Pretreatment Efficiency for Physical Refining of Sunflowerseed Oil

Etelka Dimic*, Dj. Karlovic and **J. Turkulov**
University of Novi Sad, Faculty of Technology, 21000 Novi Sad, Yugoslavia

The appropriate pretreatment of crude oil is of crucial significance for the application of physical refining. This paper presents a simplified process for the preparation of sunflowerseed oil by applying multistep acid degumming as the only pretreatment step. Amorphous silica hydrogel was used instead of treatment with bleaching earth. The results obtained showed that samples of crude-pressed and extracted sunflowerseed oil differ significantly with respect to the content and composition of phosphatides, which is important for the pretreatment. The proper choice of oil and the application of multistep acid degumming results in an effective pretreatment of sunflowerseed oil for physical refining.

KEY WORDS: Degumming, phosphatides, physical refining, sunflowerseed oil.

To obtain a stable high-quality edible oil by physical refining, it is necessary to prepare the crude oil in a special way. According to Ong (1), the residual content of undesirable compounds should be even lower than for alkaline refining, because deacidification by distillation (i.e., deo-neutralization) is performed at higher temperatures than classical deodorization.

Among the undesirable compounds that have to be removed from the oil before deo-neutralization, the phosphatides are important. The residual content of phosphatides after the pretreatment process is even considered as the criterion for suitability of oil for physical refining (2). The removal of nonhydratable phosphatides (NHP), which are mainly Ca- and Mg-salts of phosphatidic and lysophosphatidic acid (3), is one of the biggest difficulties in the pretreatment process of oil for deo-neutralization. The NHP can be removed from the oil by applying acid, usually phosphoric or citric, or agents that will form complexes with Ca/Mg, i.e., enable their precipitation in the form of insoluble salts. Treatment with these acids is the basis of several processes for the pretreatment of oil before deo-neutralization. These processes are known as "Unidegumming" (Unilever, Vlaardingen, The Netherlands) (4), "Special degumming" (Alfa-Laval, Tumba, Sweden) (5) and "Top-dry" processing (Vandemoortele Coordination Centre, Izegem, Belgium) (6). Several other processes have been patented but were not given special names (7,8). Most of the mentioned processes are developed for soybean oil processing, which is harder to refine than sunflowerseed oil.

Principally, the oil pretreatment process for physical refining includes two phases: (i) The first step is hydratation of phosphatides to decrease their content below 0.15% (phosphorus content <50 ppm). Values below 0.09% (phosphorus content <30 ppm) are desirable, which can be achieved by multistep acid degumming, as described by Segers (9); and (ii) The residual phosphatides are removed in the second stage by adsorption on bleaching earth. Some authors recommend the use of synthetic amorphous silica gel instead of bleaching earth or in combination with it (10,11). Oil treated in this way contains 2–5 ppm phosphorus. At the same time, iron is also removed.

*To whom correspondence should be addressed at Faculty of Technology, 21000 Novi Sad, Bul. cara Lazara 1, Yugoslavia.

The results of our preliminary investigations indicate that the NHP content of our sunflowerseed oil is rather low because the degumming is performed easily. After the degumming of different-quality crude oil by applying water or some acid, the residual phosphorus content was 8 to 20 ppm (12–14). For soybean oil, such low values can be reached by applying the multistep degumming process (15).

The pretreatment process of oil for physical refining, which is mainly applied in the industry, involves the combination of several phases and operations, like heating, tempering, separating, washing and drying (16). All these processes are complex and need great amounts of auxiliary material. According to our research, such a reinforced pretreatment of sunflowerseed oil is not necessary. The bleaching process is considered particularly undesirable, as large amounts of bleaching earth promote a loss of tocopherols and increase the conjugated trienes content, further affecting the oil stability.

For this reason, we investigated a simplified pretreatment process for sunflowerseed oil in which only multistep acid degumming is applied. Subsequent treatment of oil with bleaching earth was avoided. The possibility of applying amorphous silica hydrogel was also investigated.

MATERIALS AND METHODS

Fresh crude sunflowerseed oil, produced under usual industrial conditions, was used for the investigations. Two samples of crude oil were taken from the processing line: pressed oil and extracted oil, which was obtained by hexane extraction of oilcake. Equal amounts of pressed and extracted oil were mixed to prepare the third sample, which is called mixed oil.

The preparation of oil for deo-neutralization was performed in two ways, Procedure A and Procedure B, as shown in Scheme 1. Procedure A involved only multistep degumming with 50% citric acid solution. In Procedure B, after the multistep acid degumming, the oil was subsequently treated with adsorbent, i.e., 0.3% amorphous silica hydrogel (TriSyl; Grace GmbH, Worms, Germany) without bleaching earth. The methods used for the quality and stability investigation of samples are presented in Table 1.

