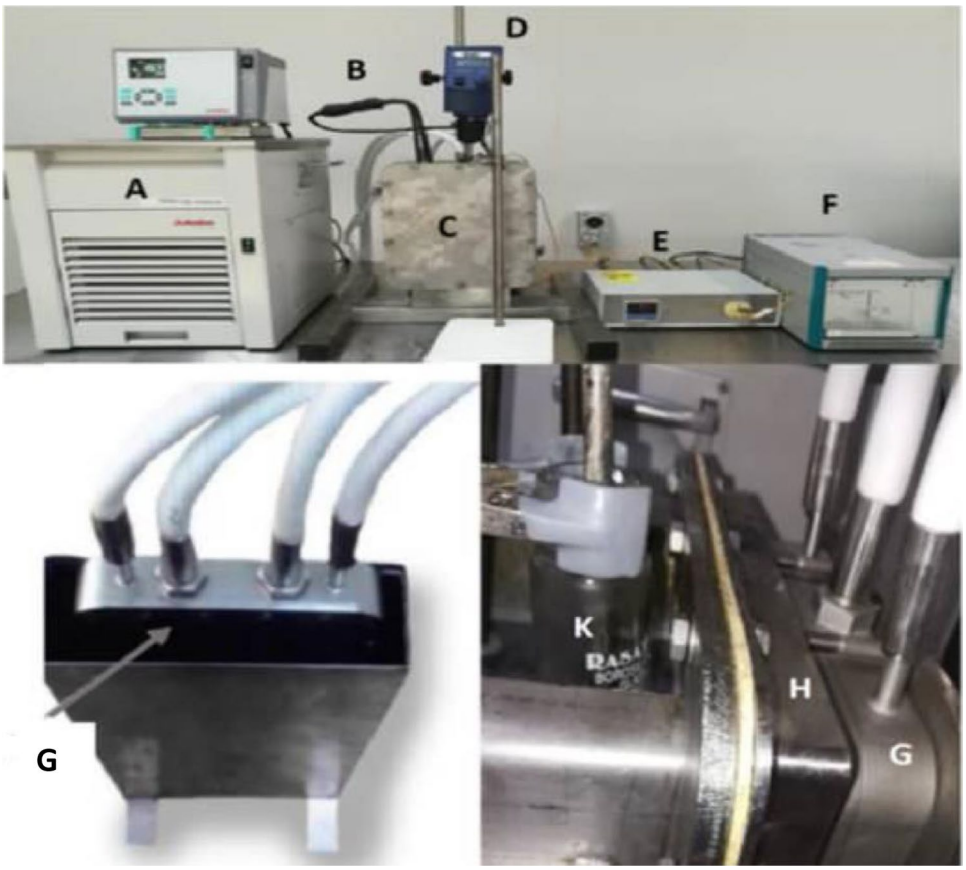

Fig. 1 Experimental setup for non-megasonic and megasonic-assisted degumming. A: cooling system; B: electrical heater; C: megasonic reactor, D: electrical stirrer; E: temperature control; F: generator; G: transducer plate; H: cooling jacket; K: glass container

Method I: Determination of Entrained Oil in Gums Using Hexane Extraction (Wet Gum Basis) Hexane extraction was performed by mixing 20 mL of hexane with the wet filtered gums (containing the entrained oil) in a 50-mL centrifuge (falcon) tube. The tube was heated for 10 min in a 60 °C water bath and then centrifuged (Centrifuge J6-MI, Beckman Coulter, Pasadena, USA) at 3000 × *g* for 20 min at 25 °C. The hexane layer was transferred into a pre-weighed 50-mL centrifuge tube for overnight drying in a centrifugal vacuum solvent evaporator (SpeedVac, Savant SC250EXP, Thermo Scientific, Australia) with a refrigerated vapour trap (Savant RVT4104, Thermo Scientific, Australia) and weighed again to determine the amount of residual unreleased oil, expressed on a wet gum basis [15, 28, 29].

Method II: Determination of Entrained Oil in Gums Using Acetone Extraction (Wet Gum Basis) This is a similar procedure to Method I, which follows the industrial standard method for determining the oil content in gums [29]. The extraction was carried out with cold acetone at 0 °C on a wet gum–solvent ratio of 1:1.5 w/v, with continuous shaking for 30 min. After resting for 15 min the extract was separated by filtration. The gums were extracted twice, and the extracts were pooled. The oil was recovered by overnight evaporation of the pooled acetone extracts using the Speedvac concentrator at 40 °C, and the residual unreleased oil in gums was then determined gravimetrically [29].

