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ULTRASONIC DEGUMMING OF SOYBEAN OIL

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ABSTRACT

The present work discusses an alternative process for degumming of soy bean oil (SBO) using ultrasonic waves. The main advantages of this method are exclusion of acid treatment and heating that are required in the conventional degumming method, no heat treatment required, very short time of processing is needed. Increasing ultrasonic intensity to 80% of the maximal ultrasound power during degumming of SBO for 5 seconds caused sharp decrease in the phosphorus content of the investigated oil by 77.5%, since it reached 19.5ppm. With regard to PV, *p*- Av, Totox and conjugated triene the neutralized ultrasonic degummed SBO was superior to the neutralized acid degummed SBO (industry scale).The newly developed degumming technique shows promise in producing good-quality soy bean oil for this step of refining.

INTRODUCTION

There are four major steps in the chemical refining process of soybean oil (SBO); degumming, deacidification, bleaching, and deodorization. Refining is designed to remove free fatty acids (FFA), phospholipids, and pigments. The removal of these components increases the shelf stability, palatability, visual appeal, and marketability of the product (Lai,*et al*.,2008). Degumming, removes a range of substances from the oil which would separate out on storage (McKevith, 2005). Pan *et al*. (2000) reported that, during degumming hydratable phospholipids (HP) ,are eliminated by thermal treatment with water followed by treatment with other degumming agents such as phosphoric acid or citric acid to remove nonhydratable phospholipids (NHP). Hydration conditions are reported to be addition of 2% water by volume to the oil, and heating at 70C for 0.5-1 h. Phosphatides, including lecithin are removed efficiently from the oil by centrifugation. The acid degumming can be applied to oils that have been water degummed or not.

Commercial degumming of soybean oil includes treatment of oil with 85% concentrated phosphoric acid (represents 0.2% of the total weight of oil) .This process requires mixing for 4 h at 85 C (Erickson and Wiedermann, 2008) followed by neutralization using NaOH and separation of soap by centrifugation .Soap includes most of the gums and portion of oil . This is a time consuming, chemical consuming and results in 2-3% loss of the oil in the sludge (Phospholipid +Soap).Besides it eliminates the utilization of gums (Phospholipid) or commercial lecithin.

Chemical refining results in excessive neutral oil loss and the removal of some bioactive compounds.

Recently, novel approaches to physical refining have been developed in parallel, leading to a commercially viable physical refining process for SBO. A prerequisite for the successful process of physical refining is a very low content of phosphatides, i.e., a phosphorus content of less than 15 ppm, (Yang, *et al*. 2006).

Enzymatic degumming using phospholipase was reported to be successful in reducing the phosphorus content (Yang *et al*., 2006) but its economic viability has yet to be established.

The ultrafiltration process is still a new method in the oil industry as membrane fouling, which will lead to a poor economic performance, is still a serious problem. Till now, there is still no good degumming method that is qualified for the physical refining for all oils irrespective of their initial quality (Yang *et al*., 2008).

Moulton and Mounts (1990) studied the feasibility of a continuous ultrasonic degumming process as an alternative to chemical refining .They reported that optimization of the technique will be required for application.

Erickson and Wiedermann (2008) recommended the adoption of a philosophy for Minimum Treatment Practices (MTP) to ensure maximum finished oil quality in spite of crude oil quality variations.

The objective of this work was to evaluate: - the efficiency of ultrasonic technology under different % intensity of the ultrasonic power for the degumming_of water degummed (partially degummed) soybean oil, and the oxidation status of the ultrasonically degummed oil in comparison with the oil degummed by commercial method (phosphoric acid degumming process).

MATERIALS AND METHODS

Water degummed (partially degummed) and water-acid degummed-neutralized soybean oil samples were provided by Cairo Oil and Soap Co., El- Aiyat Factory, Giza, Egypt. All chemicals used were of analytical grade (Sigma-Aldrich Co.,USA).

