ХІМІЧНІ НАУКИ / ХИМИЧЕСКИЕ НАУКИ

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TEMPERATURE FACTOR AND SUNFLOWER OIL OXIDATION

В статье исследуются процессы, происходящие при принудительном термоокислении подсолнечного масла. Результаты, полученные в ходе исследования, показали большое влияние термоокисления. Индекс кислотности свежего подсолнечного масла увеличился в 13,7 раза и составил 2,46 мг КОН г$^{-1}$ жира для термоокисленного масла по сравнению с исходным значением 0,180 мг КОН г-1 жира. Термоокисление подсолнечного масла привело к значительному снижению индекса омыления, что свидетельствует о значительной степени полимеризации и приводит к увеличению вязкости исследуемого подсолнечного масла. Установлено, что применяемая обработка способствует как образованию вторичных карбонильных соединений, так и одновременному образованию гидропероксидов и триглицеридов, содержащих гидроксилированные группы. Накопление гидропероксидов и триацилглицеридов с гидроксильными функциями облегчило протекание реакций полимеризации, которые должны увеличивать вязкость термоокисленного исследуемого подсолнечного масла..

Ключевые слова: *образование, химический эксперимент, химия, виртуальная лаборатория, видеофрагменты.*

This article investigates the processes that take place during the forced thermo-oxidation of sunflower oil. The results obtained in the study showed a major impact of thermo-oxidation. The acidity index of fresh sunflower oil increased 13.7 times, with a value of 2.46 mg KOH·g^{-1} of fat for the thermo-oxidized oil compared to the initial value of 0.180 mg KOH·g^{-1} of fat. The thermo-oxidation of sunflower oil caused a significant decrease of the saponification index, which indicates a significant degree of polymerization and leads to viscosity increase of the studied sunflower oil. It was established that the applied treatment favoured both the formation of carbonyl secondary compounds and the simultaneous formation of hydroperoxides and triglycerides containing hydroxylated groups. The accumulation of hydroperoxides and triacylglycerides that have hydroxyl functions have facilitated the course of polymerization reactions, which are to increase the viscosity of thermo-oxidized studied sunflower oil.

Keywords*: sunflower oil, thermal oxidation, IR spectroscopy, peroxide index, acidity index, epoxides, trans- and cis- fatty acid isomers.*

Introduction

Lipid oxidation is one of the main problems of deterioration in food (edible oils and beverages) and cosmetic (skin cream) products, affecting their chemical, physical, and sensory properties [1]. In fact, lipid auto-oxidation and its inadequate storage contribute significantly to the deterioration of vegetable oils life causing changes in colour, texture, odor and aroma, as well as loss of constituent vitamins [2]. The understanding of lipid oxidation mechanisms in food and oils is deemed essential as we can construct effective prevention measures against the lipid oxidation in these commodities by identifying and targeting the responsible oxidation mechanisms. Oxidation of unsaturated lipids especially that of unsaturated fatty acids linoleic acid and linoleic acid ethyl ester, occurs according to three mechanisms: photo-oxidation, auto-oxidation and enzyme-oxidation.

The peroxide and acid indexes have become the most common indicators for lipid oxidation levels. These analysis methods do not provide enough information about the mechanisms of lipid oxidation. In general, the mechanisms of lipid oxidation have been well known including photo-oxidation (singlet-oxygen induced oxidation) and auto-oxidation (radical oxidation), and it has been found that each mechanism forms different characteristic lipid hydroperoxides with different regio and geometric (cis/trans) isomers [3]. Photo-oxidation is initiated by UV light in the presence of photo-sensitizers (chlorophyll, riboflavin or hemoproteins) and catalyzed by singlet oxygen and enzymatic oxidation is initiated by yeast lipo-oxygenases.

