Improved Oil Treatment Conditions for Soft Degumming

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ABSTRACT: "Soft degumming" is a new physicochemical degumming process. It involves the complete elimination of phospholipids by using a chelating agent, EDTA, in the presence of an emulsifying additive. To study the optimal cost of the process, a laboratory study was undertaken to find a method based on substituting the emulsifying additive by endogenous phospholipids. The phospholipids were first extracted from the oil by an initial hot-water treatment. In a second stage, a solution containing a chelating agent was incorporated. The mixture was then vigorously stirred to form an emulsion. The degummed oil was obtained after centrifugation. A comparative study carried out on several oils provided an indication of the efficiency of this alternative procedure. The phospholipid content of the processed oils was about 5 ppm phosphorus.

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KEY WORDS: Chelating agent, degumming, emulsifying additive, oil, phospholipids, refining, soft degumming.

Crude vegetable oils contain variable amounts of nonglyceride impurities, including free fatty acids (FFA), nonfatty materials generally classified as "gums" or phosphatides, color pigments, sterols, tocopherols, waxes, hydrocarbons, pesticides, and traces of metals (1–3). Most of these impurities, notably the phospholipids, are detrimental to color, flavor, foaming, and smoke stability (1) of the finished product and must be removed by purification.

To obtain a physically refined oil of good quality, it is essential to have a phosphorus value lower than 5 ppm before steam-stripping. For this reason, physical refining has mainly been used for oils high in acidity and low in phospholipids. Three main degumming techniques (excluding water degumming) have been developed: (i) acid degumming; (ii) acid-basic degumming; and (iii) other degumming processes such as dry, membrane, enzymatic, and the present soft degumming.

Acid degumming processes are generally carried out at elevated temperatures using high-shear mixers. Phosphoric acid is often used to make phospholipids hydratable; in this case, the side reaction (i.e., increased phosphorus content in the crude oil) can be suppressed either by using citric acid or by reducing both the acid concentration and the treatment time. In the super degumming process proposed by Unilever (4), milder temperatures are used in a multiple holding-step process, which makes the process rather complicated. However, the residual phosphorus content is generally below 30 ppm, probably because of the increased phosphate hydration.

In acid-basic degumming processes, the oil is treated with a degumming acid and partially neutralized with a NaOH solution. The metal–phospholipid complexes are dissociated by a strong acid into insoluble metal salts and phospholipids in their acid form, which are still soluble in oil. By raising the pH with NaOH, the phospholipids are converted into Na salts, which are more hydratable and therefore more easily removed from the oil (5).

Among the other degumming processes, dry degumming is an acid degumming process that uses concentrated acid followed by mixing with bleaching earth. This process is limited to oils with low phospholipid contents. Membrane degumming consists of the formation of micelles when the oil rich in phospholipids comes in contact with hexane (6). The micelles are separated from the oil by ultrafiltration. However, in practice this process is costly in terms of capital and operating costs and has not found industrial application. In the enzymatic degumming process developed by Lurgi (7), phospholipase A_2 specifically catalyzes the hydrolysis of the fatty ester at the *sn*-2 position of the phospholipids and releases hydratable phospholipids. This process is most suitable for crude oils containing relatively low levels of phosphatides; with phosphatide-rich oils, a prior water-degumming step is recommended.

In soft degumming (8), the crude or water-degummed oil is treated with an aqueous solution of a chelating agent, EDTA or one of its salts. In the chemistry of complexes, the p*K* value represents the ability to form stable entities; the higher the p*K*, the more stable the complex. The p*K* values of complexes of phosphatidic acid/calcium and of phosphatidic acid/magnesium are 4.6 and 4.0, respectively. The metal ions can easily be displaced with the addition of EDTA to form EDTA/calcium and EDTA/magnesium complexes with p*K* values of 10.7 and 8.7, respectively. The EDTA/iron complex is even more stable, with a p*K* for EDTA/Fe of 14.3 or 25.1, depending on its stage of oxidation. The four carboxylic oxygen and two nitrogen groups of the amine molecule of EDTA take part in the coordinated bond with the central metal ion (Ca, Mg, or Fe), forming a three-dimensional structure. This ion exchange between the oil-soluble ions and the water-soluble EDTA can only operate efficiently if the contact between