Method III: Determination of Entrained Oil in Gums using Hexane Extraction (Dry Gum Basis) The water content in the wet gums may vary as the gums may show different water binding properties, which may add variations in the gum retained oil assessment. This method ensured that water in the gums was removed before using hexane to extract the oil from the gum. This procedure followed Method I, except that wet gums were freeze-dried before the residual oil was hexane extracted for oil quantification as explained in "Method I: Determination of Retained Oil in Gums Using Hexane Extraction (Wet Gum Basis)." The amount of residual unreleased oil was expressed on a dry gum basis.

Measurement of Oil Quality Parameters

Phosphorus content: The phosphorus content in the oil is a surrogate measure of the amount of phospholipid gums

in the oil and, as mentioned above, is used as an indicator of degumming efficiency. The phosphorus content in the oil was measured using the nephelometric phosphorus determination method (AOCS official method Ca 19–86) (Wang and Zhou 2017). The oil sample (8 g) was placed into a 50-mL volumetric flask and mixed with acetone. Turbidity was measured in the diluted mixture by using the standard turbidity range (0.02, 2, 20, and 100 Nephelometric Turbidity unit (NTU)). The measured turbidity was used to calculate the phosphorus level using the following equation as referenced in the AOCS method (Wang and Zhou 2017).

$$\text{Phosphorus content} = (5.32 * \text{turbidity}) + 3.38 \quad (1)$$

The method was also cross-checked and validated with a reference method on phosphorus content (Firestone and Society 1998) by analysing 10 samples of non-megasonic and megasonic degummed oil.

Free fatty acids and peroxide value: The determination of the free fatty acids and peroxide value was carried out using the procedures given by IUPAC "Standard methods for the analysis of oils, fats and derivatives" (No's 2.501, 5.501, 2.421) [30].

Chlorophyll content: The chlorophyll content was determined by the method described by Barthet and Daun [31] using the absorption spectra at 470 nm and 670 nm according to the following equations:

$$\text{Chlorophyll (ppm)} = (A * 106)/613 * 100 * L \quad (2)$$

where A is the absorbance and L is the spectrophotometer cell thickness (10 mm).

Statistical Analysis

All experiments were carried out in triplicate. Results are expressed as mean value ± standard deviation. Table 2 indicate the variables used for the factorial designs used for each experiment. The differences in mean values between samples were assessed with the Minitab 18 software (Minitab Inc., PA, USA). An analysis of variance (ANOVA) at the 95% confidence level was applied to determine the difference between treatments for each degumming parameter (see Table 2).

Results and Discussion

Effect of Mixing Techniques and Megasonics on Canola Oil Degumming Efficiency

The phosphorus removal efficiency of three mixing methods, shaking, ultra-turrax one-pass, and ultra-turrax two-passes, was compared during phosphoric acid degumming, without and with a megasonic application in the oil and phosphoric acid mixture (Table 2, Experiment 1). The ultra-turrax one-pass mixing method gave the greatest reduction of phosphorus content at both degumming temperatures of 40 °C and 80 °C (Fig. 2). After applying the ultra-turrax one-pass mixing,

