UDC 665.1.09

A. Demydova [a], I. Levchuk [b], O. Aksonova [c], S. Molchenko [a], I. Demidov [a]

COMPARISON OF ACID DEGUMMING METHODS AND THEIR INFLUENCE ON THE FORMATION OF 3-MCPD-ESTERS AND GLYCIDYL ESTERS IN SUNFLOWER OIL DEODORIZATION

[a] National Technical University «Kharkiv Polytechnic Institute», Kharkiv, Ukraine
[b] Ukrmetrteststandart, Kyiv, Ukraine
[c] Kharkiv State University of Food Technology and Trade, Kharkiv, Ukraine

Degumming is the first stage in processing of vegetable oils, and it is aimed at removing phospholipids. The article compares the results of degumming by phosphoric and citric acids, their effects on the extraction of calcium and magnesium ions from oils, these ions being the main components of nonhydratable phospholipids. We showed the appropriateness of combining citric and succinic acids (the final content of phospholipids in oil was 0.034%, whereas it was equal to 0.048% when citric acid was used) and citric and ascorbic acids (the final content of phospholipids in oil was 0.040%). We studied the effect of acid degumming on the formation of 3-MCPD-esters and glycidyl esters. The content of glycidyl esters after degumming with citric acid and phosphoric acid was 310 μg kg^{-1} and 200 μg kg^{-1}, respectively. After degumming with citric acid and phosphoric acid, the content of 3-MCPD-esters in the deodorized oil was 680 μg kg^{-1} and 470 μg kg^{-1}, respectively. On the contrary, aqueous degumming does not increase the content of these esters in the deodorized sunflower oil (the content is less than 100 μg kg^{-1}) and its implementation can be recommended as one of the ways to prevent the formation of these toxic substances during deodorization.

Keywords: acid degumming, sunflower oil, phospholipids, MCPD-esters, glycidyl esters.

DOI: 10.32434/0321-4095-2021-137-4-50-57

Introduction

Degumming is the first stage of refining, which is aimed at extracting the largest group of polar lipids, phospholipids, from the oils. The content of phospholipids in unrefined pressed sunflower oil varies from 0.6 to 1.2%, and the oils obtained by extraction show a higher content of phospholipids than those obtained by pressing [1]. Among the main types of oils, soybean oil exhibits the highest content of phospholipids (Table 1).

Table 1

The content of phospholipids in the main types of oils

Oil	The amount of phospholipids, % (relative to the oil)	Reference
Soybean oil	1.0–3.0	[1]
Sunflower oil	0.6–1.2	[1]
Rapeseed oil	1.2–2.6	[2]
Palm oil	0.03–0.1	[2]
Corn oil	0.7–2.0	[1]

The main phospholipids of vegetable oils are phosphatidylcholine, phosphatidylethanolamine, phosphatidylinositol, and phosphatidic acid and its salts.

The simplest and safest way to remove phospholipids from unrefined oils is water degumming. When water is added to oil, phospholipids, due to the presence of polar groups in their molecules (Fig. 1), line up on the surface of water droplets, immersing their polar part in the middle. As a result of the difference in density, water with phospholipids settles to the bottom of the hydration apparatus and is separated from the oil by separation or decantation. The process of water hydration has been used for industrial purposes for almost a century [3].

However, the degree of interaction of different groups of phospholipids with water is different and