Ultrasonic treatment

The water degummed (partially degummed) soybean oil was treated with ultrasound without heating. Successive amounts of 20 g of the soy oil and 1g of distilled water were placed in a beaker and treated with ultrasonic irradiation. Sonication was achieved using ultrasonic generator (Fisher Sonic, Model 300,50 Hz, USA) fitted with an immersible probe that emits the sound vibration into the solution via a titanium alloy rod (19 mm diameter). The probe tip was placed in the centre of the liquid sample and was positioned in the oil phase at a distance (X cm) above the oil–water interface, where X = <0.5 cm according to the findings of Cucheval and Chow (2008). The ultrasound power was controlled by changing the ultrasonic output level to 40, 60 and 80% of its maximal power (300 Watt). The oil-water mixture was subjected to ultrasonic vibration till almost complete emulsion took place and time required to achieve this goal was recorded. .After sonication, samples were centrifuged at 4000 rpm (1200 g) for 45 min (Hettich Universal D-7200 Centrifuge) . Clear degummed oil was decanted from the settled gums and analyzed.

Laboratory caustic refining.. The quantity of NaOH required was calculated and 10% excess NaOH over that required to neutralize the FFA was used. A 20° Baume (nearly 15% w/w) solution of NaOH (in water) was prepared with this NaOH. The oil was heated to 60°C (with constant stirring) and the NaOH

solution was then added dropwise. After stirring for 20 min the oil was centrifuged at 4,000 rpm (1200 g) for 30min to discard the soap phase. Finally, the oil was washed with hot water to remove the residual soap and the water phase was separated by centrifugation at 4,000 rpm (1200 g) for 30min.The oil phase was dried over anhydrous sodium sulphate before filtration.

Analytical procedures

Phosphorus determination: Phosphorus content was determined in oil samples according to AOCS official method (1997). The method determines phosphorus by ashing the sample in the presence of zinc oxide, followed by the spectrophotometric measurement of phosphorus as a blue phosphomolybdic acid complex using Spekol 11 spectrophotometer (Carl-Zeiss, Jena, Germany) at 650 nm.

Free fatty acids %(as oleic Acid), peroxide value (meq.O_2/Kg), and *p*-Anisidine were determined according to AOCS methods (1997). Conjugated dienes and trienes were determined as specific extinctions at 232 and 268 nm , respectively according to Anwar *et al*.(2007).. Samples were analyzed in a 10 mm cuvettes using UV-Visible 1650 PC Spectrophotometer (Shimadzu Co., Kyoto, Japan).

The color of the oil samples was measured by a Lovibond Tintometer (Tintometer Ltd., Salisbury, Wiltshire, United Kingdom), using 1 inch cell.

Accelerated oxidation test. A Rancimat apparatus (Rancimat 679, Metrohm) was used to determine the induction time of the tested oil samples . The temperature was set at 100°C, the air flow was 20 L/h, and the oil sample was 5 g.

RESULTS AND DISCUSSION

Evaluation of the degumming process:

Results in Table 1 indicated that phosphorous content of water degummed (partially degummed) oil was 86.7 ppm . De-Gryet and Kellens (2000) reported that phospholipids content of crude soybean oil ranged from 1 to3%. According to the quality specifications and trading rules of the U.S. adopted by the National Oilseed Processors Association (NOPA) (2007) the degummed soybean oil should contain no more than 0.02% of phosphorous.

Results showed that time required for complete emulsification of oil with 5% water using ultrasonic decreased sharply from 16 min to 0.08min (5sec) with the increase of ultrasonic intensity from 40% to 80% of the maximal ultrasonic power. Pan *et al.* (2000) reported that the optimal contact time for the quantitative removal of the NHP was 35 min for phosphoric acid. Erickson and Wiedermann (2008) reported that time of mixing during water and acid degumming of soy oil extends to1 and 4 h, respectively.

Results in the same Table 1 also showed that ultrasonic degumming of soy bean oil at 40% of the maximal ultrasonic power in presence of 5% water eliminated its phosphorus content by 56.4% .Increasing ultrasonic intensity to 80% of the maximal ultrasound power during degumming of SBO

for 0.08 min (5 seconds) caused sharp decrease in the phosphorus content of the investigated oil by 77.5%, since it reached 19.5 ppm. This treatment was selected for neutralization.