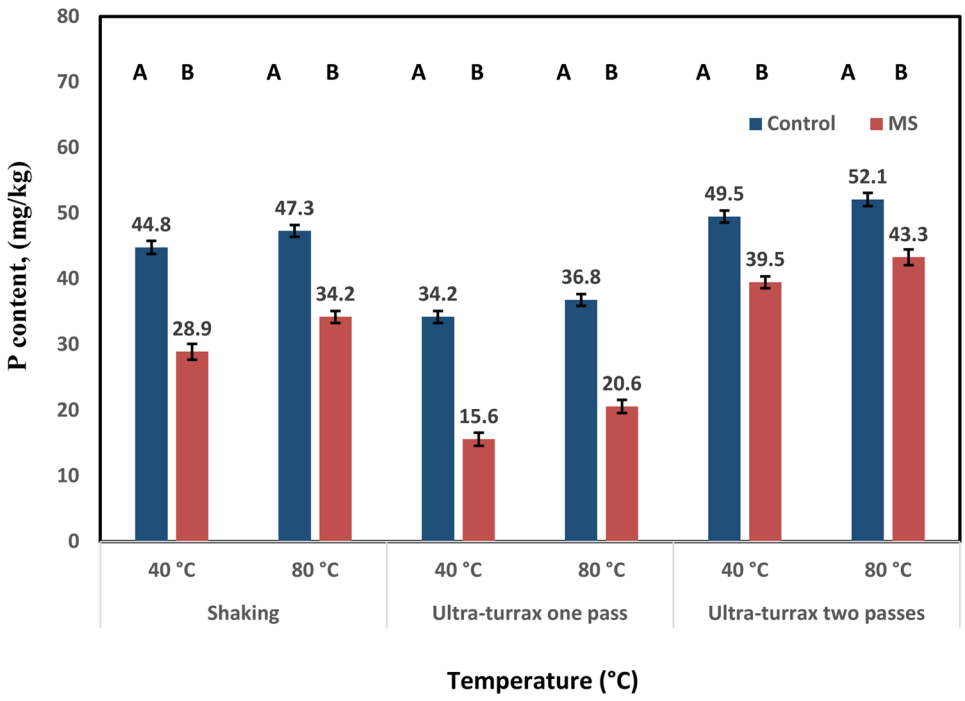

Fig. 2 Three mixing techniques applied for phosphoric acid degumming in canola oil and degumming efficiency as indicated by the residual phosphorus content. Megasonic (MS) treatment was carried out at 2 MHz, 40 °C, and 20 min. The control was a non-megasonic treatment (ultrasound OFF). Different uppercase letters indicate significant ($p < 0.05$) differences between control and MS at a selected temperature for each method of mixing

the megasonic treatment significantly ($p < 0.05$) reduced the phosphorus content in the canola oil by 35.5% and 27.7% at 40 °C and 80 °C, respectively , compared with their respective non-megasonic controls. The megasonic treatment therefore performed better in reducing phosphorus content in the oil when degumming using the ultra-turrax one- pass method at 40 °C, compared with 80 °C. This was also the case for the other two mixing methods when operating at 40 °C (Fig. 2).

As expected, the non-megasonic ultra-turrax one-pass mixing method showed a superior phosphorus removal efficiency than the shaking method. However, the shaking method followed by a megasonic application further reduced the residual phosphorus content to levels below the non-megasonic ultra-turrax one- pass mixing method (Fig. 2). This indicates that only shaking the oil and phosphoric acid followed by a megasonic treatment may reduce the need for shearing during degumming.

The ultra-turrax two-pass mixing was the least effective mixing method, producing oil with the highest phosphorus content on both non-megasonic and megasonic samples, both at 40 °C and 80 °C. This is because the second shear mixing re-dispersed some of the phospholipids gums and increased the phosphorus content in the degummed oil. Because of the superior phosphorus reduction achieved with the ultra-turrax one-pass at 40 °C followed by the megasonic treatment, this mixing method was used in all subsequent experiments.

Effect of Oil-Acid Mixing Time and Megasonics on Canola Oil Degumming Efficiency

The degumming efficiency was examined at 40 °C after varying three canola oil-phosphoric acid mixing times (3, 6, and 10 min) by using the ultra-turrax one-pass method, without and with a subsequent megasonic treatment (Table 2, Experiment 2). Figure 3 shows that the mixing time had no significant effect ($p > 0.05$) on the residual phosphorus content reduction of the degummed oil for all tested conditions. These results are consistent with those reported by Diosady et al. [32] where mixing time between 10 and 30 min using maleic anhydride and citric acid did not affect the residual phosphorus content in degummed canola oil. As there was no significant difference in the phosphorus content with mixing time, 3 min was selected for all subsequent experiments. The mixing time established here applies for the current set up that uses a laboratory scale device for shearing; however, further research is required at pilot to industrial scale with high shear mixing pumps.

Megasonic-Assisted Degumming of Canola, Soybean, and Sunflower Oil

As mentioned, previous work has demonstrated that megasonic treatments applied during degumming significantly reduced the residual phosphorus content in canola oil obtained from expeller processing (canola oil I) [27]. This section evaluates the effect of megasonic treatments on the degumming of hexane extracted canola (II), as well as expeller pressed soybean and sunflower oils (Table 2, Experiment 3) and compares with previous results on expeller extracted canola oil (I).