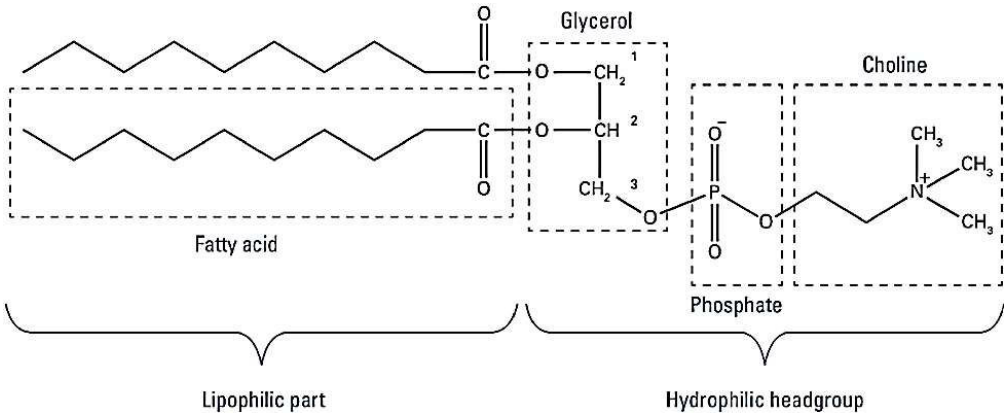

Fig. 1. The structure of the phosphatidylcholine molecule

the depth of their removal during aqueous degumming also differs. There are two types of phospholipids: hydratable (HPL) and nonhydratable (NHPL). The most hydrophilic phospholipids (i.e. including those capable of being removed from oils during aqueous degumming) are phosphatidylcholine (because its structure does not form an internal salt at any pH value and always remains hydrophilic) and phosphatidylinositol (it has five free hydroxyl groups on a fragment of inositol). Thus, phosphatidylinositol and phosphatidylcholine are completely removed from the oil when degumming is carried out in the presence of sufficient amount of water [4].

The phosphatidylethanolamine molecule carries a positive charge (i.e. becomes hydrophilic) at a pH value of two. As the pH rises, more and more phosphate groups dissociate and therefore zwitterion is formed: a positive amino group forms an internal salt with a negatively charged phosphate group. The positive and negative charges are so close to each other that the hydrophilicity of this zwitterion is quite weak and the aqueous degumming of phosphatidylethanolamine is incomplete. Thus, acid degumming is optimal for its removal from oil [3].

The molecule of phosphatidic acid in an acidic environment does not dissociate. When the pH rises to values greater than 5, the molecule acquires a negative charge, which makes it hydrophilic.

Alkaline earth metal salts of phosphatidic acid remain in the oil at any pH value, because divalent calcium and magnesium form a salt with two dissociated hydroxyl groups of the phosphate residue. They are part of the so-called non-hydrated groups of phospholipids [5].

Thus, even after thorough aqueous degumming, phosphatidic acid salts, phosphatidic acid and partially phosphatidylethanolamine remain in the oil.

The simplest way to increase the efficiency of degumming is the introduction of acid solutions. In addition, phosphatidylethanolamine molecules are removed, degumming time is reduced and phase separation is simplified. The biggest disadvantage of acid degumming is that phosphatidic acid and its salts remain in the oil. However, they are removed at the stage of chemical neutralization, so acid degumming is one of the most optimal ways of degumming in the refining process, including neutralization. Phosphoric or citric acids are most often used to this end.

According to current research, the method of hydration (composition of the hydrating agent) affects the formation of MCPD-E and glycidyl esters.

2,3-MCPD-esters (MCPD-E) and esters of glycidyl (GE) are a new type of fat-soluble food contaminants (Fig. 2), which are formed mainly at high temperatures: greater than 200^{0}C in case of esters of glycidyl and from 160 to 200^{0}C in case of esters of MCPD-E [6].

Let's consider the toxic effect of these esters. First of all, this is a genotoxic effect which negatively affects the cellular genetic material or DNA with the possibility of mutations (it applies to glycidyl esters, 3-MCPD-E being not genotoxic carcinogens [6]). In addition, the toxic effect of the esters under consideration implies carcinogenic action (increasing the likelihood of cancer (non-genotoxic)), nephrotoxicity (kidney disease), reduction of erythrocyte function by reducing hemoglobin (anemia), and destructive action on fertility in men and women (infertility in laboratory animals). Glycidol is classified as a human carcinogen (group 2A) [6].

Since September 2020, the content of 3-MCPD and glycidol is regulated by the requirements of Regulation (EU) 2020/1322 of 23 September 2020 amending Regulation (EC) No 1881/2006 as regards maximum levels of 3-monochloropropanediol

