The quality of food is the result of such points as its nutritional, health or sensory properties. These qualities depend, not only on the original composition of raw materials used to its production, but also on preserving safety and proper method of conducting all processes that foodstuffs are subjected to during their lifecycle.

In transport, foodstuff undergo many transformations, due to physical, biochemical and microbiological factors. In reference to edible oils, this could result in inducing the reactions such as oxidation, hydrolysis, polymerization and various types of physical transformations, which reduce oils utility for producers and consumers. According to that, it is important to broaden knowledge, which enables to avoid harmful effects, which could occur in discussed type of liquid cargo, for example during maritime transport.

ABSTRACT: In order to provide quality and safety of liquid cargo carried by sea, it is necessary to obey the rules of its protection. During maritime transport edible oils are prone to detrimental influence of many external factors such as supply of oxygen, of water, of metal ions and of pollution, as well as changes of temperature and mixing caused by ship movement. Due to them, they could undergo oxidation reactions, hydrolysis, polymerization and various types of physical transformation. On account of them the deterioration of nutritional, health and sensory qualities of fat could occur.

The aim of the study was the assessment of the dynamic of changes with oxidative character (peroxide value and TBA index) which could appear in edible oils depending on their storage conditions.

The analysis, which lasted 12 weeks, concerns rapeseed oil. Oxidative changes were registered every two week. The storage conditions in the atmospheric air induced danger connected with oxygen presence, whereas nitrogen blanketing eliminated this risk factor. The assessment also includes the influence of temperature of storage (indoor temperature 20˚C or refrigeration temperature 4˚C) and mixing of the fats.

The results indicate that nitrogen blanketing, lowering the temperature and eliminating the mixing during storage of oil have highly positive impact on reduction of oxidative changes in fats.

1 INTRODUCTION

The quality of food is the result of such points as its nutritional, health or sensory properties. These qualities depend, not only on the original composition of raw materials used to its production, but also on preserving safety and proper method of conducting all processes that foodstuffs are subjected to during their lifecycle.

Available literature, subjected to this issue, usually describes the transformations to which edible fats may be exposed, but it rarely presents possible methods, applicable in practice, for reducing negative changes and their dynamics.

The paper focuses on vegetable oils market, on characteristic of rapeseed oil, on changes to which it is subjected during storage (also in maritime transport) and on conditions and methods of its protection from external factors. Assumption of the study was that
Polish oil industry are oils such as: rape seed oil, and olive oil [Wroniak and Ratusz, 2014]. The basic of soybean, rapeseed, sunflower, cotton, peanut, coconut foundation of their global production are: oil palm, sunflower oil, soybean oil, peanut oil and mixed oils. The production as well as consumption of oils have been constantly increasing for many years. The index were examined and then their dynamics in varied ambient conditions were compared.

2 MARKET AND COMMODITY CHARACTERISTICS OF EDIBLE OILS

The production as well as consumption of oils have been constantly increasing for many years. The foundation of their global production are: oil palm, soybean, rapeseed, sunflower, cotton, peanut, coconut and olive oil [Wroniak and Ratusz, 2014]. The basic of Polish oil industry are oils such as: rapeseed oil, sunflower oil, soybean oil, peanut oil and mixed oils (for example rapeseed oil with sunflower oil or soybean oil) [Palich at al. 2006]. In 2016, 602 000 tons of vegetable oils (worth EUR 516 million) were exported from Poland. 68% of which was rapeseed oil. In the first half of 2017, around 492 000 tons of crude rapeseed oil were produced in Poland. About 392 000 tons of which were refined [Oil Express, 2017].

At the same time, 720 000 tons of vegetable oils were imported to Poland (worth EUR 702 million). 81 000 tons of that was rapeseed oil [Oil Express, 2107]. The balance of import and export of vegetable oils within 8 years between 2009 and 2016 has been presented in Figure 1.

![Figure 1. Foreign trade of vegetable oils in 2009-2016 [Oil Express, 2017]](image)

Rapeseed oil takes third place in the world production of oils. Its main producers are countries such as: Canada, China, India and in Europe: Germany, France, Great Britain, Poland, Russia and Ukraine [Wroniak and Ratusz, 2014]. This oil is widely used as edible oil. It is characterized by a high smoke point and it could be applicable also in other sectors, not only in the food industry, for example in the production of biofuels.