Table (1): Phospholipids content of the ultrasonic degummed soybean oil

Parameter	Water degummed oil	Ultrasonic intensity % of maximal ultrasonic power		
		40	60	80
Time required to reach almost complete emulsification (min)	-	16	1	0.08
Phosphorus content (ppm)	86.7	37.8	25.97	19.5
Phosphlipids content (ppm)*	2748.3	1198.2	823.2	618.1
% Elimination**	-	56.4	70	77.5

*** Phospholipids content = phosphorous content x 31.7**

**** % Elimination of phospholipids = (phospholipids content in water degummed oil - phospholipids content in the ultrasonic degummed oil) x 100/ (phospholipids content in water degummed oil).**

Phosphorus content, FFA% and color of the Ultrasonic degummed neutralized oil (laboratory scale) were compared with those of the acid degummed neutralized oil (industry scale) and results were tabulated in Table 2 .

Results in Table 2 showed that residual phosphorus in the ultrasonic degummed-neutralized soybean oil was 10.4ppm,the same as that of the acid degummed neutralized oil (11.73ppm).Both processes succeeded in the elimination of $\geq$ 87% of the phosphorus content of the soybean oil. Phospholipids content of the ultrasonic degummed-neutralized soybean oil was 329.6 ppm while phospholipids content of the acid degummed neutralized oil was 358.2ppm. These results indicated that phospholipids were efficiently removed from the oil and its content was reduced to an acceptable level with respect to the degumming and neutralization refining processes used.

Moulton and Mounts (1990) applied ultrasonic energy (750 W) to continuous degumming for the efficient removal of phospholipids from crude soybean oil (phosphorus content =446 ppm). The crude oil and water (2.5% by weight) were pumped through an ultrasonic processing cell, the oil-water mixture was subjected to ultrasonic vibration for 0.8 second. Ultrasound power to the horn varied from 20 to 100% (full power). Oil and hydrated gums were separated by centrifugation. The degummed oil had a residual phosphorus content of 30 ppm. Nasirullah (2005) found that the water-degummed soybean oil, when treated with 2% of electrolyte solution, prepared by mixing aqueous solution of 1.5% of potassium chloride and 0.5% of sodium chloride in a ratio of 95: 5 (v/v), yielded degummed soybean oil with phospholipid contents as low a 0.05 %.

Results in the same Table 2 showed that FFA %was reduced through neutralization to an acceptable level (0.127 %) for industrial application (<0.3% according to Egyptian Standard, 2005) for refined soybean oil.

Results in Table 2 showed that color of the SBO under investigation (determined by Lovibond Tintometer and 1 inch cell) was 4.4 R and 20Y. The color of the neutralized ultrasonic degummed oil and neutralized acid degummed oil was 3.2 R and 2.4R, respectively at 20Y indicating the efficiency of the neutralization process in removing pigments from oil through soap phase.

Table (2): Phospholipids content , FFA% and color of ultrasonic degummed neutralized soybean oil

Parameter	Water degummed oil	Ultrasonic degummed neutralized oil **	Acid degummed neutralized oil *
Phosphorous content (ppm)	86.7	10.4	11.73
Phospholipids content (ppm)	2748.3	329.6	358.2
% Elimination***	-	88	87
FFA %(as oleic acid)	0.55	0.127	0.085
Color (Lovibond, 1 inch cell) Y20 R	4.4	3.2	2.4

*** Industry scale using phosphoric acid**

**** Ultrasnoic intensity 80% of the maximal ultrasonic power**

***** % Elimination of phospholipids = (phospholipids content in water degummed oil - phospholipids content in the degummed neutralized oil) x 100/ (phospholipids content in water degummed oil).**

The results of analysis of PV, *p*-anisidine value, absorption at 232 and 268 nm of 1% oil in cyclohexane and induction period determined by Rancimat are given in Table 3. Results in Table 3 indicated that primary oxidation products, determined by the PV (1.81 meq/kg oil), and secondary oxidation products (aldehydes), determined by the *p*-ansidine value (0.871), of the water degummed soybean oil (partially degummed) increased with extending time of exposure to ultrasonic waves (40% of maximal ultrasonic power) to 16 min .