All degumming procedures tested (non-megasonic and megasonic) gave oils that met the industrial specification for maximum residual phosphorus content, with values below 100 mg/kg [33]. Megasonic-assisted acid degumming resulted in a lower phosphorus content in all the tested oils

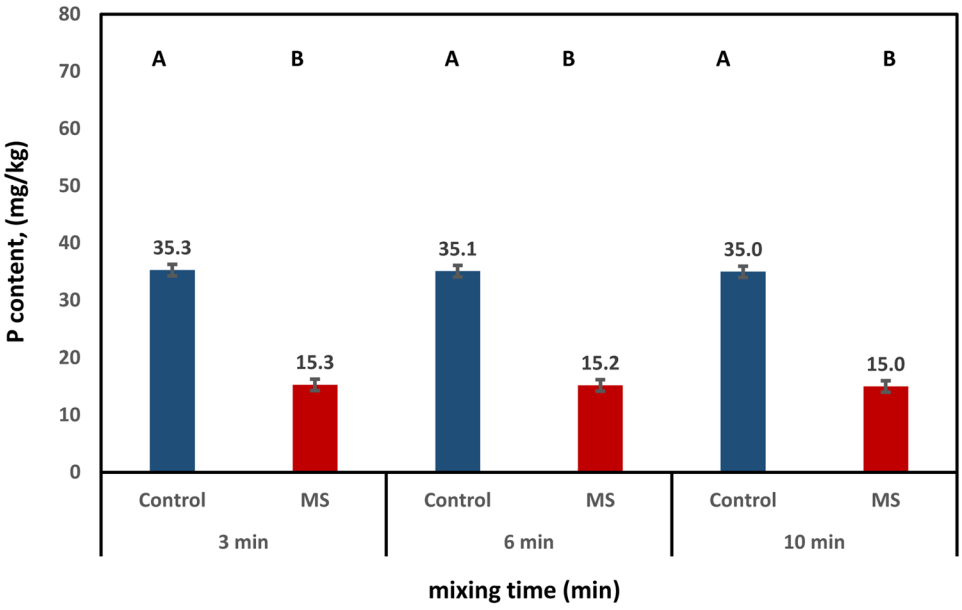

Fig. 3 Megasonic (MS) effect on the contact period for phosphoric acid degumming in canola oil. Megasonic treatment was carried out at 2 MHz, 40 °C, and 20 min. The control was a non-megasonic treatment (ultrasound OFF). Different uppercase letters indicate significant differences ($p < 0.05$) between control and MS treatments for different mixing times

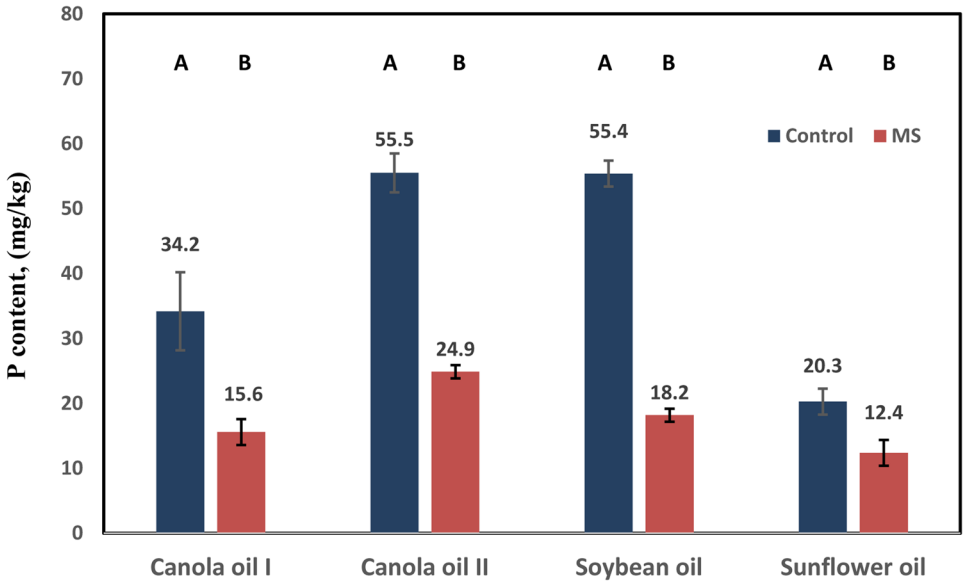

Fig. 4 Megasonic (MS) effect on the phosphorus content for canola, soybean and sunflower oils. Megasonic treatment was carried out at 2 MHz, 40 °C, and 20 min. The control was a non-megasonic treatment (ultrasound OFF). Different upper-case letters indicate significant differences ($p < 0.05$) between control and MS for each crude oil. Canola I, soybean, and sunflower are crude oils obtained from expeller pressing, with canola oil I data taken from our previous work [11] . Canola II is a crude oil obtained from hexane extraction from the canola cake after pressing

compared with non-megasonic degummed oils (Fig. 4). The reduction in phosphorus content with megasonics was more pronounced in soybean oil with a 67% reduction, compared with the non-megasonic control. Less reduction was achieved in both canola oils I and II (55%) and in sunflower oil (39%) after a megasonic application.

