THE PHYSICAL-CHEMICAL MECHANISM OF THE EDIBLE OILS DEEP REFINING

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Abstract: Deep or soft degumming mechanism was treated in the present research paper. Deep degumming is a physical-chemical refining process, which involves the complete removing of total oil phosphatides by using a chelating agent (EDTA) in the presence of an emulsifying additive (sodium dodecyl sulfate – SDS).
The direct hydratable phosphatides are, in the first stage, separated from the crude oil by water classic degumming process and, in the second stage, a chelating treatment is applied in order to remove the heavy metals which imposed the non-hydratable phosphatides to separate from the partial degummed oil.

Keywords: *deep degumming, oil, phosphatides*

INTRODUCTION

Purification of the neutral part from crude oils is the major objective of the oils refining process. Crude vegetable oils contain variable amounts of nonglyceride impurities,

including free fatty acids (FFA), gums or phosphatides, color pigments, sterols, tocopherols, waxes, hydrocarbons, water, pesticides, and traces of metals [1-3].
The refining of edible oils and fats is conducted by using two technological routes: chemical and physical refining. In the chemical refining, wastewater and discharge are produced and higher refining oil losses are caused especially for oils with high FFA content. Physical refining is a modern refining procedure, ecological and with low processing costs. The reducing of the phosphorous content in the degummed oil less than 5 ppm (optimum 2 ppm) is the principal goal of the degumming process [4].
The removal of phospholipids (oil degumming) is the first stage of crude edible oil refining process.
In the classic water/acid degumming process, the crude oil is treated with water, salt solutions (NaCl, $CaCl_2$), or dilute acid (citric acid, phosphoric acid) to remove phospholipids. The phosphatides are changed into hydrated gums, insoluble in oil, which are separated by sedimentation, filtration or centrifugation.
The classic water degumming process leads to a considerable loss of neutral oil, large amount of wastewater and energy consumption. The phospholipid content of soybean oil is reduced to 1800 ppm, which correspond to phosphorus content of 60 ppm.
The acid degguming process induced an increasing of the phosphatidic acid salts hydratability by addition of either phosphoric or citric acid, which determined the decreasing of the phospholipid content to 1500 ppm.
Super-degumming and total degumming are modified processes of acid degumming. Super-degumming process determined degummed oil with a maximum residual phospholipid content of 900 ppm. The amount of acid used in the acid-degumming process varies between 0.05 and 0.2% of the oil weight and 0.5% in the case of oils that contain an initial phospholipid content of 6000 ppm and higher.
Enzymatic degumming is the biotechnological process in which lipase enzymes are used to hydrolyze nonhydratable phospholipids and transform them in hydratable form. Enzymatic degumming under optimal technological conditions leads to a low residual phosphorous content (10–15 ppm) in degummed oil. For successful industrial applications, only three enzymes, a phospholipase A2 from porcine pancreas and two kinds of microbial phospholipase A1 from *Fusarium oxysporum* and *Thermomyces lanuginosus*/ *Fusarium oxysporum* are available for enzymatic oil degumming [5].
Membrane degumming is a simple procedure of vegetable oils refining, characterized by the low energy consumption, ambient temperature operation, free chemical technology and retention of nutrients and other biological active oil compounds [6].
Deep degumming is a physico-chemical methods of primary edible oils refining which eliminated the acid degumming, as a dramatically method of chemical processing for remove the non-hydratable phosphatides. In deep degumming, the water pre-degummed oil is softly treated with a sequestrant agent, such as EDTA or one of its salts [7-8].

MATERIALS AND METHODS

The physical-chemical mechanism of the soybean oil deep degumming is analyzed in a two stage refining process:

(i) The water degumming, applied for the removing of the easily hydratable phosphatides and extracting these phospholipids (the hydratable, or easy-to-extract phosphatides) with hot water (2 wt% of water to the oil at 75 °C);
(ii) The de-salting treatment of pre-degumated oil and the extracting of the remaining heavy hydratable phosphatides from a W/O stabilized emulsion.

The chelating agent is EDTA and the emulsifying agent for W/O emulsion is SDS.

RESULTS AND DISCUSSIONS

The deep-degumming mechanism can be separated into four stages:
(i) The preliminary water degumming process, in order to remove the easy hydratable fraction of the phosphatides;
(ii) The Ca, Mg, Fe salts complexing, leading to increased the hydration degree of the phosphatidic acid and phosphatidylethanolamine;
(iii) The transfer of residual phosphatides phase into the aqueous phase with an emulsifying additive;
(iv) The separating of the complete degummed oil from the aqueous phases by decanting (in a batch operation) or by centrifuging (in a continuous processing).

The mechanism of deep degumming is based on the different stability of EDTA salts created by the interaction with the heavy metals of crude/pre-degummed oil and the stability of EDTA non-hydratable phosphatides salts.
In the chemistry of EDTA 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 hydratable phosphatides are removed, in the current industrial procedure, by water degumming.