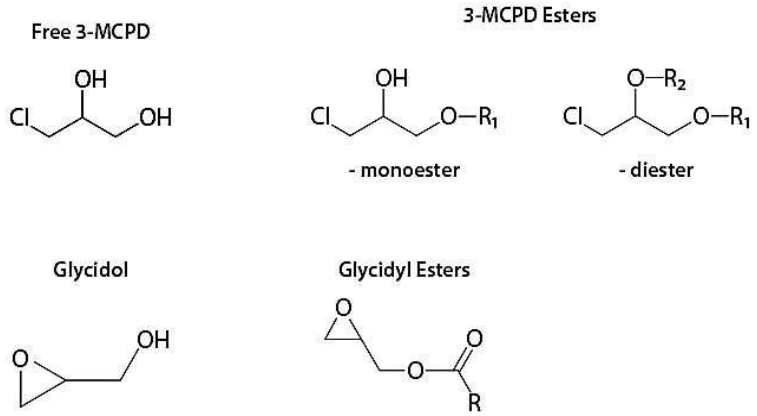

Fig. 2. General formulas of the MCPD group of toxic pollutants

(3-MCPD), 3-MCPD fatty acid esters and glycidyl fatty acid esters in certain foods. These maximum levels with respect of the sum of 3-monochloropropanediol (3-MCPD) and 3-MCPD fatty acid esters in terms of 3-MCPD should be as follows [7]:

– 1250 μg kg^{-1} for oils and fats from coconut, maize, rapeseed, sunflower, soybean, palm kernel and olive oils (1000 mg kg^{-1} for glycidyl fatty acid esters in terms of glycidol);

– 2500 μg kg^{-1} for other vegetable oils (including pomace olive oils), fish oils and oils from other marine organisms and mixtures of oils and fats with oils and fats only from this category;

– 750 μg kg^{-1} for vegetable oils and fats, fish oils and oils from other marine organisms destined for the production of baby food and processed cereal-based food for infants and young children (500 μg kg^{-1} for glycidyl fatty acid esters in terms of glycidol).

When a 0.02% solution of phosphoric acid in oil was used for degumming, 2.1 mg kg^{-1} of 3-MCPD-E was formed, while the use of water without added acids reduced the concentration of 3-MCPD-E to 0.75 mg kg^{-1} (an increase by 64%) [8].

Due to the fact that palm oil is characterized by a low content of phospholipids, «dry» degumming is most often carried out by treating palm oil with solutions of phosphoric or citric acids. However, this approach leads to the formation of increased amounts of MCPD-E and GE. The effect of water washing after dry degumming was determined as follows: the contents of 3-MCPD-E and GE were decreased by 25% (from 2.8 to 2.1 mg kg^{-1}) and by 16% (from 3.5 to 3.0 mg kg^{-1}), respectively [9]. Washing by ethanol yielded a decrease in the content of 3-MCPD-E and GE by 36% and 26%, respectively [9]. When using the method of physical refining via replacing acid degumming (with phosphoric acid) by aqueous degumming, the content of 3-MCPD-E in palm oil was decreased by 80% [10]. However, these studies were performed using palm oil, which is the leader among vegetable oils in the possible content of 3-MCPD-esters and esters of glycidyl. The effect of aqueous and acid degumming on the content of MCPD-E and GE in deodorized sunflower oil should be investigated.

The aim of this work is to compare the results of different methods of acid degumming and establish the effect of the composition of degumming agents on the content of 3-MCPD-esters and esters of glycidyl in deodorized sunflower oil.

Experimental

Unrefined crude press sunflower oil was selected as the object of the study. Degumming of sunflower oil was performed using a magnetic stirrer with a thermocouple at a temperature of 60^0C at a constant stirring rate (360 rpm). The sample volume was 500 cm^3 and the temperature was controlled with an error of $\pm 0.1^0$C. A magnetic stirrer was used during all experiments (RIVA-04.4, RIVA-STAL, Ukraine) and a centrifuge (RC-6, Dastan, Russia) operated at 1000 g. The amount of water for degumming was 1%. The amount of acids was 0.1–0.2%. Duration of degumming was 15 min at a temperature of 60^0C. After degumming, the mixture was cooled to room temperature, exposure was continued for 60 min. The mixture was separated in a centrifuge for 10 minutes to obtain two phases: degumming oil and wet gum.

The following acids were used for acid degumming: citric, succinic, ascorbic acids in powder form, phosphoric acid (80% solution), and lactic acid (40% solution).

To determine the content of phospholipids in oils, an express analyzer of phospholipids AMDF-1A (MERA, Russia) was used. The range of measurements of the mass fraction of phospholipids

(in terms of stereooleocytin) in sunflower oil was 0.02–2.0. The relative error of measurements (p=0.95) in the ranges of mass fraction (0.02–2.0)% was on average 8.5%.