The phosphorus content reduction effect in all megasonic treated oils (Fig. 4) may be attributed to increased mass transfer of phosphoric acid into the oil phase, induced by megasonic phenomena such as microstreaming and milder, localised, cavitation [27]. Megasonic phenomena enhanced the overall reaction between phosphoric acid and crude oil, thereby facilitating gum precipitation and separation after centrifugation.

Megasonic-Assisted Reduction of Gum-entrained Oil

This section demonstrates the potential recovery of entrained oil in gums, resulting from megasonic treatment during the degumming process, by using three extraction methods to measure gum-entrained oil (Table 2, Experiment 4).

Method I: Hexane Extraction Method (Wet Gum Basis)

Table 3 shows the residual entrained oil in gums obtained after phosphoric acid degumming, without and with megasonic treatment (see "Method I: Determination of Retained Oil in Gums Using Hexane Extraction (Wet Gum Basis)"). The gum-entrained oil, measured after megasonic-assisted acid degumming of the two types of canola oil (I and II), was reduced by 46.0% and 47%, respectively, compared with a non-megasonic treatment (control). Similarly, megasonics reduced the oil entrained in soybean and sunflower gums by 35% and 24%, respectively, compared with the non-megasonic control. Therefore, megasonics reduced the oil entrained in gums in the tested seed oils to different extents and increased the oil yield after degumming.

Method II: Cold Acetone Extraction Method (Wet Gum Basis)

The residual entrained oil in gums obtained by method II (see "Method II: Determination of Entrained Oil in Gums Using Acetone Extraction (Wet Gum Basis)"), which is known as the industry's standard method, corroborated the results obtained by method I (Table 3). In this case, the megasonic treatment reduced the gum-entrained oil, by 50.0%, 45.0%, 35.3%, and 28.4% when processing canola I, canola II, soybean, and sunflower oils, respectively. As above, percentages use the gum-entrained oil obtained by non-megasonic treatment as a basis.

Method III: Hexane Extraction Method (Dry Gum Basis)

Method III (see "Method III: Determination of Entrained Oil in Gums Using Hexane Extraction (Dry Gum Basis)") measured the gum-entrained oil after drying the gum before hexane extraction. The method showed that the moisture content in the gum did not impact on the trends observed above (Table 3). When using Method III, the megasonic treatment reduced the gum-entrained oil by 50.0%, 45.0%, 35.3%, and 28.4%, for the canola I, canola II, soybean, and sunflower oils, respectively; compared with the non-megasonic treatment.

Table 3 The entrained oil in gums obtained without and with megasonic treatment. Megasonic treatment (MS) was carried at 2 MHz, 40 °C for 20-min sonication time and the non-megasonic experiment was replicated with the megasonic OFF

	The residual entrained oil in gums (g/kg of crude oil)[1]							
Gum origin[2]	Canola I[4]		Canola II[5]		Soybean[4]		Sunflower[4]	
Method[3]	C	MS	C	MS	C	MS	C	MS
I	20.0 ± 2.3Aa	10.8 ± 4.5Ba	40.2 ± 11.3Aa	21.3 ± 5.5Ba	50.0 ± 10.2Aa	32.5 ± 11.5Ba	39.5 ± 8.0Aa	30.0 ± 7.5Ba
II	25.5 ± 4.5Aa	12.5 ± 3.1Ba	45.5 ± 12.7Aa	25.0 ± 10.3Ba	98.4 ± 12.2Ab	63.7 ± 15.5Bb	85.5 ± 12.0Ab	61.2 ± 14.5Bb
III	15.1 ± 2.5Ab	7.5 ± 1.5Ba	22.4 ± 7.5Ab	10.4 ± 5.3Ba	30.2 ± 6.0Ac	19.5 ± 7.5Bc	20.5 ± 3.1Ac	15.5 ± 2.2Bc

[1]Different uppercase letters indicate significant ($p < 0.05$) differences between non-megasonic or control (C) and megasonic treatment (MS) for selected oils. Different lowercase letters indicate significant ($p < 0.05$) differences between non-megasonic or control (C) and megasonic treatment (MS) of each method for selected oils

[2]Gums separated from the oils

[3]Method I: n-hexane extraction method (wet basis); Method II: acetone extraction method (wet basis); Method III: n-hexane extraction method (dry basis)