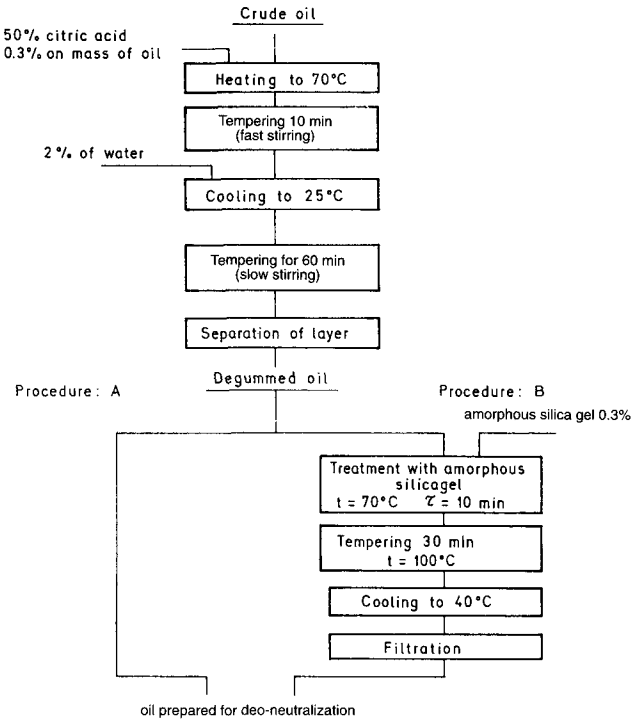
The content of hydratable phosphatides was determined by the centrifugation method (HPc), proposed by the Institute for Oil and Fat from Petrograd (20). The essence of the method is that the phosphatides are hydrated by addition of 2–3% water at 40–50°C and separated by centrifugation. The obtained layer is washed with acetone and dried to constant weight. The percentage of hydratable phosphatides is calculated with the formula:

$$HP_c\ (\%) = \frac{M_{HF}}{M_o} \times 100 \qquad [1]$$

where M_{HF} = mass of hydrated phosphatidic layer (grams) and M_o = mass of initial oil (grams).

The content of NHP, determined by the centrifugation method, is obtained from the difference:

$$NHP_c\ (\%) = TP - HP_c \qquad [2]$$



SCHEME 1

where TP = total phosphatides content (%), and HP_c = content of hydratable phosphatides determined by the centrifugation method (%).

The content of NHP was determined also by atomic absorption spectrometry (NHP_{AAS}) from the Ca, Mg and P contents in the oil by applying the following formula (11):

$$NHP_{AAS}\ (\%) = \frac{(Ca/40.1) + (Mg/24.3)}{(P/31)} \times TP \qquad [3]$$

where Ca = Ca content (ppm), Mg = Mg content, (ppm), P = P content (ppm) and TP = total phosphatides content (%).

RESULTS AND DISCUSSION

The main quality parameters and stability of crude sunflowerseed oil samples are presented in Table 2. The results obtained show that the oil used is of high quality with low content of free fatty acids and oxidation products.

Table 3 presents the contents of phosphatides, i.e., hydratable and NHP, as determined by centrifugation and AAS methods. The contents and compositions of phosphatides of crude oil samples are different. Though the phosphatide content of extracted oil is the highest, the ratio of NHP is the lowest. This fact leads to the conclusion that the degumming of this oil could be performed simply. On the other hand, although the total phosphatides content of crude pressed oil is considerably lower, the NHP ratio is about 60%.

Previous work by Russian investigators has shown that the treatment of seed before oil removal and the conditions of processing can have decisive effects on the quality, quantity and ease of removal of phospholipids from the oil (26). It is thought that NHP are the result of phospholipase D activity during slow heating of the seed in the cooking process. The activity of phospholipase can be prevented by intensive heating of the material. In this way, oil with low content of NHP can be obtained (27).

The content and ratio of NHP in oil differs significantly, depending on the method applied (Table 3). A certain agreement between the centrifugation and AAS results was observed for the pressed oil. The values for the NHP content are significantly lower in extracted and mixed oils, as determined by the centrifugation method. The questions arise: what is the reason for these differences, and which method can be accepted as the realistic one. It seems that the correlation between the Ca and Mg contents and NHP content for sunflowerseed oil is not as strong as for soybean oil, according to some authors (11). The correlation between the NHP contents by both methods is straight but negative.