The acid value of oils was determined according to the official method of AOCS Cd 3a-63 (AOCS, 1997). The peroxide number was determined according to the official AOCS method Cd 8b-90 (AOCS, 2017). The amounts of calcium and magnesium were determined by inductively coupled plasma (ICP) optical emission spectroscopy by the official method AOCS Ca 17-01 (AOCS, 1997).

Deodorization was performed under laboratory conditions in the following way. The degumming oil after separation of the wet gum was washed with distilled water to remove acid residues after acid degumming. The separation of the oil-wash water phases was performed on a separating funnel to reach a neutral pH of the wash water. The oil was then placed in a 250 cm^3 flask for deodorization, heated to 240^{0}C and kept at atmospheric pressure for 2 hours. The sample volume was 150 cm^3; the temperature was controlled with an error of ±0.1^{0}C. Stirring was performed using a magnetic stirrer at 120 rpm. Heating was carried out using a heating ring and the temperature was monitored using an electrical contact thermometer TPK-7-P (the measuring range being 0–300^{0}C). After deodorization, the oil was cooled and stored at 5±0.5^{0}C.

The content of 3-monochloropropanediol (3-MCPD) and glycidol was determined by gas-liquid chromatography using an Agilent 7890V/5977B gas-liquid chromatography-mass spectrometer with an automated sample preparation system based on MPS Robotic (ISO 18363-1:2015 (modified)).

All measurements were repeated three times. The significance of the differences between the average values of all measurements was determined at p=0.05 (i.e. 5%).

Results and discussion

The efficiency of degumming, i.e. the final amount of phospholipids in degumming oil, is influenced not only by the nature of degumming agent, but also by the characteristics of the degumming process, namely: the initial amount of phospholipids in oil, their fractional composition, degree of interaction between oil phases–degumming agent, duration, temperature degumming, and a method of separating the phases. Therefore, it is possible to compare the results of different methods of degumming only based on the same initial sample and under the same conditions of degumming.

The results of comparative degumming are given in Table 2. The amount of water for degumming was 1%, and the amounts of phosphoric and citric acids were 0.1% and 0.2%, respectively, which approximately close to the amounts commonly used in industry. The content of calcium and magnesium as the main metals that are part of the NHPL was also determined (Table 2).

Thus, as a result of aqueous degumming, about 88% of phosphorus-containing substances were removed. Brevedan et al. [11] reported the removal of 83% of phospholipids as a result of aqueous degumming of sunflower oil.

The efficiency of acid degumming by phosphoric and citric acids is close to 95% and 94% of the extracted phospholipids, respectively.

The most modern and effective method of degumming is enzyme degumming [12]. It allows reducing the phosphorus content to 10–25 mg kg^{-1} and even lower. However, enzymes are expensive, the duration of enzymatic degumming is several hours (from 2 to 8 and above), and the process requires a very thorough mixing of phases. Most importantly, a final phosphorus content of less than 0.05% is required only if the stage of physical refining is performed after degumming. In other cases, after the degumming stage, chemical neutralization is performed, which also removes phospholipids; the final phosphorus content is approximately the same low values as after careful enzymatic degumming [13]. Therefore, in our opinion, it is advisable to use acid degumming in the refining cycle, including alkaline neutralization.

The most effective metal ions in the NHPL complex are removed by citric acid (residual content of calcium and magnesium in degumming oil is

Table 2

Influence of water, phosphoric and citric acids on the content of phospholipids in hydrated oil and on the content of calcium and magnesium ions

Oil sample	The content of phospholipids in the oil, in terms of stereooleocytin, %	Content of Ca, mg kg^{-1}	Content of Mg, mg kg^{-1}
Pressed crude sunflower oil	0.541±0.0130	29.7±2.0	19.5±1.8
Oil after water degumming	0.065±0.0036	11.3±1.2	6.8±1.3
Oil after degumming with phosphoric acid	0.033±0.0049	6.9±1.6	3.3±1.5
Oil after degumming with citric acid	0.029±0.0054	5.2±1.2	2.1±1.4

5.2 mg kg^{-1} and 2.1 mg kg^{-1}, respectively) due to its ability to form complex compounds. The logarithm of the stability constants of complex compounds of citric acid with calcium and magnesium is 4.84 and 3.96, respectively (at 25°C and ionic strength of 0–0.2 mol L^{-1}) i.e. citric acid forms more stable complexes with NHPL metals than phosphatidic, converting them into a hydrophilic form. This is due to the low final content of phospholipids in the oil after degumming with citric acid (Table 2).

