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N.E. Alzhaxina, A.B. Dalabaev, K.Z. Zhunussova,*
K.A. Baigenzhinov, N.Zh. Muslimov

Astana branch of «Kazakh Research Institute of Processing and Food Industry» LLP
Nur-Sultan, Kazakhstan
nazjomka@mail.ru, dalabaev_askhat@mail.ru, zhunusovakz@mail.ru,*
baigenzhinov@inbox.ru, n.muslimov@inbox.ru

TYPES OF CONTAMINANTS AND THEIR CONTENT IN VEGETABLE OILS

Abstract

The article discusses the groups of pollutants most commonly found in the food industry. The results of the content of pollutants in vegetable oils are also presented, which indicates a fairly wide range of concentrations of monoglycerides, diglycerides and triglycerides. Various technological parameters of the deodorization process lead to such a wide range of values and require further research and development of technologies aimed at reducing the content of these compounds. The classification of pollutants is presented, individual groups of pollutants are considered in more detail, and the main measures for the prevention and prevention of the content of pollutants in food products are given. Therefore, knowledge about impurities and pollutants in food is of great practical importance and is considered an important food safety issue. The presence of impurities in food products that have no nutritional and biological value or are completely toxic threatens human health. Thus, in order to reduce the risks associated with the consumption of these compounds, it is necessary to develop effective technological methods for reducing the content of pollutants that can be used not only in production, but also on an industrial scale. And one of the important processes of reducing the content of pollutants in vegetable oils is the improvement of the oil purification process using various solvents.

Key words: *glycidyl ethers, vegetable oils, contaminants, deodorization, food products, mycotoxins, refining process, impurities.*

Introduction

Every person consumes food on a daily basis and must be sure that they do not pose a danger to either his health or the health of his loved ones. The growing globalization of food markets poses more and more challenges to the society responsible for ensuring the safety of food products, including fat and oil. One of such tasks is to minimize the content of pollutants in vegetable oils, which poses a potential risk to human health

Up to 70% of chemical compounds released in large quantities as a result of industrial development, chemicalization of agriculture, through the food chain enters the animal body with feed, and then enters the human body with finished products. In addition to contaminants-pollutants, special attention is paid to food additives associated with technological necessity. Therefore, knowledge about pollutants is of great practical importance [1].

As you know, the problem of the negative impact of environmental pollution on human health in recent years has become more acute, which has outgrown national boundaries. The intensive development of industry, the chemicalization of agriculture and the environment provokes the appearance of large quantities of chemical compounds that are harmful to the human body. At the same time, there are scientific and technological solutions that make it possible to regulate the content of these harmful substances and bring their concentration to safe levels. This applies to both the entire environment and individual food products. It is known that in the process of eating, a significant part of foreign substances, for example, heavy metals, can enter the human body [2].

The formation of chemical compounds, toxic carcinogens during food processing is one of the important safety problems of the food industry. Among these carcinogenic chemical compounds, special attention is paid to glycidyl ether or so-called contaminants that can be formed during the refining of vegetable oils, especially in palm oil, as well as in some processed foods. These substances pose a danger to the health of some population groups due to their toxic and carcinogenic properties.

Thus, in order to reduce the risks associated with the consumption of such chemical compounds, it is necessary to develop effective technological methods for reducing the content of glycidyl esters or precursors of contaminants that can be used for production purposes. It is also necessary to establish clear mechanisms for the formation of contaminants in vegetable oils and thereby reduce their content by improving the process of refining and deodorization of vegetable oils using various solvents [3].

Methods and materials

Vegetable oils were the object of the research. The research was carried out in accordance with GOST 30418-96 «Vegetable oils. Method for determination of fatty acid content». The method is based on the conversion of monoglycerides, diglycerides and triglycerides of fatty acids into methyl (ethyl) esters of fatty acids. The method is applicable in the range of mass fractions of fatty acids 0.1-100%. The studies were carried out using a UV-1900i bi-beam spectrophotometer.