The basic ingredient of edible fats are triacylglycerols. They make up 99% of the composition of refined oils. These are esters of glycerol and fatty acids. At a temperature of 15°C the density of vegetable oils is between 910 and 970 kg/m³ and it decreases linearly when temperature increases. The coefficient of thermal changes of density is 0,67kg/m³ for 1°C [Wiktor, 1994]. All vegetable oils are combustible. However, due to the fact that they are characterized by high flash point, they are not classified as hazardous materials [Leśmian-Kordas and Pilawski, 1992].

Rapeseed oil is composed mainly of monoenic and polyenic fatty acids, which influence its utility properties. According to principles of human nutrition, rapeseed oil is characterized by relevant participation of acids ω-6 to ω-3 (ca. 2:1), which makes it really valuable foodstuff. Acids ω-3 are especially important in relation to dietetics because they improve proper functioning of the human nervous and immune system, as well as brain activity. They could also reduce the risk of cardiovascular diseases and diabetes, which are civilization diseases in developed countries. Rapeseed oil, in comparison to other oils available in market, contains also the greater number of sterols, including brassicasterol.

Food durability was defined by the Institute of Food Science and Technology and is understood as the time when the foodstuff, properly stored, is safe and maintains its organoleptic, physical, chemical and microbiological qualities at the assumed level and also keeps declared nutrition properties [Samotyja, 2016]. Food durability is an important factor of food quality and determines its availability.

Edible oils during storage or transport can undergo many different chemical reactions [Klopotek et al. 2017]. Overall transformations which occur in them, are referred as rancidity. It results in change of chemical composition of oil, which could lead to the deterioration of the product, to the change of its sensory attributes or to the loss of its healing properties [Nierzwicki 2013]. Products of these reactions are usually free fatty acids, oxides and peroxides, aldehydes and ketones and products of their polymerization as well. Some of emerging chemicals could even have harmful effects on the human body. Aldehydes, ketones and acids are classified as biologically active substances. Their actions could lead to damage of cell membranes and intercellular structure and also to reduction of enzyme activity. These could also cause cytotoxic or mutagenic effect. [Cichosz and Czeznot, 2011].

Fatty acids, especially unsaturated, present in edible oils, are prone to oxidation reactions. As a result of these reactions hydroperoxides are formed. The growth of hydroperoxides content in composition of oil, leads to increase of peroxide value (PV) and causes reduction of iodine value (IV) [Czechowska-Liszka, 2012]. Process of oils oxidation is stimulated by many environmental factors such as temperature, oxygen presence, occurrence of catalytic metal ions (for example: copper, cobalt, iron, chromium), pH of surrounding environment, storage time and access to light [Palich, 2000], especially ultraviolet radiation and radiation of blue light [Leśmian-Kordas and Pilawski, 1992].

Another type of transformation, which could occur in the oil composition, is hydrolysis. It leads to the breakdown of triacylglycerols and to the release of free fatty acids, monoacylglycerols, diacylglycerols and glycerol [Czechowska-Liszka, 2012]. This results in growth of fat acidity and causes the increase of acid value (AV). Sensory changes of fats, which are
Edible fats qualify as perishable products. They could undergo rancidity as an effect of different external factors such as admission of light and oxygen or high temperature. Therefore, they require to be kept in suitable conditions to avoid their premature deterioration. Spaces which are devoted to storage and transport of edible oils, should be clean, dry, and dark, or illuminated with diffused light [Palich, 2000; Wroniak and Ratusz, 2014]. In these areas, relative humidity of the ambient air should vary from 75% to 85%. It is worth noticing that decreasing the temperature allows to reduce the speed of chemical reactions, the development of microorganisms and the occurrence of biological changes [Nierzwicki, 2013]. Due to that fact, temperature in the discussed areas, should range from +4 to +6°C. Such way of storage enables to preserve the oil durability for 6 months, while maintaining the temperature not exceeding 15°C shortens this period to 3 months.

The most suitable containers for storing edible oils are narrow, tall, vertical tanks with a circular cross section. They should have a conical or sloped bottom to allow self-flow [Berger, 1985].