The removal of metals from oils is associated not only with a decrease in residual phosphorus, but also with the oxidative stability of oils. It is known that the strongest catalysts for lipid oxidation are metals of variable valence. Therefore, the oil after acid degumming is more stable to oxidative stress. It is safer and more environmentally friendly to use food acids for hydration.

The complexing constants of different food acids with metals (pK) are different. Therefore, it is advisable to analyze the results of degumming with mixtures of food acids to increase the efficiency of NHPL removal from oils. Based on the above data, we decided to use citric acid as the basic acid. The results were compared with the data on degumming with individual food acids (Table 3). The amount of degumming agents to obtain data that can be compared (significant values of phospholipids in degumming oil with less study error) was reduced to 0.1% relative to the oil.

Lactic acid turned out to be the worst degumming agent. It practically did not increase the efficiency of degumming (as compared with water degumming). The best results were obtained with succinic acid and a mixture of succinic and citric acid.

The synergistic effect of mixtures of citric acid with other food acids on the extraction of phospholipids is explained by various constants of complexation of the studied food acids with calcium, magnesium, iron, etc.

The combination of citric and ascorbic acids proved to be quite effective. Ascorbic acid is also a strong antioxidant [14] and its presence in lecithin will positively affect the stability of this product against oxidative damage. The disadvantage of using ascorbic and succinic acids is their high cost as compared with citric or phosphoric acids.

For many oil companies, the degumming stage is the final stage and degumming oil is the final product. Therefore, it is necessary to establish the effect of acid degumming on those quality indicators of sunflower oil that change during this process (Table 4).

No significant increase in acid value was detected after acid degumming. A decrease in peroxide value when using acids during degumming (from 3.04 to 2.36 and 2.05 for phosphoric acid and citric acid, respectively) is due to the destruction of peroxides during contact with acid molecules [15].

The effect of the degumming method on the formation of 3-MCPD-esters and esters of glycidyl as a result of laboratory deodorization was characterized. The results are given in Table 5.

The results revealed a contribution of lowering the pH during degumming to the formation of

Table 3

The effect of food acids and their mixtures on the excretion of phospholipids from sunflower oil (water content 1%)

The composition of the degumming agent	The content of phospholipids in the oil, in terms of stereooleocytin, %	The composition of the degumming agent	The content of phospholipids in the oil, in terms of stereooleocytin, %
Citric acid (0.1%)	0.048±0.0037		
Citric acid (0.05%)+succinic acid (0.05%)	0.034±0.0028	Succinic acid 0.1%	0.045±0.0045
Citric acid (0.05%)+lactic acid 40 % (0.1%)	0.052±0.0042	Lactic acid (40% solution) 0.2%	0.060±0.0051
Citric acid (0.05%)+ascorbic acid (0.05%)	0.040±0.0039	Ascorbic acid 0.1%	0.053±0.0039

Table 4

Qualitative indicators of sunflower oil after degumming

Oil sample	Acid value, %	Peroxide value, mmol ½O/kg	Color, mg of I_2
Pressed crude sunflower oil	0.31±0.011	3.04±0.31	10
Oil after water degumming	0.27±0.009	3.16±0.27	5
Oil after degumming with phosphoric acid	0.31±0.013	2.36±0.22	5
Oil after degumming with citric acid	0.29±0.015	2.05±0.21	5

Table 5

The effect of water and acid degumming on the content of 3-MCPD-E and GE in deodorized sunflower oil

Oil sample	Mass fraction of 3-monochloropropanediol (3-MCPD), μg kg^{-1}	Mass fraction of esters of glycidyl fatty acids in terms of glycidol, μg kg^{-1}
Oil after water degumming, deodorized	Less than 100	Less than 100
Oil after degumming with phosphoric acid, deodorized	470±30	200±30
Oil after degumming with citric acid, deodorized	680±30	310±30

increased amounts of 3-MCPD esters and glycidol during the deodorization of sunflower oil. The effect of citric acid is more noticeable, which is explained by the introduction of more H^+ ions, the amount of phosphoric and citric acids in degumming being 0.1% and 0.2%, respectively. In general, it should be noted that acid degumming does not lead to exceeding the maximum allowable levels (1250 μg kg^{-1} for sunflower oil [7]). It is also important that degumming is not the final stage before deodorization. Stages of neutralization and adsorption purification also affect the formation of esters of 3-MCPD and glycidyl [8,10].