Auto-oxidation is the most common fatty acids that can be subjected to this process both in free form and being combined (glycerol-lipids or glycol-lipids). Moreover, it has been observed that a poly-unsaturated fatty acid esterified in position 2 of glycerin molecule is better protected against oxidation than when it is esterified in position 1 of glycerin [4]. As well, lipids containing unsaturated fatty acids may undergo spontaneous peroxidation. Auto-oxidation is catalyzed by temperature, metal ions, free radicals, etc. This type of oxidation leads to the formation of numerous compounds, from unstable intermediate products of hydroperoxide type to stable final products (aldehydes, cyclic compounds, polar compounds and polymers). This spontaneous oxidation is an auto-catalytic reaction, which is responsible for the devaluation of food and the denaturation of tissues in living organisms.

The peroxidative change of unsaturated lipids can be caused by reactions triggered by free radical species such as peroxyl-radicals and non-radical species such as singlet oxygen. The latter is excited form of oxygen (O_2), very reactive from a chemical point of view, due to the presence of unpaired valence electrons. The formation of singlet oxygen is often related to the presence of a photo-sensitizer, which catalyzes the transmission of electrons excitation energy to molecular oxygen, with the formation of singlet oxygen, which is about 1500 times more reactive than triplet oxygen. Oxygen in its reactive form can attach directly to the double bonds of unsaturated fatty acids. In the absence of photo-sensitizers, an initiation step with free radicals is required to allow this fixation and formation of hydroperoxides [3]. Decomposition of hydroperoxides by heating or by the catalytic action of transition metal ions can produce peroxyl- and alkoxyl-radicals [5]. The formation of the peroxyl-radical is the main stage of the oxidation propagation stage during which free radicals "attack" fatty acids. Antioxidants can convert these radicals into an inactive, much more stable form, thus blocking this propagation reaction [6].

Hydroperoxide, as an unstable primary product, decomposes rapidly into secondary compounds, forming volatile compounds: aldehydes, acetones, organic acids, epoxides or polymers, which give a pungent and strong characteristic taste. This accelerates the oxidation of dyes, flavours and constituent vitamins, which makes the food containing oxidized unsaturated lipids completely rancid (accumulation of peroxyl-radicals) [7]. As well, reactive oxygen species (such as hydroxyl –OH or peroxyl-radicals –ROO•), formed in human tissue cells by endogenous agents and / or exogenous causes cause extensive oxidative damage, which in turn can contribute in aging, cancer and other human diseases [8, 9]. In order to control and reduce oxidative changes, nature uses several types of compounds, known as antioxidants, which react rapidly with free radicals at firsts stages of the oxidative process, to delay or reduce the degree of oxidative damage of the constituent compounds [10, 11].

Experimental part

The study used 100 % native vegetable oil extracted from sunflower seeds species *Héliantalus Annus*. This oil contains a high proportion of linoleic acid in the form of fatty acid triglycerides. A decrease in the proportion of this poly-unsaturated acid is used as an indicator of lipid oxidation.

The oxidation procedure of sunflower oil was performed according to the previously published method [12]. The experimental thermo-oxidation installation consists of a 1 L balloon capacity which is mounted on a hot plate, equipped with thermo-couple and temperature control. The air is supplied by a pump and the flow is regulated by a manometer. The device is equipped with a speed adjustable magnetic stirrer. Operationally, a volume of 500 ml of oil was introduced into the reactor, ensuring intense agitation. The oil temperature was maintained at 90 ± 2 °C and air was bubbled through the reaction mixture at a rate of $8 \div 10\ L \cdot h^{-1}$ for 50 hours.

Thermo-oxidation was performed under laboratory conditions that excluded the direct action of sunlight to exclude photo-oxidation of studied sunflower oil. At the end of the process, the thermo-oxidized oil samples were distributed in sealed 100 mL bottles and stored at 0 °C until used for analysis, and the fresh oil was stored under the same storage conditions. During the study, the following physico-chemical indicators of sunflower oil were assessed and evaluated dynamically – acidity, acidity index, saponification index, iodine index, peroxide index, the density and humidity.