As suggested by Ong (1), the phosphatides content of soybean oil before physical refining should be below 0.06% (phosphorus content, maximum 20 ppm). Considering

TABLE 1

Methods Used

Method Use	Method type (reference)
For oil quality characteristics determination	
Free fatty acid (FFA) content	ISO method (17)
Moisture content	ISO method (18)
Phosphorus/phosphatides content	Spectrophotometric method (19)
Hydratable phosphatides (HP_c) content	Centrifugation method (20)
Color	Spectrophotometric method (21)
For oxidation state and stability determination	
Peroxide value (PV)	ISO method (22)
Anisidine value (AV)	IUPAC method (23)
Total oxidation (TOTOX) value (2 PV + AV)	IUPAC method (23)
Specific absorbance	IUPAC method (23)
Rancimat test at 100°C	(24)
For Determination of metal in oil	
Ca and Mg content	AAS[a] method (25)

[a]Atomic absorption spectroscopic method. ISO, International Standards Organization, Geneva, Switzerland.

TABLE 2

Quality and Stability Characteristics of Crude Sunflowerseed Oil Samples

Characteristics	Crude sunflowerseed oil		
	Pressed	Extracted	Mixed[a]
FFA (% oleic acid)	0.39	0.69	0.51
Moisture content (%)	0.14	0.38	0.26
Color (% T_{455} nm)	38	27	32
PV (mmol/kg)	0.81	2.02	1.60
AV (100 A_{350} nm)	1.44	1.00	0.71
TOTOX value (2 PV + AV)	3.06	5.04	3.91
Specific absorbance			
A_{232}	2.33	2.56	2.54
A_{270}	0.24	0.31	0.30
Stability—Rancimat test induction period at 100°C (h)	9.80	15.30	13.07

[a]Mixed pressed and extracted oil in ratio 1:1. See Table 1 for abbreviations.

the data for NHP obtained by centrifugation, the extracted and mixed oils fulfill this criterion after simple water degumming. On the other hand, on the basis of values obtained by the AAS method, it seems that oil with a low content of NHP could not be obtained by water degumming of the abovementioned samples. However, the centrifugation method, which is, in fact, degumming of oil with water, denies this assumption. For this reason, we consider the centrifugation method to be a more convenient method for the determination of NHP in sunflowerseed oil.

INFLUENCE OF MULTISTEP ACID DEGUMMING AND ADSORBENT TREATMENT ON THE PHOSPHORUS/PHOSPHATIDES CONTENT OF OIL

Table 4 presents the phosphorus content in oil samples after acid degumming and amorphous silica hydrogel treatment. The results show that the multistep acid degumming was the most satisfying for extracted oil, although the total phosphatides content of this oil was the highest. The residual phosphorus content in the citric acid-degummed samples of extracted and mixed oil was only 10 ppm. With soybean oil, such values can be obtained only by subsequent washing of degummed oil (9). The efficiency of acid degumming on NHP removal (determined by the centrifugation method) is evident from Figure 1. The results obtained show that about 60 to 70% of NHP (NHP_c) was removed by degumming with citric acid. The successful removal of NHP from the mixed oil could be explained by assuming that the interaction between the phosphatides in the pressed and extracted oil samples is positive, making their removal from the mixed

TABLE 3

Content of Total, Hydratable and Nonhydratable Phosphatides of Crude Sunflowerseed Oil

Characteristics	Crude sunflowerseed oil		
	Pressed	Extracted	Mixed
Total phosphatides (TP, %) (P × 30)	0.24	1.32	0.70
HP and NHP content determined by centrifugation method			
Hydratable phosphatides (HP_c, %)	0.098	1.28	0.61
Nonhydratable phosphatides content (NHP_c, %)	0.14	0.04	0.09
Ratio of NHP:			
NHP_c/TP × 100 (%)	59	3	13
NHP_c determined by AAS[a] method			
P (ppm)	80	440	240
Ca (ppm)	22	33	25
Mg (ppm)	22	49	36
NHP_{AAS}, (%)	0.135	0.26	0.19
Ratio of NHP:			
NHP_{AAS}/TP × 100 (%)	56	20	27

[a]Atomic absorption spectroscopy. NHP_{AAS} content calculated on the basis of Ca, Mg and P content in the oil.

TABLE 4

Phosphorus Content After Acid Degumming and Adsorbent Treatment of Oil

Oil	P (ppm)		P^a removed (%)	P (ppm) After adsorbent treatment	P^b removed %
	Crude	After degumming			
Pressed	80	20	75	10	50
Extracted	440	4	99	<1	100
Mixed	240	10	96	2	80

[a]Percent of phosphorus removed by acid degumming compared to crude oil.
[b]Percent of phosphorus removed compared to degummed oil.