According to the fact that main factor which influence the oxidation of fats is presence of oxygen, oils could be preserved by using modified atmosphere packing (MAP), and taking advantage of nitrogen [Wroniak and Ratusz, 2014]. It enables to maintain their nutritional and organoleptic quality, and also allows to extend durability, preserve taste and consistency of product, and protect it from mechanical damage. Even when liquid oils are purged with inert gas only once, the oxygen could be flushed out and its content in the product may be reduced by as much as 80-90%. It is possible to conduct inertisation while storing the oil in the tanks, as well as during bottling it [Airlquide, 2017].

When oil is being delivered, means of transport act as temporary warehouses. They must protect the product against the adverse effects of external factors. It is also important to properly arrange and fasten cargo that could be exposed to moisture and lateral pressures during sea transport during the sea transport [Czarniecka-Skubina, 2010].

3 BLANKETING OF OILS IN INERT ATMOSPHERE

The main factor decreasing the final quality of oil is the oxygen content, which was dissolved in fat [Wroniak et al., 2015]. In order to minimize the effect of this factor, inert gases such as carbon dioxide (CO₂) and nitrogen (N₂) can be used while storing.

When temperature is decreasing, the solubility of CO₂ in fats and water increases.

CO₂ has bacteriostatic properties, and may also be an inhibitor for some enzymes. It is able to lower the pH of food by forming carbonic acid in an aqueous environment, and its gas fraction can inhibit the growth of microorganisms.

N₂ doesn't have bacteriostatic properties and is poorly soluble in fats and water. However, its usage in oil storage, gives the opportunity to create an anaerobic environment in the packaging, which limits oxidation processes. The removal of air above the oil also reduces the amount of water contained in it, which may have a beneficial effect on the inhibition of the hydrolysis process and on the changes in the sensory characteristics of fat which are associated with it.

Accordingly, the usage of inert gases could be an effective, as well as safe, from a health point of view, method to reduce unfavorable changes occurring in oils. Although better results were achieved with carbon dioxide, nitrogen is more often used, for economic reasons [Jedrzejkiewicz and Krygier, 2008].

During storage and transport of fats, deterioration of their quality may occur due to long-term contact with oxygen from the air. The time necessary for oil transport depends on the type of oil (its origin) and the conveyance route. This could take from several weeks to several months for cargo to reach its destination [Takashina et al. 1994]. Therefore, ships and oil storage tanks which are high quality, or which are devoted to long term storage, should have facilities for bubbling and covering the load with an inert gas. Moreover, filling the stream of pumped oil with pressurized nitrogen, may be an effective way to protect refined fats [Berger, 1985; FAO/WHO, 2015]. For this purpose, nitrogen with a concentration not less than 99.5% is used [Takashina et al. 1994] because too low purity of nitrogen, could lead to problems with the stability of vegetable oils.

Changes which may occur in fats during storage or transport could be characterized by different quality indicators. First of these are the peroxide value and the TBA index. Their changes, associated with the
storage of edible oil under different conditions, have been experimentally determined and described in the empirical part of this work. In addition, there are also the acid number, saponification number and iodine number, which could be indicated or Kreis test which could be conducted [Stasiuk and Przybyłowski 2008].

4 AIM AND METHODS OF RESEARCH

The aim of the study was to define the dynamic of oxidative changes, which could appear in edible oils depending on their storage or transport conditions. The object of research was refined rapeseed oil. The study was a multifactorial analysis. Research focused on factors such as: 1) presence of oxygen or nitrogen in the sample tube; (2) oil storage temperature; (3) mixing of the sample; (4) time of oil storage. It was subjected to define the influence that these factors have on the changes of the peroxide value and the TBA index during 12 weeks of storage.

A zero test and four repetitions were carried out for each of the 6 prepared samples - after 3, 6, 9 and 12 weeks, and their peroxide number and TBA index were indicated.

Six samples were taken from these same bottle of refined rapeseed oil. Each of them was placed in a previously prepared utensil, which enabled to fill it with air or nitrogen, as shown in Figure 2.

![Figure 2. Scheme of the utensil for sample storage](image)

The utensil was filled out with such volume of sample that after placing it in a horizontal position its content did not leak out through the taps. Afterwards, when inlet and outlet were opened, air or nitrogen, depending on the sample, was blown through the utensil, in order to eliminate the presence of other gases. The subsequent step was to fill the utensil tightly with the eligible gas.