[4]Crude oils obtained from expeller pressing

[5]Crude canola oil obtained from hexane extraction from the canola cake after pressing

Therefore, all three gum-entrained oil quantification methods consistently showed greater reductions of entrained oil in gums after a megasonic intervention. However, except for Methods I and II for canola oil, all methods gave different residual oil values in both control and megasonic samples. Acetone has shown to be more effective than hexane in de-oiling dried gums during soybean lecithin manufacturing, and this also reflects in higher oil values obtained by method II, compared with method I. The same applied for sunflower when comparing methods I and II. Furthermore, method I provided higher oil values than method III. Freeze drying the gum during method III may have changed the physicochemical properties of the gum and therefore its solubility in hexane and oil retention.

The different phospholipids composition of the three seed oils could create different gum structures, trapping different amounts of oils. These structures may interact differently with megasonic waves, thereby trapping and releasing oil to different extents, depending on the phospholipid composition. The reduction of entrained oil in gums may be attributed to solid gums agglomeration at the low-pressure nodal planes, while the oil droplets move to the anti-nodal planes[21, 27, 34, 35]. This phenomenon may compact the gums at the nodes and coalesce the oil in the antinodes, facilitating further oil separation as a result of the acoustic waves. To better understand how megasonic waves affect oil entrapment and release, further studies are required to examine the effect of individual phospholipids and other constituents present in the gums. . However, no previous work has considered the behaviour of gums under a high frequency acoustic field.

Megasonic-Assisted Enhancement of Gum Recovery

The gums weight of the four crude oil samples, without and with megasonic treatments, were quantified after de-oiling by hexane extraction (see "Method I: Determination of Retained Oil in Gums Using Hexane Extraction (Wet Gum Basis)"). Results in Table 4 proved that the megasonic treatment increased the gum yield for all four oils compared with non-megasonic treatment.

The gum yield of the degummed canola oil II was 22.5% (crude oil basis) after the megasonic treatment and 17.5% (crude oil basis) after the non-megasonic treatment (Table 4). The yield of canola oil II gums was about tenfold higher than canola oil I gum, without or with a megasonic treatment. Higher yield of gums in hexane extracted crude oil may be explained by the enhanced acid solubility of its phospholipids compared with residual phospholipids in the oil after expeller pressing. This has been also validated by the lower phosphorus content

Table 4 Gum yield of tested crude oils, with and without megasonic (MS) treatment. Megasonic treatment was carried at 2 MHz, 40 °C for 20 min and the non-megasonic experiment was replicated under the same conditions with the megasonic OFF

	Gums weight (g/100 g of crude oil)[1]			
	Canola I[2]	Canola II[3]	Soybean[2]	Sunflower [2]
Control (non-megasonic)	1.7 ± 0.3A	17.5 ± 0.9A	16.5 ± 0.9A	14.2 ± 0.6A
Megasonic treated	2.2 ± 0.3B	22.5 ± 1.0B	20.3 ± 1.2B	16.9 ± 0.5B

[1]Different uppercase letters indicate significant ($p < 0.05$) differences in gum weight between control and megasonic treatments at a selected degumming treatment method ± standard deviation

[2]Crude oils obtained from expeller pressing

[3]Crude canola oil obtained from hexane extraction from the canola cake after pressing

found in the expeller pressed canola oil (canola oil I) compared with the hexane extracted canola oil (canola oil II). The higher extractability of phospholipids in canola oil II may result from high temperatures (60–80 °C) and extended extraction time utilised during the oil hexane extraction process [14, 16].

Due to megasonic treatment, the gum yield increased from 16.5 to 20.3 oil g/100 g oil, for soybean, and from 14.2 to 16.9 g/100 g oil, for sunflower. These increases are attributed to the enhanced phosphorus removal discussed earlier (see "Megasonic-Assisted Degumming of Canola, Soybean, and Sunflower Oil"), therefore having an effect on gum yield. This effect provides a more efficient contact between the oil–water interphases [15], assisting the phospholipid gum precipitation. Therefore, there are two simultaneous material separation mechanisms occurring during megasonic treatment in the four tested oils: (a) phosphorus removal from higher reactivity between acid and oil [27], giving high gum yields, and (b) gum-entrained oil reduction resulting from the effect of the acoustic field.

Economic Benefits from Megasonic-Assisted Degumming

While the current proof of concept is unprecedented and novel, it has now been demonstrated at a laboratory scale in a batch process. Further optimisation and scale up is required to perform a more realistic economic evaluation of the technology.