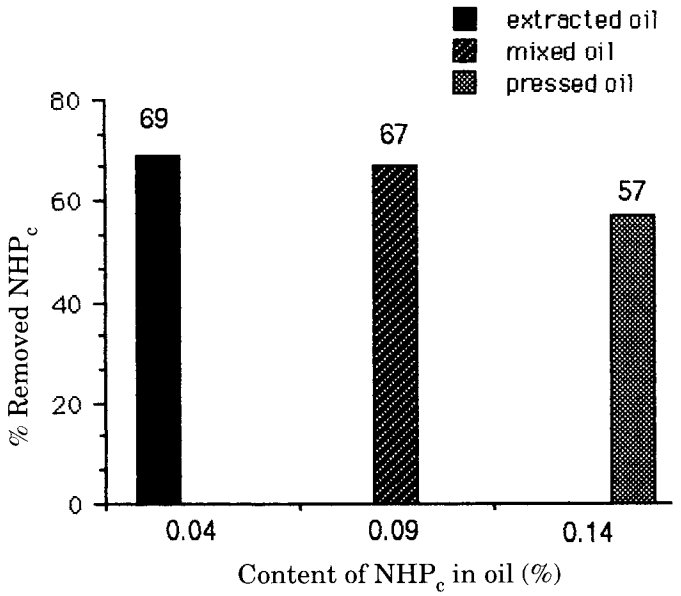


FIG. 1. Influence of NHP_c content of sunflowerseed oil on the removal efficiency by acid degumming; NHP_c—nonhydratable phosphatides determined by centrifugation.

oil easier. It seems that a part of NHP is withdrawn with the hydrated phosphatidic layer. This concept is supported by the recommendations given in Unilever's "Superdegumming" process: "If needed, 'hydratable lecithin' should be added to the crude oil" (28).

The treatment of oil with amorphous silica hydrogel resulted in a further decrease of phosphorus content, due to the affinity of this sorbent to phospholipids (Table 4). The efficiency of phosphatides removal by sorbent in pressed oil was 50%, while they were practically completely removed from the extracted oil. However, the phosphorus content of the extracted oil before the treatment was already low. The residual phosphorus content of pressed oil after the treatment was 10 ppm. A further decrease of this content could probably be achieved by increasing the sorbent amount, taking care on the economy of the process.

Considering the criterion most mentioned, that the phosphorus content in oil prepared for deo-neutralization should be below 5 ppm, the extracted and mixed oil samples are quite satisfactory.

From the standpoint of total phosphatides removal, the efficiency of the applied process for the pretreatment of sunflowerseed oil could be discussed on the basis of data presented in Table 5.

The multistep acid degumming was successful for extracted and mixed oils, but subsequent treatment was necessary for the pressed oil. This means that the proper choice of oil for processing can influence the pretreatment efficiency of sunflowerseed oil intended for physical refining.

CHANGE OF OIL QUALITY DURING PRETREATMENT

The changes of some quality and stability parameters of samples during the preparation for deo-neutralization are presented in Table 6. During the pretreatment process,

TABLE 5

Influence of Pretreatment on the Removal Efficiency of Phosphatides from Sunflowerseed Oil

Oil	Total phosphatides content (%)	Residual phosphatides content (%)		Efficiency of phosphatides removal (%)	
		A[a]	B[b]	A	B
Pressed	0.24	0.06	0.030	75	88
Extracted	1.32	0.01	<0.003	99	100
Mixed	0.72	0.03	0.006	96	99

[a]Procedure A includes only multistep acid degumming.
[b]Procedure B includes degumming and oil treatment with amorphous silica hydrogel.

TABLE 6

Changes in Quality and Stability of Oil During Pretreatment for Deo-Neutralization

Characteristics	Kind of oil					
	Pressed		Extracted		Mixed	
	A[a]	B[b]	A	B	A	B
Color (%T_{455} nm)	38	48	27	33	32	37
PV (mmol/kg)	1.16	1.37	3.06	3.30	2.05	2.39
AV (100 A_{350})	1.32	1.58	1.30	1.38	0.78	0.81
TOTOX value	3.64	4.32	7.42	7.98	4.81	5.59
Specific absorbances						
A_{232}	2.26	2.27	2.17	2.17	2.40	2.65
A_{270}	0.26	0.45	0.26	0.33	0.35	0.39
Stability—Rancimat test, induction period at 100°C (h)	9.3	9.0	10.0	8.9	8.7	8.4

[a]Degummed oil—Procedure A. See Table 1 for abbreviations.
[b]Degummed oil treated with amorphous silica hydrogel—Procedure B.

a slight increase of the oxidative state and decrease of stability of the oil samples was observed. Neither the color nor the content of oxidation products was changed under the influence of the applied sorbent.