The utensils filled with air or nitrogen were divided into 3 groups:
- stored motionless, in a refrigerator, at temperature 4°C,
- stored motionless, at room temperature 20°C,
- stored at room temperature 20°C, shaken at irregular intervals.

The special construction of the outlet taps allowed to take the sample of oil after putting the utensil in a vertical position. Therefore, it prevented the leak of the gas contained in the utensil or its mixing with outside air.

In order to imitate the conditions prevailing in the container, during the transport of oil, the utensils were protected from sunlight using aluminum foil.

At the same time, the sample was taken, to indicate the designation for the zero test on it.

4.1 Determination of peroxide value

Peroxides are products of fat oxidation reactions. The peroxide value (PV) defines the amount of substance which oxidize potassium iodide to iodine contained in one kilogram of fat. It is also connected with creation of epihydryne aldehyde [PN-EN ISO 3960:2012].

4.2 Determination of TBA index

As a result of the aldehyde rancidity process, a characteristic product - malondialdehyde - may be formed. In order to detect it, the so-called TBA index could be used [Stasiuk and Przybyłowski, 2008]. This index is determined by thiobarbituric test, which enables to follow the oxidative processes occurring in fat.

5 OVERVIEW AND DISCUSSION OF RESULTS

The peroxide values of rapeseed oil recorded during storage under the conditions of the experiment, were primary data for approximation of parameters of linear regression equations. They were subjected to describe the dynamics of changes occurring during 12 weeks of storage under different conditions (Tab. 1). Table 1 also shows the values of the coefficient of determination R², which is the proportion of the variance in the dependent variable, that is predictable from the independent variable.

| Storage type                        | Regression equation | Coefficient R² |
|-------------------------------------|---------------------|----------------|
| Nitrogen, motionless, room temperature | y=1.7771x-2.2517    | 0.8456         |
| Nitrogen, shaken, room temperature  | y=0.3455x+0.6741    | 0.6333         |
| Nitrogen, motionless, refrigerator  | y=0.1330x+0.6240    | 0.6920         |
| Air, motionless, room temperature   | y=7.3978x-9.5005    | 0.9636         |
| Air, shaken, room temperature       | y=13.379x-11.922    | 0.9837         |
| Air, motionless, refrigerator       | y=2.4849x-3.4246    | 0.7577         |

Coefficient R² (square of the correlation coefficient between the explained variables and explanatory variables)

Comparison of the course of curves describing changes in the peroxide value, enables to state that
storage conditions have significant influence on variation in the dynamics of changes of peroxide value of rapeseed oil during its 12 weeks incubation in experimental conditions.

Storage of rapeseed oil under an atmosphere of air, which contains about 21% of oxygen, caused a considerable increase in the peroxide value in all variants of the experiment. This is indicated by the high values of the regression coefficient (from 2.4849 to 13.3379), which defines how much the value of the dependent variable (PV) increased, in case of the increase of the independent variable (time) by one unit. Comparison of the values of regression coefficients for the temperature 4°C and 20°C allows to conclude that the use of low storage temperature (4°C) and at the same time limiting the oxygen access by eliminating shaking of the oil during storage, had contributed to reduction of the oxidation of fat. This reflects in the existence of relatively low peroxide values during storage. Increase of the storage temperature (20°C), whilst maintaining limited oxygen access, by eliminating shaking of oil during storage, led to a nearly three-fold increase in the regression coefficient, which resulted from the rise in dynamics of peroxides formation. On the other hand, the appearance of an additional exposure factor, in the form of shaking oil during its storage, which results in an increase of the extend of aeration, and thus oxygenation, contributed to an almost 5.5-fold increase of the regression coefficient.