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the two phases is optimal. The formation of a water-in-oil emulsion is indispensable and requires a special mixer designed for this purpose. This emulsion is stabilized by adding an emulsifying agent. The soft-degumming mechanism can be separated into two stages: (i) a stage of complexing, leading to increased hydration of phosphatidic acid and phosphatidylethanolamine, followed by (ii) a stage of phospholipid (hydratable and nonhydratable) transfer into the aqueous phase. The emulsion can finally be separated by decanting (in a batch operation) or, preferably, by centrifuging (in a continuous operation).

The main objective of the present study is to provide an industrially and economically valid process based on substituting of the action of the emulsifying additive with that of endogenous hydratable phospholipids, making it possible to obtain completely degummed oil and facilitate physical refining. This is made possible by removing practically all of the nonhydratable phospholipids.

EXPERIMENTAL PROCEDURES

Soft-degumming conditions. Oil samples (300 g) (Tirtiaux Society, Fleurus, Belgium) were heated in a 600-mL beaker on a hot plate with magnetic agitation to 75°C unless specified otherwise, and 5 wt% of an aqueous solution containing a chelating agent (EDTA) and an emulsifying additive (sodium dodecyl sulfate, SDS) was then added. The mixture was homogenized for 1 min with a homogenizer (Ultra Turrax, Heidolph, Bayern, Germany) at a speed of approximately 9500 rpm. The emulsion obtained was agitated for approximately 2 min with the magnetic stirrer, and the mixture was transferred to four centrifuge tubes. Degummed oil was obtained after centrifuging for 20 min at 5000 rpm ($4080 \times g$).

Improved soft-degumming conditions. To facilitate the contact between the oily and aqueous phases, a two-step degumming operation was utilized: (i) hydrating the easily hydratable phospholipids and extracting these phospholipids (the hydratable, or easy-to-extract phospholipids) with hot water; and (ii) following with a treatment of an aqueous solution containing a chelating agent according to the method described for soft degumming. In the first step, the procedure consisted of adding 2 wt% of water to the oil at 75°C. The mixture was stirred at 75°C for variable periods of time. In the second step, the emulsion was degummed according to the method described for soft degumming.

Phosphorus analyses. The phosphorus contents of the oils were determined according to AOCS method Ca 12-55 (9). Three grams of sample and 0.5 g of zinc oxide were measured into a crucible and heated on a hot plate to char the oil. The crucible was then placed in a muffle furnace and heated to 650°C until completely ashed. The ash was dissolved in water and HCl, neutralized with KOH, and then re-acidified to make up 100 mL. An aliquot was treated with molybdate and a reducing agent to form molybdenum blue. The absorbance was read at 650 nm using a UV/Vis 7800 spectrophotometer (JASCO, Tokyo, Japan), and the phosphorus content was determined by comparing with a standard curve prepared from solutions of NaH_2PO_4.

RESULTS AND DISCUSSION

Soft degumming. (i) Effect of chelating agent and emulsifying additive concentrations. Dephospholipidation was directly related to the increased concentration of EDTA or emulsifying agent. However, with similar emulsifier or chelating agent concentrations (Tables 1 and 2), the desired degumming effectiveness was obtained for oils with relatively low initial phospholipid contents (H46). For low-phospholipid samples (46 ppm P), the elimination was nearly complete starting from concentrations ≥100 mM in chelatant or 50 mM in emulsifying additive. The differences in effectiveness between the H46 and H180 oil samples were due to the cation content. The cation concentrations were most probably greater for H180 than for H46. EDTA and emulsifier synergistic effects should also be noted. Insufficient EDTA or emulsifier resulted in poor degumming.