Results and discussion

One of the objectives of this study was to investigate the forced oxidation of sunflower oil. For this, the thermal stability at 90 °C was analyzed for a series of oil samples for a period of 50 hours and the following parameters were determined: the peroxide index: the acidity index, the oil acidity, the iodine index, the saponification index, refractive index, density and humidity (table 1).

Table 1

Value of physico-chemical indices of studied oil samples

Physico-chemical analyzed indices	Sunflower oil	Oxidized sunflower oil
Organoleptic characteristics	Fluid, straw yellow	Fluid, dark color and rancid odor
Peroxide index, *meq. O2·kg*$^{-1}$	5.30 ± 0.70	144.5 ± 2.00
Acidity index, *mg KOH·g*$^{-1}$	0.18 ± 0.04	2.46 ± 0.10
Acidity, *degrees of acidity T*	0.09 ± 0.02	1.25 ± 0.06
Iodine index, *g I2· 100 g*$^{-1}$	1.23 ± 1.20	0.80 ± 1.40
Saponification index, *mg KOH·g*$^{-1}$	192.60 ± 2.00	183.79 ± 1.30
Refractive index	1.463 ± 0.035	1.476 ± 0.025
Density at 20 °C	0.912 ± 0.020	0.983 ± 0.020
Humidity, %	0.100 ± 0.02	2.00 ± 0.20

The results obtained in the study showed a marked impact of lipid oxidation on the physico-chemical indicators of the oil (table 1). The acidity index of fresh sunflower oil increased 13.7 times, with a value of 2.46 mg KOH·g^{-1} oil for the thermo-oxidized samples compared to the initial value of 0.180 mg KOH·g^{-1} oil. The acidification of the oil samples were due to the hydrolysis reaction of glycerides, this process is favoured by the water contained in the oil even in the form of traces. The intensity of the hydrolysis reaction depends on various factors, including the temperature applied to the oil, as well as its water content. These two factors contribute to the hydrolysis of triglycerides to produce mono-and diglycerides (free fatty acids and possibly glycerin). Free fatty acids accumulate in the oil, thus increasing its acidity more than 10 times.

Thermo-oxidative treatment leads to a reduction in the total degree of unsaturation sunflower oil. This change was assessed by measuring the iodine index. This index makes it possible, in fact, to measure the degree of general unsaturation of oil. Our results show a significant decrease in the value of this index after the thermo-oxidation of sunflower oilsamples. The iodine index measured in fresh sunflower oil is estimated at 1.23 mg I_2·g^{-1}, while in thermo-oxidized sunflower oil it is only 0.80 mg I·g^{-1}, fact that can be explained by the oxidation of double bonds and / or their involvement in active polymerization processes. Increase of humidity of thermo-oxidized sunflower oil during the study, could be due to the formation of water and volatile products during oxidation reactions. In fact, water and CO_2 are some of the final products of the break-down of unsaturated fatty acid hydroperoxides. The humidity of the oil also increases due to the supply of water vapor from the air supplied through the system.

The thermo-oxidation of fresh sunflower oil caused a decrease in the value of the saponification index. In the thermo-oxidized oil, a value of 183.79 mg KOH·g^{-1} of oil was recorded. The saponification index provides information on the average molecular weight of fatty acids that are part of the glycerides of oil.

The decrease in the saponification index in the thermo-oxidized sunflower oil indicates a higher degree of polymerization acid. The increase in oil density is also explained by the thermo-oxidative polymerization. The formation of polymers can cause the viscosity to increase simultaneously with the increase of the chain length and decreases with the increase of the degree of oil unsaturation [13].