When studying the content of mycotoxins in vegetable oils, GOST 30711-2001 «Food products. Methods for detecting and determining the content of aflatoxins B1 and M1».

To determine glycidyl esters in terms of glycidol, the method of gas chromatography with mass-selective detection in SIM mode (selective ion monitoring) was used according to the procedure described in ISO 18363-1:2015 «Animal and vegetable fats and oils». Determination of the content of fatty acid esters of monochloropropanediols (MCPD) and glycidol using gas chromatography with GC/MS mass spectrometric detection, also a method using rapid alkaline transesterification and measurement of 3-MCPD content and differential measurement of glycidol content.

Results and discussion

There are the following groups of pollutants most commonly found in the food industry:

Mycotoxins - are toxic metabolic products of molds that form on the surface of food and feed. These toxins are able to penetrate into the food by diffusion. Mycotoxins have a toxic effect on animals, birds and humans, causing mycotoxicosis. They are resistant to high temperatures and sunlight, do not die during long periods of storage and canning. Of the molds growing on food, approximately 60-75% should be considered toxic. The exceptions are products made using specially selected strains of mold - for example, Roquefort cheese with the noble mold Penicillium roqueforti. Today, over 400 mycotoxins are known, but the most famous are aflatoxins and patulin. Patulin, as a rule, is detected in fruit processed products - juices, fruit purees and jams, which is associated with a violation of technology and the use of non-standard raw materials [4].

Nitrates and nitrites are found in plants as normal metabolites or accumulate as a result of inappropriate use of nitrogen fertilizers. Excessive use of nitrogenous fertilizers leads to the accumulation of these contaminants, amine and amide compounds, and the formation of a highly toxic compound - N-nitrosoamines. Our body does not assimilate compounds of nitric and nitrous acids and removes them very poorly, therefore, their intake into the body leads to disruption of biochemical processes in the form of toxic and carcinogenic manifestations. products to preserve the red color. When salted, red meat dye - myoglobin, which turns into gray-brown metmyoglobin during boiling, reacts with nitrites, forming red nitrosomyoglobin. This compound, which gives meat products the typical red color of salted meat, does not change during boiling and is more resistant than myoglobin to atmospheric oxygen. Along with the stabilization of the color, nitrates and nitrites together with table salt have a preservative effect [5].

Preservatives and antioxidants are used to extend the shelf life of food by slowing down chemical and biochemical processes. The action of preservatives is primarily aimed at inhibiting the growth of microorganisms. But the human gastrointestinal tract also contains beneficial microorganisms (bifidobacteria) that live in the large intestine. By hydrolyzing hemicellulose, they supply our body with other biologically active monosaccharides. Long-term use of food products with preservatives leads to inhibition of intestinal bifidobacteria and contributes to the development of dysbiosis in humans. This is a fairly widespread problem: there are cases when the prescribed drugs did not have the desired effect on the pathogenic microflora due to their developed resistance to preservatives. Organic acids and their derivatives, inorganic compounds, as well as special groups of preservatives are used as preservatives [6].

The physicochemical parameters of the initial vegetable oils were studied. Such indicators as acid value, peroxide value, color value, degree of transparency, mass fraction of moisture and volatile substances, mass fraction of phosphorus-containing substances, mycotoxin content were determined. All indicators were determined by standard methods according to TR CU 024/2011. The results of the study are presented in table 1.

Table 1 - Physico-chemical parameters of the starting oils

Indicator name	Indicator value						
	RSO	URSO	RRO	URLO	RCO	UROO	PO
Density, kg/m3 at 20 °C	926	916	918	940	920	914	923
Refractive index at 20°C	1,475	1,473	1,472	1,480	1,471	1,466	1,454
Viscosity at 20 °C, Pa*s	0,0598	0,0546	0,0766	0,0527	0,0657	0,0713	-
Acid value, mg KOH/g	0,3	1,8	0,2	1,9	1,0	4,6	0,5
Peroxide value, mmol of active oxygen/kg	4,7	9,5	6,1	2,5	5,9	9,8	0,8
Color value, mg of iodine	1	9	2	45	4	35	1
Degree of transparency, fem	1	2	1	2	1	2	1
Mass fraction of moisture and volatile substances, %	0,01	0,05	0,01	0,01	0,1	0,2	0,09
Mass fraction of phosphorus-containing substances, %	-	0,15	-	0,03	-	0,02	-
Mycotoxin content, mg/kg (aflotoxin B1)	-	0,005	0,005	0,004	-	0,005	-