Conclusions

Aqueous acid solutions are effective degumming agents that are able to remove approximately 95% of phospholipids from sunflower oil. The content of calcium and magnesium in the oil when using citric acid as a degumming agent is reduced by 83% and 89%, respectively.

In our opinion, this result proves the feasibility of using acid degumming in comparison with other more effective but more expensive and complex methods of degumming (enzymatic, molecular sieves, etc.).

Based on the obtained data, we can assert that the most effective degumming agents are citric, succinic and ascorbic acids. The use of mixtures of food acids further increases the efficiency of degumming. Food acids are safe substances approved for use in foods that are easy to dissolve, dispense, etc.

Degumming affects the formation of 3-MCPD-esters and glycidyl esters. The presence of acids in the processing of oils (i.e. H^+-ions) can be attributed to the precursors of the formation of esters of 3-MCPD and glycidol. On the contrary, water degumming does not increase the content of these esters in deodorized sunflower oil and its implementation can be recommended as one of the ways to prevent the formation of these toxic substances during deodorization.

REFERENCES

1. *Assessment* of water degumming and acid degumming of mixed algal oil / Paisan S., Chetpattananondh P., Chongkhong S. // J. Environ. Chem. Eng. – 2017. – Vol.5. – No. 5. – P.5115-5123.

2. *Phospholipids* of rapeseeds and rapeseed oils: factors determining their content and technological significance – a review / Ambrosewicz-Walacik M., Tanska M., Rotkiewicz D. // Food Rev. Int. – 2015. – Vol.31. – No. 4. – P.385-400.

3. *Dijkstra A.J.* Questions begging for answers (Part I) – water degumming // Lipid Technol. – 2016. – Vol.28. – No. 10-11. – P.165-167.

4. *Dijkstra A.J.* About water degumming and the hydration of non-hydratable phosphatides. // Eur. J. Lipid Sci. Technol. – 2017. – Vol.119. – No. 9. Article No. 1600496.

5. *Gunstone F.D., Harwood J.L.* The lipid handbook. – 3rd ed. – Boca Raton: CRC Press 2007. – 1772 p.

6. *EFSA CONTAM* Panel (EFSA Panel on Contaminants in the Food Chain), 2016. Scientific opinion on the risks for human health related to the presence of 3- and 2-monochloropropanediol (MCPD), and their fatty acid esters, and glycidyl fatty acid esters in food // EFSA J. – 2016. – Vol.14. – No. 4426.

7. *European* Commission. Amending Regulation (EC) 1881/2006 as regards maximum levels of glycidyl fatty acid esters in vegetable oils and fats, infant formula, follow on formula and foods for special medical purposes intended for infants and young children. Available from: https://eur-lex.europa.eu/eli/reg/2018/290/oj.

8. *Effects* of degumming and bleaching on 3 MCPD esters formation during physical refining / Ramli M.R., Siew W.L., Ibrahim N.A., Hussein R., Kuntom A., Razak R.A.A., Nesaretnam K. // J. Am. Oil Chem. Soc. – 2012. – Vol.88. – No. 11. – P.1839-1844.

9. *Mitigation* strategies for the reduction of 2- and 3-MCPD esters and glycidyl esters in the vegetable oil processing industry / Oey S.B., van der Fels Klerx H.J., Fogliano V., van Leeuwen S.P.J. // Compr. Rev. Food Sci. Food Saf. – 2019. – Vol.18. – No. 2. – P.349-361.

10. *The effects* of physical refining on the formation of 3-monochloropropane 1,2 diol esters in relation to palm oil minor components / Zulkurnain M., Lai O.M., Latip R.A., Nehdi I.A., Ling T.C., Tan C.P. // Food Chem. – 2012. – Vol.135. – No. 2. – P.799-805.

11. *Changes* in composition and quality of sunflower oils during extraction and degumming / Brevedan M.I.V., Carelli A.A, Crapiste G.H. // Grasas Aceites (Seville). – 2000. – Vol.51. – No. 6. – P.417-423.

12. *Sein A., Hitchman T., Dayton C.L.* Enzymes in vegetable oil degumming processes // Ind. Enzyme Appl. – 2019. – 416 p.