According to these laboratory scale experiments, Table 5 forecasts the potential economic benefits of increased oils and gums recovery, based on an annual production of 100,000 tonne/year in an edible oil plant. It includes the additional oil yield due to recovery of gum-entrained

Table 5 Economic benefit evaluation of megasonic-assisted degumming for three crude oils

Economic evaluation parameters	Based on production rate (100,000 tonnes crude oil/year)		
	Canola oil I[3]	Soybean[3]	Sunflower[3]
Additional oil (%, tonne reduced oil loss/100 tonne initial crude oil)	0.25 ± 0.05	0.5 ± 0.04	0.15 ± 0.02
Additional oil (tonne/year)	250	500	150
Oil price (USD/tonne)	875	706	740
Profit from additional oil (USD/tonne)	220,000	355,000	110.000
Total gum production (tonne/year)[1]	200	500	300
Additional gums (%, tonne additional gum from MS/ 100 tonne gum)	22.7 ± 2	18.7 ± 1	16.5 ± 1.5
Additional gums (tonne/year)	44	93.5	49
Meal price (USD)	350	316	330
Profit from additional meal (USD/year)	15,400	29,500	16,500
Total additional profit (USD/year)[2]	235,400	384,500	126,500

[1]Gums are usually mixed with the seed meal and sold as meal—additional gum adds to the total meal sold

[2]Total additional profit = Profit from additional oil (USD/tonne) + Profit from additional gums (USD/year)

[3]Crude oils obtained from expeller pressing; additional oil recovery and gum yield results are connected to Tables 3 and 4, respectively

oils ("Method III: Hexane Extraction Method (Dry Gum Basis)"), and the additional gum yield ("Megasonic-Assisted Enhancement of Gum Recovery"). The additional oil recovered was calculated by taking the difference between the oil recovered after a megasonic and non megasonic treatment. Based on Table 3, the additional % oil recoveries were 0.24%, 0.50%, and 0.15% (g crude oil loss reduced/100 g initial oil) for the degummed canola, soybean, and sunflower oils obtained from the expeller.

For soybean oil degumming, the application of megasonics could achieve an additional oil recovery of 500 tonne/year of oil, worth nearly USD 355,000 (assuming the cost per tonne is USD 706). In addition, an extra 93.5 tonne/year of soybean gums can be mixed with soybean meal yielding an additional profit of 29,500 USD/year (Table 5), therefore giving a total additional profit of 384,500 USD/year as a result of megasonics. Similarly, the extra sales from megasonic treatment in canola and sunflower oil degumming could provide an additional total profit of 235,400 and 126,500 USD/year, respectively.

The data presented above serves as an initial guide and indicates significant earnings from additional oil and gum recovery. The next step would be to evaluate the capital and operating cost of a continuous large-scale megasonic vessel to evaluate the return on investment of commercial scale units. The megasonic technology for enhanced oil separation has been explored and scaled up in recent years in olive [22] and palm oil [35] processing as reviewed by Juliano et al. [21]. Proof of concept of megasonic technologies have been previously published and reviewed by Juliano et al. [36] showing energy requirements of 100–200 kJ/kg for laboratory scale samples of 0.07–2 kg. The technology was subsequently scaled up to 300 kg/h in continuous systems, in olive oil processing, as well as to 5 tonnes per hour and then to 45 tonnes per hour in palm oil processing [34], with lower energy requirements of 10 kJ/kg and 0.5–0.05 kJ/kg, respectively. The economical scale up of the megasonic technology is not limited by the energy requirement, but by the costs of the total amount of transducers required in the pre-separation stage [35, 37]. However, previous experience in scaling up the megasonic technology in aqueous based palm oil and olive oil processes have shown that trials at pilot and industrial scales require less specific energy due to larger distances between the transducer and the wall, which allow for larger treatment chambers and increases the oil-bearing material's residence time.

Effect of Megasonic Treatment on Oil Quality

The refined oil quality parameters of the degummed oils after non-megasonic and megasonic treatment are shown in Table 6. Results were compared with the specifications defined by the Australian Oilseeds Federation edible oil quality standards [38]. The measured oil quality parameters were free fatty acids, peroxide value, and chlorophyll, for both non-megasonic (control) and megasonic treatments. Even though slight changes can be observed in some of the quality parameters for the tested degummed oils, values were all within the quality standard limits.

There was a significant reduction ($p < 0.05$) in free fatty acids resulting from megasonics treatment in expeller extracted canola and sunflower oils (Table 6), as shown in our previous work for expeller extracted canola oil degumming [27]. A similar finding was also reported by Juliano et al. [22] who showed that FFA of olive oil was slightly reduced by high-frequency megasonic application compared with non-megasonic treated olive oil.