The studied oils according to physico-chemical parameters comply with the safety requirements of TR CU 021/2011 and TR CU 024/2011. According to physico-chemical indicators, all oils have an acid value (0,2-4,6) and a peroxide value (0,8-9,8) within the normal range. However, the presence of free fatty acids in the oils can lead to the formation of glycidyl esters. The indicators of acid and peroxide values reflect the presence of free fatty acids in vegetable oils.

Glycidyl ethers are formed during refining in all vegetable oils, without exception: in sunflower, corn, palm, olive, etc. (table 2).

Table 2 - Content of contaminants in vegetable oils

Name of the oil	Monoglyceride content,%	Diglyceride content,%	Triglyceride content,%
Soybean oil	-	1,0	97,9
Cottonseed oil	-	3,1	95,0
Palm oil	-	5,8	93,1
Corn oil	-	2,8	95,8
Sunflower oil	-	2,0	95,6
Safflower oil	-	2,1	96,0
Olive oil	0,2	5,5	93,3
Rapeseed oil	0,1	0,8	96,8

As can be seen from table 2, in the oilseed raw materials glycidyl ether contaminants are absent, but it contains precursors (precursors) of these compounds. During the ripening period, enzymatic processes take place in the seed: the lipase enzyme breaks down triglycerides of fatty acids to diglycerides and monoglycerides, which are subsequently converted to glycidyl ethers and monochloropropanediols during high-temperature processing (> 230 ° C), respectively. Formation of glycidyl esters occurs after intramolecular rearrangement, removal of fatty acid and epoxide.

In the process of industrial production of food products, changes in the quality indicators of the product and its composition occur, as a result of which various compounds (contaminants) can be unintentionally formed. Some of them have no effect on human health, others may affect the body to a greater or lesser extent.

The presence of partial acylglycerols, such as diacylglycerols (DAG) and monoacylglycerols (MAG) is associated with the formation of glycidyl esters (GE). The proposed mechanism involves intramolecular rearrangement, which leads to the elimination of fatty acids. In addition, cyclic acyloxonium ions can form under deodorization conditions and initiate the formation of contaminants. In addition, it has been suggested that the mutual conversion between 2- MCPD and 3-MCPD through an intermediate compound of glycidyl esters can occur at high temperatures. Also, the formation of 3-MCPD can be formed as a result of a reaction mediated by free radicals [7].

The available data on the content of contaminants in food products are mainly limited to refined edible oils and oil-based food products. Precursors of contaminants are formed at the stage of deodorization of oil processing processes. Glycidyl esters are also found in various refined oils and fats, such as palm oil, rice oil, soybean oil and corn oil. Among them, rice oil and palm oil are the most susceptible to the formation of contaminants that exceed 30 mg/kg of oil. The content of diacylglycerol precursors (DAG) in glycidyl esters is especially high in oil, varying from 4% to 12%, on average about 6.5% in palm oil. This fact also explains the relatively high concentrations of glycidyl esters in palm oil, while the actual reason for their high content in rice oil has not yet been discovered. Crude or unrefined oils and fats, such as extra virgin olive oil, do not contain glycidyl esters or simply do not contain traces of them [8].