Table 1. *The phosphatides content of crude edible oils [9]*

Edible Oil	Phosphatides content [%]	Phosphorus content [ppm]
Sunflower	0.5-1.3	200-500
Soybean	1.0-3.0	400-1200
Colza	0.5-3.5	200-1400
Corn	0.7-2.0	250-800
Cottonseed	1.-2.5	400-1000
Groundnut	0.3-0.7	100-300
Palm	0.03-0.1	15-30

The nonhydratable phosphatides, mainly present as Ca or Mg salts of phosphatidic acid and phosphatidylethanolamine, are lyposoluble. EDTA is an effective sequestrating agent, which forms a very stable chelate complex with all polyvalent metal ions from oil, especially with Ca^{2+}, Mg^{2+} and Fe^{2+}.

In contact with the nonhydratable phosphatides and in the presence of endogenous hydratable phosphatides, EDTA breakdown phosphatides/metal complexes and increase the hydratability degree of the phosphorus compounds, separated by centrifugation.
The technological factors which influence the deep degumming process are the followings:

(i) *The influence of chelating agent and emulsifying additive concentrations.* Degumming process is directly related with the increasing concentration of the sequestrating and emulsifying agent. For the oils with initial low-phosphatides concentration (under 50 ppm P), the degumming is quasi complete at the concentrations up to 100 mM in EDTA or 50 mM in SDS.

(ii) *The influence of the W/O emulsion ratio.* The effect of the W/O phase ratio is enhanced by increasing the proportion of the aqueous emulsion phase. The chelating agent concentration relative to the phospholipid concentration was maintained constant with diluted solution of EDTA. For constant chelating agent/phosphatides ratio, the effect of increased W/O phase ratio on degumming degree is significant for value under 2.

(iii) *The influence of temperature.* The degumming degree is in a direct relationship with the temperature. The increasing of the temperature in the range of 75-85 °C determines a more rapid and effective contact of the phases involved in the process and an efficient separation process of the gum fraction from the deggumed oil.

(iv) *The influence of degumming time.* The optimum phase's reaction time is 20 minutes, which is necessary for the interaction and complete and stable hydrating effect of the phosphatides.

CONCLUSION

The production of refined oil requires phosphatides removal from crude oil. Most phosphatides are hydratable and can be separated by aqueous degumming. The increment of nonhydratable phosphatides diminishes the degumming efficiency.
In the water degumming process, water is mixed into crude oil, and phosphatides hydrate and settle out as gum. The physical stability of the degummed oil is improved and bleaching & drying processes generate the commercial lecithin.
Chemical refining leads to important neutral oil loss and removes the bioactive oil compounds.
The conventional phosphoric acid treatment is unable to remove completely the phosphatides.
Enzymatic degumming using phospholipase is reported to be successful in reducing the phosphorus content under the level of 5 ppm, but it's a high cost refining method. The re-esterification of FFA through enzyme biorefining and by chemical methods was unsuccessful because of its poor refining efficiency high processing costs.
The membrane physical refining for the removing of the gum and wax is a future alternative method for physical refining of commercial edible oils.
The deep degumming is the most efficient method of edible oils degumming (residual phosphatides under 0.01%, below 5ppm phosphorus respectively). Applicable for the most edible oils, such sunflower, canola or corn oils, is a gently procedure of industrial

processing in which the degumming degree is similar with the ultrafiltration degumming and much better than the water/degumming process (residual phosphatides under 0.01-0.04%, under 5-15 ppm phosphorus respectively), but at a lower processing costs and in the ecological condition of refining, with the protection of the active biological compounds of edible oils (tocopherols, orysanol, fitosterols, vitamins).

REFERENCES

1. Dahlke, K.: *Oléagineux Corps Gras Lipides*, **1997**, **4**, 55–57;
2. Gibon, V., Tirtiaux, A.: *Un Raffinage S.O.F.T.*, **1998**, 371–377;
3. Denise, J.: Raffinage des Corps Gras, *Manual des corps gras*, Tec & Doc Lavoisier, Paris, Vol. 2, **1992**, 789–880;
4. Vintila I.: *Tehnologia uleiurilor vegetale* (in Romanian), Ed. Didactica si Pedagogica, Bucuresti, **2003**, 265-269;
5. Pryde, E.H.: *Handbook of Soy Oil Processing and Utilization*, American Soybean Association and American Oil Chemists' Society, Champaign, **1990**, 13–31;
6. Dijkstra, A.J., van Opstal, M.: Process for Producing Degummed Vegetable Oils and Gums of High Phospholipidic Acid Content, *U.S. Patent 4,698,185*, **1987**;
7. Ferrari, A.R., E. Schuttle, L. Bruhl, K.D. Mukherjee: Minor Constituents in Vegetable Oils During Industrial Processing, *J. Am. Oil Chem. Soc.*, **1996**, **73**, 587–592;
8. Hui, Y.H.: *Bailey's Industrial Oil and Fat Products, Volume 4: Edible Oil and Fat Products: Processing Technology*, 5th ed., Wiley Interscience, New York, **1992**, 160;
9. www.alfalaval.com