Similar to what has been reported elsewhere [27], peroxide value slightly but significantly ($p < 0.05$) increased by 2 to 3 ppm for all three crude oils because of megasonic treatment. These levels are still under the maximum quality

Table 6 Quality parameters of the degummed oils obtained without and with megasonic treatment and refined oil industrial specifications. Megasonic treatment was carried at 2 MHz, 40 °C for 20 min and the non-megasonic experiment was replicated under the same conditions with the megasonic OFF

Quality specifications	Units	Canola oil I[1]		Soybean oil[1]		Sunflower oil[1]		Refined oil industrial specifications
		C	MS	C	MS	C	MS	
FFA	%	0.86 ± 0.1A	0.63 ± 0.05B	0.62 ± 0.1A	0.61 ± 0.1A	0.42 ± 0.05A	0.40 ± 0.05B	2–2.5
Peroxide value	meq O_2/kg	5.0 ± 0.3A	8.2 ± 0.2B	7.5 ± 0.2A	8.2 ± 0.2B	7.7 ± 0.2 A	9.5 ± 0.3 B	10
Chlorophyll	mg/kg	2.8 ± 0.2A	2.4 ± 0.2B	1.1 ± 0.1A	0.8 ± 0.1B	1.9 ± 0.1A	1.5 ± 0.05B	30–50
Phosphorus	mg/kg	34.2 ± 3.0A	15.6 ± 1.0B	55.4 ± 6.0A	18.2 ± 2.0B	20.3 ± 2.0A	12.4 ± 2.0B	100

Different uppercase letters indicate significant ($p < 0.05$) differences in oil quality between control and megasonic at a selected degumming treatment method. ± standard deviation

Abbreviation: *C* control or non-megasonic, *MS* megasonic, *FFA* free fatty acids, *PV* peroxide value

[1]Crude oils obtained from expeller pressing

standard levels. It is well known that peroxide value increases after degumming and alkali neutralisation [39] due to the exposure of the oil to water and shearing, creating greater exposure to oxygen. A megasonic treatment may have also enhanced the oxidation processes as it provided further interaction between water-based reagents and the oil. However, these low peroxide levels may not be of industrial concern since the bleaching and deodorisation steps commonly reduce the peroxide values and therefore the level of oxidised compounds [27].

Chlorophyll content reduced by 0.4 ppm for all three-crude oils because of the enhanced megasonic treatment. Chlorophyll reduction was also reported elsewhere [27] after using megasonics to degum expeller extracted canola oil by various degumming methods. This previous work demonstrated the enhanced pigment separation, potentially including chlorophyll, as a result of megasonic treatments during degumming.

In summary, quality results observed in Table 6 showed that the application of megasonics is not expected to have a deleterious effect on the oxidative stability of the oil.

Conclusions

The application of megasonic treatments during acid degumming of crude seed oils further enhanced phosphorus reduction, with greater effects in soybean oil compared with canola and sunflower oil. Megasonic-assisted acid degumming reduced the amount of gum-entrained oil in canola, soybean, and sunflower oil, therefore showing its potential to increase refined oil production during degumming. Furthermore, the megasonic treatment concomitantly increased the gum yields from crude canola, soybean and sunflower oils, as a result of additional phospholipid removal. The oil quality parameters for all the non-megasonic and megasonic degummed oils met the industrial standards. Therefore, a megasonic treatment enhanced the phospholipids removal, oil yield, and gum yield on degumming expeller pressed oils and hexane extracted canola oil. This suggests a significant economic benefit due to the increased oil and gum yield resulting from the megasonic treatment. However, further work needs to be carried out to validate the efficacy, viability, and cost-effectiveness of this novel megasonic-assisted degumming process for vegetable oil refining at pilot and industrial scales.

Acknowledgments The authors would like to acknowledge Dr. Cheryl Taylor, Dr. Kai Knoerzer, and Dr. Henry Sabarez (CSIRO, Werribee, Melbourne, Australia) for their academic support. The authors also acknowledge the industrial experts Mr. Alan Thomson (Cargill CO, Melbourne, Australia), Mr. Peter Lymberis, and Mr. David Kwamsuk (GrainCorp Foods, Melbourne, Australia) for their contribution in this project.

Funding The authors received financial support from the Commonwealth Scientific and Industrial Research Organization (CSIRO) and University of New South Wales (UNSW), Sydney, Australia.

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