The amount of glycidyl esters (GE) in oil-based foods is due to the addition of contaminated oils and fats, as well as high temperatures in production processes. The appearance of GE in refined edible oils has attracted considerable attention regarding the mechanism of formation, including the precursors of GE and the factors influencing the formation of GE. The stage of deodorization in the process of oil processing significantly affects the formation of GE. In initial studies, GE was considered as a pathway for the formation of 3-MCPD esters or their degradation. Subsequently, it was proposed that GE, as well as 3-MCPD esters, form an intermediate compound of the 1st acyloxonium ion and then rearrange through charge migration, eventually forming GE. However, it was also taken into account that GE and 3-MCPD esters can be formed in different ways, depending on the applied temperature and reaction time. In this article, attention is focused on 3 aspects of GE formation from the macroscopic and microscopic points of view, that is, on the precursors and factors influencing the formation of GE for the macroscopic slice, and on the reactive mechanisms for the microscopic slice [9].

The following methods can be used to reduce the content of contaminants in vegetable oils.

Thus, the effectiveness of reducing the content of contaminants can be achieved by washing unrefined vegetable oil with polar solvents, such as water or a water-alcohol mixture, in order to remove polar chlorine-containing compounds from the oil. Due to the possibility of the transformation of polar chlorine-containing compounds into non-polar ones during the sterilization of fruits, it is proposed to remove the indicated chlorine donors not from the obtained unrefined oil, but from the pulp.

Analysis of the physico-chemical parameters of unrefined oils showed that the acid number of oils varies in the range of 1,8-4,6 mg KOH/g. However, in unrefined olive oil (UOO), the acid number index exceeds the norm of 4,0 mg KOH/g. This indicates that it contains free fatty acids and the oil is oxidized. The value of the peroxide number of oils is in the range of 2,5-9,8 mmol of active oxygen/kg, which corresponds to the norms of regulatory and technical documentation. The color number of olive oil exceeds the norm of 15 mg of iodine. The degree of transparency, the mass fraction of moisture and volatile substances, the mass fraction of phosphorus-containing substances and the content of mycotoxins, which are indicators reflecting the microbiological safety of oils, comply with the norms of regulatory and technical documentation. The results of studies of the physico-chemical parameters of refined oils are presented in Table 3.

Table 3 - Physico-chemical parameters of refined oils

Indicator name	Indicator value							
	RSO	Standard	RRO	Standard	RCO	Standard	SO	Standard
Acid value, mg KOH/g	0,3	0,4	0,2	0,4	1,0	0,35	0,5	0,2
Peroxide number, mmol of active oxygen/kg	4,7	10	6,1	10	5,9	10	0,8	0,9
Color number, mg of iodine	1	10	2	30	4	18	1	30
Degree of transparency, fem	1	2	1	2	1	2	1	2
Mass fraction of moisture and volatile substances, %	0,01	0,1	0,01	0,1	0,1	0,1	0,09	0,1
Mass fraction of phosphorus-containing substances, %	-	-	-	-	-	-	-	-
Mycotoxin content, mg/kg (aflatoxin B1)	-	-	0,005	0,005	-	0,005	-	0,005

The results of studies of the physico-chemical parameters of refined oils showed that the indicator of the acid number of oils varies in the range of 0,2-0,5 mg KOH/g. However, in refined corn oil (RCO) and sunflower oil (SO), this indicator of the acid number exceeds the norm of 0,35 and 0,2 mg KOH/g. This indicates that they contain free fatty acids, which ultimately can lead to the formation of glycidyl esters. The value of the peroxide number of oils is in the range of 0,8-5,9 mmol of active oxygen/kg, which corresponds to the norms of regulatory and technical documentation.

An additional reduction in the content of glycidyl ethers and related compounds can be facilitated by the use of soils with a low salt content for growing oilseeds, the use of chlorine-free fertilizers, irrigation water, herbicides and insecticides. In addition, to reduce the content of free fatty acids in vegetable oils, it is rational to harvest the crop as soon as the first ripe bunches are found, and also, if possible, shorten the time interval between harvesting and the extraction of oil from seeds [10, p. 803].

Another effective way to reduce the thermal load on the oil and, most importantly, virtually eliminating the formation of glycidyl esters, is molecular distillation of oils instead of deodorization or in combination with deodorization under mild conditions. The biocatalytic method is also promising, which allows using enzymatic processes to remove esters from refined oils [11].