The elimination of the atmosphere, which has an oxidative characteristics, improved the storage stability of rapeseed oil. In reliance to undoubted low values of the regression coefficient of the linear function (from 0.1330 to 1.7771) describing changes in time of 12 weeks of incubation, storage of rapeseed oil under the nitrogen atmosphere significantly reduced the increase of peroxide value in all variants of the experiment. It is worth noticing that due to storage at low temperature (4°C) and elimination of oil mixing during storage, the fat oxidation occurred at extremely low dynamics (0.1330). What is more, the high protective efficiency of nitrogen, in comparison to air, which is the source of oxygen, is demonstrated also by the comparison of the values of regression coefficients, which describe the changes occurring under conditions of increased temperature and increased temperature combined with mixing. Higher value of the regression coefficient of the function describing changes of the peroxide value over time, obtained when oil was stored at increased temperature with restriction of mixing (1.7771) in comparison to regression coefficient describing changes of the peroxide value over time determined for the experimental variant assuming oil storage at increased temperature with exposure to mixing (0.3455), undoubtedly indicates that there had to be leakage during the test. As a result of this, oxygen got to the utensil together with the air, which led to a significant acceleration of the peroxide value growth rate. According to that, this value should be considered as increased in a way which is not related to the assumptions of the experiment. At the same time, it is worth emphasizing that very low value of regression coefficient (0.3455) referring to changes of the peroxide value during storage of rapeseed oil under nitrogen atmosphere, at increased temperature and under conditions of its mixing (extreme conditions), is an evidence of stability of rapeseed oil in terms of changes in oxidation, conditioned by the protective function of nitrogen. In reliance to that, it could be assumed that if there had not been any leakage of utensil during oil storage under nitrogen atmosphere, at room temperature, without exposing it to mixing, the regression coefficient of the linear function would have been lower than 0.3455.

Oils kept in utensils filled with air featured higher dynamics of changes of peroxide value than oils stored in nitrogen. Regardless of the composition of gas atmosphere in which oils are stored, keeping them at low temperature (cooling), positively reduces the dynamics of changes of their peroxide values. Cyclical mixing of oils stored in the air-filled utensils, resulted in a higher dynamics of peroxide number changes, in comparison to storage under conditions which avoid mixing of liquid. For samples filled with nitrogen, this regularity occurred only during the first six weeks of sample storage. The maximum peroxide value, specified by the standard on the level of 5 [mEq O2/kg], has not been exceeded in case of oil, which was:
- stored in nitrogen, motionless, at room temperature – during the first nine weeks of storage,
- stored in nitrogen, shaken, at room temperature – during the first twelve weeks of storage,
- stored in nitrogen, motionless, in a refrigerator – during the first twelve weeks of storage,
- stored in air, motionless, at room temperature – during the first three weeks of storage,
- stored in air, motionless, in a refrigerator – during the first nine weeks of storage.

In case of oil stored in air, at room temperature and shaken, the defined peroxide value has significantly exceeded appointed value after the first 3 weeks of storage (13.1396 mEq O2/kg).

Comparison of the course of curves describing changes of the absorbance value of a rapeseed oil distillate over time (TBA test) using the analytical method (Tab. 2.), leads to the conclusion that storage conditions have the significant influence on variation in the dynamics of its changes during 12 weeks incubation in experimental circumstances.

Table 2. Linear regression equations describing the dynamic of changes of the absorbance value of a rapeseed oil distillate during 12 weeks of storage under different conditions together with values of coefficient of determination R²

| Storage type                      | Regression equation          | Coefficient R² |
|----------------------------------|------------------------------|----------------|
| Nitrogen, motionless, room temp. | y=0.1163x-0.153              | 0.8068         |
| Nitrogen, shaken, room temp.     | y=0.0476x+0.0396             | 0.919          |
| Nitrogen, motionless, refr.      | y=0.0081x-0.2970             | 0.036          |
| Air, motionless, room temp.      | y=0.1535x-0.1727             | 0.8792         |
| Air, shaken, room temp.          | y=0.1752x+0.0935             | 0.9225         |
| Air, motionless, refr.           | y=0.0621x+0.0434             | 0.9487         |
In case of storing rapeseed oil in the atmosphere of air, the increase in the radiation beam absorbance value assigned to distillate was observed in all variants of the experiment. This is indicated by values of the regression coefficient ranging from 0.0621 to 0.1752. Keeping the oil at low temperature (4°C) with elimination of oil mixing, allowed to reduce the absorbance value. The increase of the storage temperature (20°C), whilst maintaining limited oxygen access, by eliminating shaking of oil during storage, led to a nearly 2.5-fold increase in the regression coefficient. This regularity resulted from the increase of dynamics of formation of malondialdehyde, which is responsible for absorbance. On the other hand, the appearance of an additional exposure factor, in the form of shaking oil during its storage, which results in an increase of the extend of aeration, and thus oxygenation, contributed to an almost threefold increase of the regression coefficient.