The Totox or oxidation value (OV), which is equivalent to 2 X peroxide value + anisidine value, was suggested for the assessment of oxidation in oils (Jelen *et al*.,2007).The Totox value of SBO was 4.491 and increased after 16 min of exposure to ultrasonic waves at 40% of the maximal ultrasound power to 7.313. Shorten time of exposure of SBO to ultrasonic waves during degumming to 1 min and 0.08 min (5 sec) at 60 and 80 % of the maximal ultrasonic power, respectively, yielded degummed oil samples with peroxide ,anisidine and Totox values lower than those of the oil subjected to ultrasonic for longer period. Peroxide, *p*-anisidine and Totox values of ultrasonic degummed SBO at 80% of the maximal ultrasonic power with 5% water for 0.08 min were 1.16 meq O_2/kg oil, 0.79 and 3.11, respectively. According to guidelines for good-quality prebleached oil the *p*-anisidine value has to be less than 4(Gupta, 2003).

On the other hand, results in the same Table 3 showed that induction period (determined by Rancimat at 100C) of the water degummed SBO (partially degummed) was 13.2 h and was not much influenced with the ultrasonic degumming since relative stability of the degummed oil samples

was >90% of that of the SBO before degumming regardless of the ultrasonic intensity (40, 60 or 80% of the maximal ultrasonic power) and exposure time (16,1 and 0.08 min) used.

Results in the same Table 3 showed also that formation of conjugated diene (absorbance of 1% oil in cyclohexane at 232 nm using cuvette of 1cm) $\mathbf{K_{232}}$ of the SBO increased slightly from 2.501 before ultrasonic degumming to 2.82 after degumming at all investigated ultrasonic degumming conditions.

Chemat *et al*. (2004) found that PV increased substantially in sunflower oil treated with ultrasound from 5.38 meq. O_2/kg oil for untreated oil to 6.33 meq. O_2/kg oil after irradiation of sunflower oil (20 kHz; 150 W; 2 min), while conjugated diene was almost constant.

On the other hand ,results in Table 3 indicated that formation of conjugated triene (absorbance of 1% oil in cyclohexane at 268 nm using cuvette of 1cm) $\mathbf{K_{268}}$ of the SBO was 0.359 .Formation of the conjugated triene was highly affected by the duration of the ultrasonic treatment rather than ultrasonic intensity used, since it reached 0.445 ,0.432 and 0.416 when ultrasonic degumming was carried out at 40,60 and 80% of the maximal ultrasonic power for 16 , 1 and 0.08 min (5 sec), respectively.

From results in Tables 1 and 3 and Fig 1 one can conclude that degumming of soybean oil in presence of 5 % H_2O with high ultrasonic intensity (80 % of the maximal ultrasonic power) for short time of exposure (5 seconds) reduced phosphorus content of oil by 77.5% and kept its quality characteristics.

Table (3): Oxidative status of ultrasonic degummed SBO

Parameter	Water degummed oil	Ultrasonic intensity % of maximal ultrasonic power			Neutralized	
		40	60	80	Ultrasonic degummed oil **	Acid degummed oil *
P.V (meq O_2/kg oil)	1.81	3.2	2.14	1.16	0.29	1.18
p- Anisidine	0.871	0.913	0.833	0.790	0.608	1.320
Totox ***	4.491	7.313	5.113	3.11	1.188	3.68
Oxidative stability (h)****	13.2	12.8	12.6	11.9	9.72	10.3
Relative stability %	-	96.9	95.4	90.1	73.6	78
K_{232}	2.501	2.825	2.826	2.817	3.145	2.932
K_{268}	0.359	0.445	0.432	0.416	0.375	1.443

*** Industry scale using phosphoric acid.**
**** Ultrasnoic intensity 80% of the maximal ultrasonic power .**
***** Totox =2X peroxide value+ anisidine value **** Rancimat Induction Time (h)**