Thus, in order to reduce the content of glycidyl ethers in vegetable oils, it is advisable to act in 3 directions:

1) reduction of the content up to the complete elimination of precursors in oilseeds and unrefined oils;

2) adjustment of the conditions for the extraction of oils and refining processes with the possible inclusion of additional stages of refining in the full cleaning cycle;

3) reduction of glycidol content in refined oils using appropriate sorbents or by enzymatic methods [12].

The formation of contaminants can be minimized in several ways:

1. By optimizing the deodorization process while reducing the heat load at $t<240^0$C, which will improve the safety characteristics of food products.

2. The use of two-stage deodorization (with a short-term treatment at a higher temperature, followed by a longer treatment at a reduced temperature) is used on an industrial scale as an effective risk reduction measure to achieve a minimum level of glycidyl esters in refined oils.

3. Contaminants can also be removed from refined edible oils in high vacuum at high temperature (260^0C), since they have the same volatility parameters as monoacylglycerides (MAG).

4. During post-bleaching with non-HCl activated bleach clay, glycidyl esters give very low levels (<0,5 ppm) and turn into monoacyglycerides (MAG). This is provided that post-deodorization is carried out at a low temperature ($\leq 230^0$C).

5. A reduction in the formation of glycidyl esters can be achieved by using the process of enzymatic esterification of free fatty acids into diacylglycerides (DAG) in raw or bleached palm oil. This will increase the overall oil yield during the refining process.

6. The process of chemical transesterification, followed by post-bleaching with non-HCl activated bleach clay and deodorization at moderate temperature ($<220^0$C), thanks to which refined edible oils with very low levels of glycidyl esters or contaminants can be obtained [13].

Employees of the Astana branch of the Research Institute of the Processing and Food Industry, in accordance with the program of the Ministry of Agriculture of the Republic of Kazakhstan, invert registration number BR10764977, are working to determine the content of glycidyl ethers in vegetable oils.

Conclusion

Based on the foregoing, the content of contaminants in vegetable oils, even at levels below hygienic standards, can affect the health of the population in the form of both carcinogenic and chronic non-carcinogenic effects. Protection of a person from the harmful effects of contaminants is effectively ensured by a barrier of hygienic standards and regulations, but as a result of their non-observance, acute and chronic poisoning and other health disorders can occur.

Currently, the overwhelming majority of agricultural manufacturers are seriously concerned about the problems of environmental safety of food and make great efforts to minimize the risk of contamination of feedstock. In order to obtain guaranteed clean raw materials for their production, they often organize their own, so-called organic-biological farming. Achieving this goal begins with a careful selection of farms with healthy fertile soil in ecologically clean areas, away from industrial zones and highways, taking into account the wind rose. Finally, all raw materials entering the plant are first checked by the laboratory for the presence of harmful substances in it and only after confirming their safety are they allowed into production [14].

Of course, the given example is not the only one of its kind, but it illustrates the possibility of producing clean products even in difficult modern conditions. To create environmentally friendly food products, it is necessary to assess the environmental conditions of their production at all stages of the biotechnological chain.

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Н.Е. Альжаксина*, А.Б. Далабаев, К.З. Жунусова,
К.А. Байгенжинов, Н.Ж. Муслимов
«Қазақ қайта өңдеу және тағам өнеркәсіптері ғылыми-зерттеу институты» ЖШС
Астана филиалы, Нур-Султан қ., Казахстан
nazjomka@mail.ru, dalabaev_askhat@mail.ru, zhunusovakz@mail.ru,*
baigenzhinov@inbox.ru, n.muslimov@inbox.ru