Taking advantage of a reducing atmosphere, in the form of nitrogen, improved the storage stability of rapeseed oil. Keeping rapeseed oil under a nitrogen atmosphere, reduced the increase in malondialdehyde concentration, in all variants of the experiment, which is indicated by lower, in comparison to the air atmosphere, values of the regression coefficient (from 0.0081 to 0.1163). The low temperature of storage (4°C) and the elimination of oil mixing during storage, resulted in extremely low dynamics of fat rancidity (0.0081). The effectiveness of the nitrogen as protective gas, in comparison to air, which is the source of oxygen, has been demonstrated by comparing the values of regression coefficients, describing the changes occurring under conditions of increased temperature and increased temperature combined with mixing. Higher value of the regression coefficient of the function, describing changes of the absorbance value of the tested oil samples during storage, obtained when oil was kept at increased temperature with restriction of mixing (0.1663), in comparison to the regression coefficient describing changes of the absorbance value over time, determined for an experimental variant, assuming oil storage at increased temperature with exposure to mixing (0.0476), once again indicates that there had to be leakage during the test. As a result of this, oxygen got to the utensil together with the air, which led to a significant acceleration of malondialdehyde formation. According to that, this value should be considered as increased in a way which is not related to the assumptions of the experiment. At the same time, it is worth emphasizing that very low value of regression coefficient (0.0476), referring to changes of malondialdehyde concentration during storage of rapeseed oil under nitrogen atmosphere, at increased temperature and under conditions of its mixing (extreme conditions), is an evidence of stability of rapeseed oil in terms of being prone to rancidity, conditioned by the protective function of nitrogen. In reliance to that, it could be assumed that if there had not been any leakage of utensil during oil storage under nitrogen atmosphere, at room temperature, without exposing it to mixing, the regression coefficient of the linear function would have been lower than 0.0476.

In case of oil kept in nitrogen, ones which were stored motionless at room temperature, and shaken at room temperature, and in case of oil kept in air, ones which were stored motionless at room temperature, and motionless in refrigerator, have TBA index relatively constant during the first 6 weeks of the study. A comparatively large increase in the TBA index was observed in these samples after 12 weeks.

Weighing all above considerations, the following conclusions could be made:

- blanketing the vegetable oil with nitrogen contributes to a significant slowdown of fat oxidation reaction, in comparison to oil stored in the air, at the same time;
- decreasing the storage temperature of vegetable oil leads to the reduction of its oxidation process;
- shaking the oil during keeping it in the air, at room temperature, has significant influence on acceleration of its oxidation process, in comparison to oil stored motionless. Lack of parallel principle for oil stored in nitrogen, could result from probable leakage which occurred after 6 weeks (sample stored in nitrogen, motionless, at room temperature), and which could contribute to higher peroxide value and higher TBA index;
- in case of oil stored in air, only keeping it motionless, in refrigerator enables to obtain comparatively low degree of oxidative deterioration, in comparison to oil stored in nitrogen.

6 CONCLUSIONS

Edible oils are exposed to many external factors during maritime transport. This could lead to deterioration of their nutritional and sensory quality, as well as affect their safety for consumer health. In order to avoid the adverse effects of these changes, the appropriate rules for transport of this specific liquid cargo should be obey, as well as proper methods of its protection should be applied.

First of all, the preservation of edible oils should mainly consist of the elimination of oxygen, light, water and pollution supply, as well as should possibly restrain its mixing and temperature changes.

The conducted research enables to determine to what extent the selected factors, applicable in practice, could favorably extend the time of oxidation stability of fat during its transport. In reliance to obtained results, it could be pointed that the storage of rapeseed oil under the nitrogen atmosphere, restraining its mixing and decreasing the temperature, contributes to the reduction of the rate of adverse changes occurring in this fat. Moreover these results indicate that blanketing the oil with nitrogen has highly positive impact on reduction of changes, which cause deterioration of the edible oils quality.

Last but not the least, the discussed analysis allows to conclude that there are advantages of high efficiency of combined methods of liquid cargo protection.
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