REFERENCES

1. Ong., T.L., *Fette Seifen Anstrichm. 82*:169 (1980).
2. Dimić, E., Dj. Karlović and J. Turkulov, *Uljarstvo 28*:(3-4) 3 (1991).
3. Hvolby, A., *J. Am. Oil Chem. Soc. 48*:503 (1971).
4. Van de Sande, R.L.K.M., and J.C. Segers, European Patent Application 0 348 004 (1989).
5. Nilsson-Johansson, L., U. Brimberg and G. Haraldson, *Fat Sci. Technol. 90*:447 (1988).
6. Cleenewerck, B., L. Bevernage, F. Dewulf and A.J. Dijkstra, European Patent Application 92200543.4 (1992).
7. Kaji, T., European Patent 0 269 277 (1988).
8. Rohdenburg, H., K. Csernitzky, B. Chikany, J. Peredi, A. Borodi and A. Fabicsne Ruzsics, European Patent Application 0 473 895 (1992).
9. Segers, J.C., *Fette Seifen Anstrichm. 84*:159 (1982).
10. Bogdanor, J.M., and W.A. Welsh, Silica Refining of Edible Oils, 78th AOCS Annual Meeting, New Orleans, 1989.
11. Drube, P., R.B. Morton and F. Griselli, TRISYL and Bleaching Earths: A Superior Combination for the Physical Refining of Edible Oils, Chevreul Congress, Angers, 1989.
12. Hadaći, E., Phosphatides in Sunflowerseed Oil and Their Removal, B.S. thesis, (in Serbian), University of Novi Sad, Novi Sad, 1977.
13. Zakula, B., Quality of Degummed Sunflowerseed Oil Obtained by Pressing, B.S. thesis, (in Serbian), University of Novi Sad, Novi Sad, 1981.
14. Sidji, G., Refining of Low-Quality Sunflowerseed Oil, B.S. thesis, (in Serbian), University of Novi Sad, Novi Sad, 1983.
15. Segers, J.C., *Fette Seifen Anstrichm. 87*:541 (1985).
16. Dijkstra, A.J., Degumming, Refining, Washing and Drying, Paper presented at AOCS World Conference, Oilseed Technology and Utilization, Budapest, Hungary, 1992.
17. International Standards Organization, Geneva, ISO Method 660 (1983).
18. International Standards Organization, Geneva, ISO Method 662 (1980).
19. Paquot, C., J. Mercier, D. Lefort, A. Mathieu and R. Perron, *Les Methodes Analitiques des Lipides Simples* (in Serbian), Business Association of Vegetable Oil Producers, Beograd, 1967.
20. *Rukovostvo po metodam issledovaniya tekhnokhimicheskomu kontrolyu i uchetu proizvodstva v maslozhirovoi promishlenosti*, edited by B.P. Rżehin, and A.G. Sergeev, Tom I, Vol. 2, VNIIZh, Leningrad, USSR, 1967.
21. Oštrić-Matijaševiš, B., J. Turkulov and Dj. Karlović, *Chemical Industry 30*:(1)101 (1976).
22. International Standards Organization, Geneva, ISO Method 3960 (1977).
23. Paquot, C., and A. Hautfenne, *IUPAC—Standard Methods for the Analysis of Oils, Fats and Derivatives*, Blackwell Scientific Publications, Oxford-London-Edinburgh, 1987.
24. Karlović, Dj., J. Turkulov and E. Dimić, *Uljarstvo 25*:(3-4), 157 (1983).
25. Rowe, C.J., *Food Analysis by Atomic Absorption Spectroscopy*, Varian Techtron Pty. Ltd., Springvalle, Australia.
26. Arutjunjan, N.S., V.M. Kopejkovskij and L.A. Mihtarjans, *Proceedings of the 7th International Sunflower Conference*, Krasnodar, 1976.
27. Matshuk, Yu.P., V.V. Beloborodov, E.A. Semenov and G.T. Semyakina, *Trudy VNIIZh 28*:41 (1971).
28. Segers, J.C., and R.L.K.M. van de Sande, *Degumming—Theory and Practice*, World Conference Proceedings, Edible Fats and Oils Processing: Basic Principles and Modern Practices, Maastricht. Netherlands, 1989.

[Received December 29, 1993; accepted August 31, 1994]