(ii) Effect of the oily phase/aqueous phase ratio on removal of phospholipids. The effect of the oily phase/aqueous phase ratio (Table 3) was enhanced by increasing the aqueous-phase volume and keeping the oily-phase weight constant. The chelating-agent concentration relative to the phospholipid concentration was maintained by diluting the aqueous solution.

TABLE 1
Phosphorus Content of Soybean Oil as a Function of the EDTA Concentration[a]

EDTA (mM)	Phosphorus (ppm)	
	H46[b]	H180[c]
2	26.7	43.3
5	23.3	43.2
10	23.3	40.0
20	20.0	39.7
50	13.3	30.0
100	6.2	23.2
200	0.0	16.8

[a]50 mM emulsifying additive; pH 10; temperature 75°C.
[b]H46: 46 ppm in phosphorus.
[c]H180: 180 ppm in phosphorus.

TABLE 2
Phosphorus Content of Soybean Oil as a Function of the Emulsifying Additive Concentration[a]

Emulsifying additive (mM)	Phosphorus (ppm)	
	H46	H180
0	16.2	41.2
5	15.9	37.3
10	14.9	34.6
15	14.6	33.5
30	14.2	24.1
50	6.6	23.3
70	6.6	23.6
100	6.4	20.5

[a]100 mM EDTA; pH 10; temperature 75°C. For abbreviations see Table 1.

TABLE 3
Phosphorus Content of Soybean Oil According to the Oily Phase/Aqueous Phase Ratio[a]

Aqueous phase (%)	Oily phase/aqueous phase ratio	EDTA (mM)	Phosphorus (ppm)
5	20.0	50.0	23.2
10	10.0	25.0	19.9
20	5.0	12.5	19.8
50	2.0	5.0	19.0
70	1.4	3.6	3.3
100	1.0	2.5	0.0

[a]Oil: 76.6 ppm phosphorus; pH 10; 50 mM emulsifying additive.

TABLE 5
Phosphorus Content of Soybean Oil as a Function of the EDTA Concentration[a]

EDTA (mM)	Phosphorus (ppm)
0	24.4
50	22.2
100	9.6
150	1.7
200	1.7
250	0.3
300	0.3

[a]H167 oil with 167 ppm phosphorus; 150 mM EDTA.

For a constant chelating agent/phospholipid ratio, the effect of increased oily phase/aqueous phase ratio on dephospholipidation is significant for ratios lower than 2. With these ratios, it was difficult to separate the emulsion formed by using the Ultra Turrax. On the basis of these results, it would be preferable to continue working with an aqueous phase percentage of 5%.

(iii) Effect of temperature. Results were as follows (temperature, °C; P, ppm): 22, 14.6; 45, 15.3; 65, 9.9; 75, 3.2; 95, 3.0 (for 100 mM EDTA and 50 mM emulsifying additive). For some of the chelating agent and emulsifier concentrations, temperatures greater than 65°C were necessary for effective degumming. With temperatures lower than 65°C, the phospholipid contents remained greater than 10 ppm. This phenomenon (dephospholipidation) is in direct relationship to the temperature, which depends on the phospholipid structure.

Improved soft degumming. (i) Effect of incubation times. The phospholipid contents in the oily phase remained the same after 20 min of stirring (Table 4). This time is sufficient for hydrating all of the phospholipids. However, after that time, the phospholipid content started to increase. This phenomenon was attributed to scattering of the phospholipidic esters as fine particles in the oily phase and therebay reducing centrifugation efficiency.

Immediately after homogenizing the oil and EDTA mixture (Table 4), the phospholipid content in the oily phase was at a minimum. The increased phospholipid contents was due to their scattering in the oily phase. Stirring had a negative effect on the dephospholipidation during the second stage.