ӨСІМДІК МАЙЛАРЫНДАҒЫ КОНТАМИНАТТАРДЫҢ МӨЛШЕРІ ЖӘНЕ ОЛАРДЫҢ ТҮРЛЕРІ

Аңдатпа

Мақалада тамақ өнеркәсібінде жиі кездесетін ластаушы заттар топтары қарастырылады. Сондай-ақ, өсімдік майларындағы ластаушы заттардың нәтижелері ұсынылған, бұл моноглицеридтердің, диглицеридтердің және триглицеридтердің концентрациясының кең спектрін көрсетеді. Дезодорация процесінің әртүрлі технологиялық параметрлері осындай көптеген мәндерге әкеледі және осы қосылыстардың құрамын төмендетуге бағытталған технологияларды одан әрі зерттеу мен дамытуды қажет етеді. Ластаушы заттардың жіктелуі ұсынылған, ластаушы заттардың жекелеген топтары толығырақ қарастырылған, сонымен қатар Тамақ өнімдеріндегі ластаушы заттардың алдын-алу және алдын-алу бойынша негізгі шаралар келтірілген. Сондықтан Тамақ өнімдеріндегі қоспалар мен ластаушы заттар туралы білім үлкен практикалық маңызға ие және тамақ қауіпсіздігінің маңызды мәселесі болып саналады. Тағамдық және биологиялық құндылығы жоқ немесе толығымен улы болып табылатын тамақ өнімдерінде қоспалардың болуы адам денсаулығына қауіп төндіреді. Осылайша, осы қосылыстарды тұтынумен байланысты қауіптерді азайту үшін ластаушы заттардың құрамын төмендетудің тиімді технологиялық әдістерін жасау қажет, оларды тек өндірісте ғана емес, сонымен қатар өнеркәсіптік ауқымда да қолдануға болады. Өсімдік майларындағы ластаушы заттарды азайтудың маңызды процестерінің бірі-әртүрлі еріткіштерді қолдана отырып, майды тазарту процесін жақсарту.

Кілт сөздер: глицидил эфирлері, өсімдік майлары, ластаушы заттар, дезодорация, тамақ өнімдері, микотоксиндер, тазарту процесі, қоспалар.

Н.Е. Альжаксина*, А.Б. Далабаев, К.З. Жунусова,
К.А. Байгенжинов, Н.Ж. Муслимов
Астанинский филиал ТОО «Казахский научно-исследовательский институт
перерабатывающей и пищевой промышленности», г. Нур-Султан, Казахстан
nazjomka@mail.ru, dalabaev_askhat@mail.ru, zhunusovakz@mail.ru,*
baigenzhinov@inbox.ru, n.muslimov@inbox.ru

ВИДЫ КОНТАМИНАНТОВ И ИХ СОДЕРЖАНИЕ В РАСТИТЕЛЬНЫХ МАСЛАХ

Аннотация

В статье рассматриваются группы загрязняющих веществ, наиболее часто встречающиеся в пищевой промышленности. Также представлены результаты загрязняющих веществ в растительных маслах, что свидетельствует о широком спектре концентраций моноглицеридов, диглицеридов и триглицеридов. Различные технологические параметры процесса дезодорации приводят к таким многочисленным значениям и требуют дальнейшего изучения и разработки технологий, направленных на снижение содержания этих соединений. Предложена классификация загрязняющих веществ, подробно рассмотрены отдельные группы загрязняющих веществ, а также приведены основные меры по предупреждению и предотвращению загрязняющих веществ в пищевых продуктах. Поэтому знания о добавках и загрязняющих веществах в пищевых продуктах имеют большое практическое значение и считаются важной проблемой безопасности пищевых продуктов. Наличие примесей в пищевых продуктах, которые не имеют пищевой и биологической ценности или являются полностью токсичными, представляет угрозу для здоровья человека. Таким образом, для минимизации рисков, связанных с потреблением этих соединений, необходимо разработать эффективные технологические методы снижения содержания загрязняющих веществ, которые могут быть использованы не только в производстве, но и в промышленных масштабах. Одним из важных процессов снижения загрязняющих веществ в растительных маслах является улучшение процесса очистки масла с использованием различных растворителей.

Ключевые слова: глицидиловые эфиры, растительные масла, загрязняющие вещества, дезодорация, пищевые продукты, микотоксины, процесс очистки, добавки.