Analyzing the results, a sharp increase in the value of the peroxide index was found simultaneously with the decrease of the iodine index, which demonstrates the existence of an intense oxidative process. The oxygen present in the fresh sunflower oil and the one introduced experimentally by supplied air activates a series of reactions, which generate free radicals and hydroperoxides. The peroxide index is an indicator of the presence of hydroperoxides and hydroxyperoxides in oil, called primary degradation products. Its value indicates on the degree of freshness of an oil, the smaller it is, the fresher the oil.

The peroxide index varies between 5 and 20 for crushed native oils and between 0 and 1 for refined oils. The fresh sunflower oil used in the study had a peroxide index of 5.30 meq.$O_2 \cdot kg^{-1}$, while in thermo-oxidited oil this index increases and reaches the level of 144.5 meq.$O2 \cdot kg^{-1}$. This value indicates a deep alteration (rancidity) of the heated oil. We attribute this dramatic increase in the peroxide index to the combined effects of high temperature and contact with air during prolonged heating of the oil, which induces the formation of peroxides. Similar studies on thermo-oxidized lipids suggest that an increase in oxidation temperature leads to the decomposition of hydroperoxides and therefore to a decrease in the peroxide index with the formation of oxidation by-products such as aldehydes [14]. These authors suggest that the activation energy of the decomposition reaction of primary oxidation products is significantly higher than that of their formation. In conclusion, being given the instability of peroxides, we suggest that the peroxide index cannot serve as a single parameter of the degree of oxidative degradation of oils.

Conclusions

In this study, the lipid oxidation mechanisms were determined that are most likely to be responsible for the deterioration of each samples. As a result, the thermo-oxidation was found to be the oxidation mechanism that occurred in the process of repeated frying, especially in oils. The process of forced oxidation of sunflower oil and the modification of the physico-chemical indices of the oil were investigated. It was found out, in particular, the increase of the peroxide index by 27 times and the decrease of the iodine index by 0.422 mg $I_2 \cdot g^{-1}$ which indicate the presence of an intense oxidative process. Free poly-unsaturated fatty acids are the main promoters and substrates of oxidation reactions that occur when oil is maintained longer at high temperatures. The combined action of heat and oxygen generates primary and secondary oxidation products, and the nature of these products and their concentrations depend on the oxidative conditions applied. The possible mechanisms of forced oxidation under the influence of thermal factors of unsaturated fatty acids in sunflower oil were analyzed and established.

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РАЗВИТИЕ ОБРАЗОВАТЕЛЬНОЙ СРЕДЫ КАБИНЕТА ХИМИИ

В статье раскрывается роль кабинета химии в формировании устойчивых ключевых компетентностей учащихся для жизни в условиях глобального образовательного, научного и информационного общества.

Ключевые слова: *образование, урок, химия, ИКТ, мультиборд.*

The article reveals the role of the chemistry classroom in the formation of sustainable key students for life in a global educational, scientific and information society.

Keywords: *education, lesson, chemistry, ICT, multiboard.*

Одним из главных факторов развития личности является образовательная среда, которая содержит следующее: естественное или искусственно создаваемое социокультурное окружение учащегося, включающее различные формы и средства обучения, способные обеспечивать оптимальные условия для всестороннего развития; социально-психологическая среда окружения учащегося.

При преподавании химии стараюсь акцентировать внимание не только на сознательное и прочное усвоение теоретического материала, но и формировать у учащихся интерес к предмету, умение самостоятельно получать новые знания, применять их на практике, делать выводы, проводить исследования. Содержание программы школьного курса основывается на дидактическом принципе единства обучения, воспитания и развития. Учащиеся овладевают приемами мышления, деятельности, у них формируются навыки самостоятельной работы, умения планировать и проводить эксперимент, решать различные творческие задания, обобщать и систематизировать материал, делать выводы.

Поэтому основной целью работы кабинета является сделать химию понятной, доступной, интересной, полезной для учащихся. В кабинете произведён капитальный ремонт, получено новое оборудование: приборы, модели молекул, таблицы, наборы посуды для проведения лабораторных и практических работ. В лаборантской хранятся реактивы для