TABLE 4
Phosphorus Content of Soybean Oil as a Function of Incubation Time[a]

Time (min)	Phosphorus (ppm)	
	First step	Second step
0	8.7	1.7
10	5.0	3.0
20	4.3	3.0
30	7.0	3.0
40	—	4.4
50	6.6	—
60	9.9	11.0

[a]H167 oil with 167 ppm phosphorus; 150 mM EDTA.

(ii) Effect of EDTA concentration. The hydratable phospholipids can also be removed by adding water. The nonhydratable phospholipids, mainly present as Ca or Mg salts of phosphatidic acid (PA/M^{2+}) and phosphatidylethanolamine (PE/M^{2+}), are more oil soluble. EDTA is an effective complexing agent because it forms a very stable chelate complex with all polyvalent metal ions (M^{2+}), including Ca^{2+}, Mg^{2+}, and Fe^{2+}. In contact with the nonhydratable phospholipids and in the presence of endogenous hydratable phospholipids, EDTA broke down phospholipid/metal complexes (PA/M^{2+} and PE/M^{2+}). This increased the hydratabilities of the phosphorus compounds and allowed their removal by centrifugation. Dephospholipidation was directly related to the increase in EDTA concentration (Table 5). The removal of phospholipids was almost total for concentrations >150 mM.

Comparison of soft degumming and improved soft degumming. Tests were made on various oils of different origins; Table 6 summarizes the results obtained for the three treatments. These results showed that the improved soft degumming method presented a more efficient dephospholipidation comparable with other soft-degumming techniques. In addition, the content in phosphorus was always <5 ppm. The efficiency was independent of the initial phospholipid contents and the oil origin.

TABLE 6
Phospholipid Contents (ppm) for Oils from Different Sources

Oils	Phosphorus (ppm)			
	Crude	Degumming by water	Soft degumming[a]	Improved soft degumming[b]
Linseed	490	75	9.0	6.0
Soybean	140	45	2.0	1.4
	77	—	3.2	3.0
	30	—	3.1	0.0
	23	—	0.0	0.0
Colza	34	—	1.0	1.0
	96	—	3.9	3.5
Sunflower	51	—	3.1	0.5
	85	—	3.6	3.4
Palm	6.9	—	1.3	0.0

[a]150 mM EDTA; 50 mM emulsifying additive.
[b]150 mM EDTA.

REFERENCES

1. Denise, J., Raffinage des Corps Gras, in *Manual des corps gras*, edited by A. Karleskind and J.P. Wolff, Tec & Doc Lavoisier, Paris, 1992, Vol. 2, pp 789–880.
2. Pryde, E.H., Composition of Soybean Oil, in *Handbook of Soy Oil Processing and Utilization*, edited by D.R. Erickson, E.H. Pryde, O.L. Brekke, T.L. Mounts, and R.A. Falb, American Soybean Association and American Oil Chemists' Society, Champaign, 1980, pp. 13–31.
3. Cowan, J.C., Degumming, Refining, Bleaching and Deodorization Theory, *J. Am. Oil Chem. Soc. 53*:344–346 (1976).
4. Ringers, H.J., and J.C. Segers, Degumming Process for Triglyceride Oils, U.S. Patent 4,049,686 (1977).
5. Dijkstra, A.J., and M. van Opstal, Process for Producing Degummed Vegetable Oils and Gums of High Phospholipidic Acid Content, U.S. Patent 4,698,185 (1987).
6. Gupta, A.K.S., Process for Refining Crude Glyceride Oils by Membrane Filtration, U.S. Patent 4,062,882 (1977).
7. Dahlke, K., The Enzymatic Degumming—Enzymax, *Oléagineux Corps Gras Lipides 4*:55–57 (1997).
8. Gibon, V., and A. Tirtiaux, Un Raffinage S.O.F.T., *Ibid. 5*: 371–377 (1998).
9. Mehalenbacher, V.C., T.H. Hopper, and E.M. Sallee, Phosphorus, in *Official and Tentative Methods of the American Oil Chemists' Society,* Champaign, 1970, Method Ca 12-55.

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