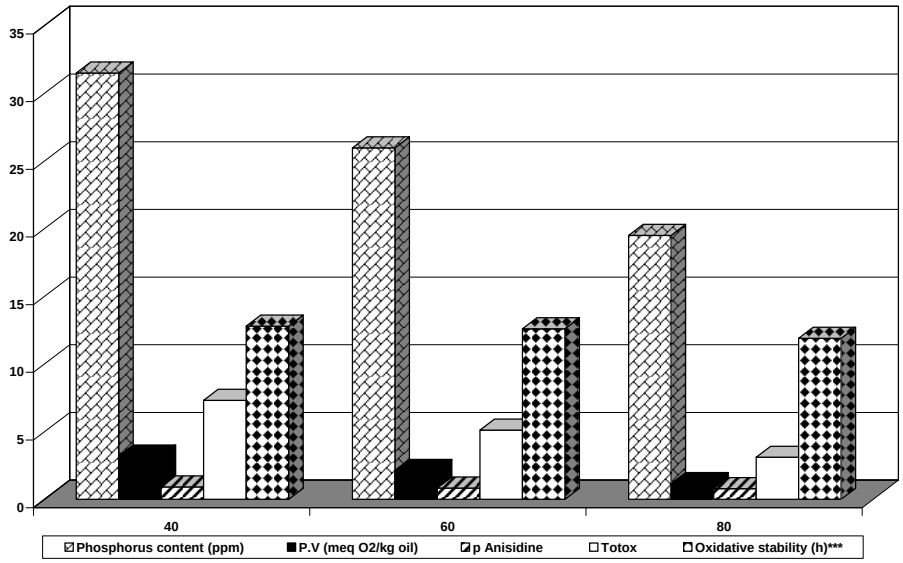
Results in Table 3 illustrated the oxidative status of the neutralized – ultrasonic degummed SBO (ultrasonic intensity representing 80% of the maximal ultrasonic power, for 0.08 min in presence of 5 % water) in comparison with that of the neutralized –acid degummed SBO (industry scale). With regard to PV, *p*- Av , Totox and conjugated triene the neutralized

ultrasonic degummed SBO was superior to the ultrasonic degummed oil before neutralization and neutralized acid degummed SBO (industry scale).The oxidation value (Totox value) and conjugated triene of the later oil samples was higher than that of the neutralized ultrasonic degummed oil by >3 and >4 times, respectively.

On the other hand, neutralization affected negatively the oxidative stability of the ultrasonic degummed and acid degummed SBO since oxidative stability of both oil samples represented 73.6 and 78 % of that of the SBO before degumming. Crude soybean oil was the most stable to the oxidation followed by deodorized, degummed, refined, and bleached oil during 6 days storage at 55 ◦C in the dark (Jung *et al*., 1989). Phospholipids act as antioxidants and prooxidants depending on their concentration and presence of metals. In purified soybean oil, which did not contain any metals, phospholipids worked as prooxidants (Choe and Min, 2006)

Results in the same Table 3 indicated that conjugated diene of neutralized ultrasonic degummed oil and neutralized acid degummed was 3.145 and 2.932 respectively.

Fig. 1: Effect of ultrasonic intensity (40, 60 & 80% of the maximal power) on phosphorus content and oxidative status of degummed soybean oil.



From these above mentioned data, it is possible to use ultrasonic at 80% of its maximal power to achieve complete degumming of SBO and separate pure gums before deacidification of the degummed oil. This process represents savings in time, chemicals, and costs besides it optimizes utilization of pure gums (commercial lecithin) ,and replaces chemical refining with a physical refining process for purification of SBO.

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التخلص من الصموغ فى زيت فول الصويا باستخدام الموجات فوق الصوتية

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تناول هذا البحث استخدام وسيلة بديلة غير تقليدية لعملية نزع الصموغ من زيت فول الصويا وذلك باستخدام الموجات فوق الصوتية وتتميز هذه الطريقة بعدم استخدام الأحماض وعدم الحاجة للتسخين وانه يمكن انجازها فى وقت قصير . ولقد أوضحت النتائج ان زيادة شدة الموجات فوق الصوتية المستخدمة إلى ٨٠% من الحد الأقصي لها خلال نزع الصموغ من زيت فول الصويا فى ٥ ثوان قد أدي إلى انخفاض حاد فى محتوي الزيت من الفوسفور بلغت قيمته ٧٧,٥% حيث أنخفض تركيز الفوسفور إلى ١٩,٥ جزء في المليون.

كما تبين أن الزيت المنزوع الصموغ (باستخدام الموجات فوق الصوتية) والمعادل يفوق فى صفاته الزيت المنزوع الصموغ (باستخدام حمض الفوسفوريك) والمعادل (على المستوي الصناعي) من حيث انخفاض رقم البيروكسيد وقيمة الانيسيدين وقيمة الأكسدة (Totox) و الـ Conjugated triene وتعتبر هذه الطريقة في التخلص من الصموغ طريقة واعدة لإنتاج زيت فول صويا ذو جودة مرتفعة.