13. *A novel* process for simultaneous degumming and deacidification of soybean, canola and sunflower oils by tetrabutylphosphonium phosphate ionic liquid / Adhami K., Asadollahzadeh H., Ghazizadeh M. // J. Ind. Eng. Chem. – 2019. – Vol.76. – No. 25. – P.245-250.

14. *Ascorbic* acid: the chemistry underlying its antioxidant properties / Njus D., Kelley P.M., Tu Y.-J., Schlegel H.B. // Free Radical Biol. Med. – 2020. – Vol.159. – No. 1. – P.37-43.

15. *Demidov I.N., Gusak V.A.* Razrushenie gidroperoksidov podsolnechnogo masla. Bulletin of NTU «KhPI». – 2008. – Vol.3. – P.54-57.

Received 22.03.2021

ПОРІВНЯННЯ СПОСОБІВ КИСЛОТНОГО ГІДРАТУВАННЯ ТА ЇХ ВПЛИВ НА УТВОРЕННЯ 3-MCPD-ЕФІРІВ І ЕФІРІВ ГЛІЦИДОЛУ ПРИ ДЕЗОДОРУВАННІ СОНЯШНИКОВОЇ ОЛІЇ

А.О. Демидова, І.В. Левчук, О.Ф. Аксьонова, С.М. Мольченко, І.М. Демидов

Гідратування – перша зі стадій перероблення рослинних олій, її мета – видалення фосфоліпідів. У статті порівнюються результати гідратування з фосфорною та лимонною кислотами, їх вплив на вилучення з олій іонів кальцію та магнію – основних компонентів негідратованих фосфоліпідів. Показана доцільність поєднання лимонної і бурштинової кислот (кінцевий вміст фосфоліпідів в олії 0,034% у порівнянні з 0,048% для лимонної кислоти) та лимонної і аскорбінової кислот (кінцевий вміст фосфоліпідів у олії 0,040%). Досліджено ефект кислотного гідратування на утворення 3-MCPD-ефірів і гліцидилових ефірів. Вміст гліцидилових ефірів після гідратування з лимонною кислотою становив 310 мкг/кг, з фосфорною – 200 мкг/кг. Після гідратування лимонною кислотою вміст 3-MCPD-ефірів у дезодорованій олії становив 680 мкг/кг, фосфорною кислотою – 470 мкг/кг. Навпаки, водне гідратування не збільшує вміст цих ефірів у дезодорованій соняшниковій олії (менше 100 мкг/кг), і його застосування може бути рекомендовано як один зі способів запобігання утворенню цих токсичних речовин під час дезодорування олій.

Ключові слова: кислотне гідратування, соняшникова олія, фосфоліпіди, MCPD ефіри, гліцидилові ефіри.

COMPARISON OF ACID DEGUMMING METHODS AND THEIR INFLUENCE ON THE FORMATION OF 3-MCPD-ESTERS AND GLYCIDYL ESTERS IN SUNFLOWER OIL DEODORIZATION

A. Demydova [a, *], I. Levchuk [b], O. Aksonova [c], S. Molchenko [a], I. Demidov [a]

[a] National Technical University «Kharkiv Polytechnic Institute», Kharkiv, Ukraine

[b] Ukrmetrteststandart, Kyiv, Ukraine

[c] Kharkiv State University of Food Technology and Trade, Kharkiv, Ukraine

[*] e-mail: ademidova2016@gmail.com

Degumming is the first stage in processing of vegetable oils, and it is aimed at removing phospholipids. The article compares the results of degumming by phosphoric and citric acids, their effects on the extraction of calcium and magnesium ions from oils, these ions being the main components of nonhydratable phospholipids. We showed the appropriateness of combining citric and succinic acids (the final content of phospholipids in oil was 0.034%, whereas it was equal to 0.048% when citric acid was used) and citric and ascorbic acids (the final content of phospholipids in oil was 0.040%). We studied the effect of acid degumming on the formation of 3-MCPD-esters and glycidyl esters. The content of glycidyl esters after degumming with citric acid and phosphoric acid was 310 μg kg^{-1} and 200 μg kg^{-1}, respectively. After degumming with citric acid and phosphoric acid, the content of 3-MCPD-esters in the deodorized oil was 680 μg kg^{-1} and 470 μg kg^{-1}, respectively. On the contrary, aqueous degumming does not increase the content of these esters in the deodorized sunflower oil (the content is less than 100 μg kg^{-1}) and its implementation can be recommended as one of the ways to prevent the formation of these toxic substances during deodorization.

Keywords: acid degumming; sunflower oil; phospholipids; MCPD-esters; glycidyl esters.

REFERENCES

1. Paisan S, Chetpattananondh P, Chongkhong S. Assessment of water degumming and acid degumming of mixed algal oil. *J Environ Chem Eng.* 2017; 5(5): 5115-5123. doi: 10.1016/j.jece.2017.09.045.

2. Ambrosewicz-Walacik M, Tanska M, Rotkiewicz D. Phospholipids of rapeseeds and rapeseed oils: factors determining their content and technological significance – a review. *Food Rev Int.* 2015; 31(4): 385-400. doi: 10.1080/87559129.2015.1022831.

3. Dijkstra AJ. Questions begging for answers (Part I) – water degumming. *Lipid Technol.* 2016; 28: 165-167. doi: 10.1002/lite.201600043.

4. Dijkstra AJ. About water degumming and the hydration of non-hydratable phosphatides. *Eur J Lipid Sci Technol.* 2017; 119: 1600496. doi: 10.1002/ejlt.201600496.

5. Gunstone FD, Harwood JL. *The lipid handbook*, 3rd ed. Boca Raton: CRC Press; 2007. 1472 p. doi: 10.1201/9781420009675.

6. EFSA CONTAM Panel (EFSA Panel on Contaminants in the Food Chain), 2016. Scientific opinion on the risks for human health related to the presence of 3- and 2-monochloropropanediol (MCPD), and their fatty acid esters, and glycidyl fatty acid esters in food. *EFSA J*. 2016; 14(5): 4426. doi:10.2903/j.efsa.2016.4426.

7. European Commission. *Amending Regulation (EC) 1881/2006 as regards maximum levels of glycidyl fatty acid esters in vegetable oils and fats, infant formula, follow-on formula and foods for special medical purposes intended for infants and young children*. Available from: https://eur-lex.europa.eu/eli/reg/2018/290/oj.

8. Ramli MR, Siew WL, Ibrahim NA, Hussein R, Kuntom A, Razak RA, et al. Effects of degumming and bleaching on 3-MCPD esters formation during physical refining. *J Am Oil Chem Soc*. 2012; 88: 1839-1844. doi: 10.1007/s11746-011-1858-0.

9. Oey SB, van der Fels-Klerx H, Fogliano V, van Leeuwen SP. Mitigation strategies for the reduction of 2- and 3-MCPD esters and glycidyl esters in the vegetable oil processing industry. *Compr Rev Food Sci Food Saf*. 2019; 18: 349-361. doi: 10.1111/1541-4337.12415.

10. Zulkurnain M, Lai OM, Latip RA, Nehdi IA, Ling TC, Tan CP. The effects of physical refining on the formation of 3-monochloropropane-1,2-diol esters in relation to palm oil minor components. *Food Chem*. 2012; 135(2): 799-805. doi: 10.1016/j.foodchem.2012.04.144.

11. Brevedan MIV, Carelli AA, Crapiste GH. Changes in composition and quality of sunflower oils during extraction and degumming. *Grasas Aceites (Seville)*. 2000; 51(6): 417-423. doi: 10.3989/gya.2000.v51.i6.460.

12. Sein A, Hitchman T, Dayton CL. Enzymes in vegetable oil degumming processes. In: Vogel A, May O, editors. *Industrial enzyme applications*. 2019. doi: 10.1002/9783527813780.ch4_2.

13. Adhami K, Asadollahzadeh H, Ghazizadeh M. A novel process for simultaneous degumming and deacidification of soybean, canola and sunflower oils by tetrabutylphosphonium phosphate ionic liquid. *J Ind Eng Chem*. 2019; 76: 245-250. doi: 10.1016/j.jiec.2019.03.048.

14. Njus D, Kelley PM, Tu YJ, Schlegel HB. Ascorbic acid: the chemistry underlying its antioxidant properties. *Free Radical Biol Med*. 2020; 159(1): 37-43. doi: 10.1016/j.freeradbiomed.2020.07.013.

15. Demidov IN, Gusak VA. Razrushenie gidroperoksidov podsolnechnogo masla [The destruction of hydroperoxides sunflower oil]. *Bulletin of NTU «KhPI»*. 2008; 3: 54-57. (*in Russian*).