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Optimization quality indicators of oils during induction heating

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Abstract. The article describes the possibility of determining the degree of hydrolysis of vegetable oils under conditions of a continuous induction heating process. Experimental methods were used to study changes in the physicochemical properties of the samples under study. The main attention is paid to the analysis of changes in the quality characteristics of oils depending on the type of heater and heating time. The article presents the results of studies of the main quality indicators that determine the degree of hydrolysis, on the basis of which it was concluded that during induction heating the changes occurring in comparison with traditional methods do not lead to a deterioration in the quality of the substance. The studies carried out allow us to speak not only about the effectiveness, but also about the safety of this heating method.

1 Introduction

Among the various methods of heating fats before deodorization or distillation neutralization in modern installations, the most common are heating using high-pressure steam (3-4 MPa). A less common method is electric, because it has a number of disadvantages, in particular the danger of local overheating, which is extremely unfavorable for thermostable products [1-4].

This article proposes induction heating as an alternative to the steam method. It should be noted that the method of heating vegetable fats (bringing them to the required temperature) in various processing technologies has a separate independent meaning. However, changes in vegetable fats under the influence of temperature under different conditions have not been studied enough and require further research.

Study the degree of hydrolysis of vegetable oils (using salomas as an example) using the induction heating method under continuous flow conditions.

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2 Research and instrumentation

Experimental studies were carried out on a bench (Figure 1). The main element of the installation is an induction heater. The working chamber of the induction heater is made in the form of two concentric cylinders made of stainless steel with fittings for supplying and draining oil.

The oil is heated by heat transfer when it comes into contact with the walls of the working chamber. The presence of a ferromagnetic core allows the use of industrial frequency current to power the coil. A short-circuited coil of copper ensures uniform heat removal to the oil from the inner and outer walls of the heating chamber. In the gap between the walls of the heating chamber, where the oil flows, an alternating electromagnetic field operates. The heater power consumption is 2000 W.

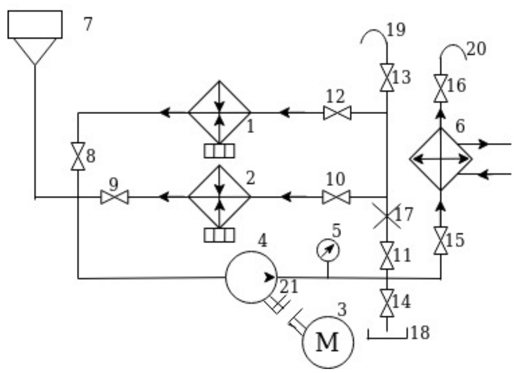

Fig. 1. Schematic diagram of the experimental setup: 1 - induction heater; 2 - electric heater; 3 - electric motor; 4 - pump; 5 - pressure gauge; 6 - sampler; 7 - funnel; 8-16 - shut-off valves; 17 - flow meter; 18 – drain tank; 19 - gander for air removal; 20 - gander for sampling, 21 – coupling.

Refined and deodorized lard was used as the object of the study (Table 1). During the operation of the experimental installation, one batch of lard was passed simultaneously through induction and steam evaporators. Saloma samples were taken when heated to 180, 200, 220 °C.

Table 1. Characteristics of oil after steam and induction heating on an experimental setup.

No	Indicators	Salomas refined	Salomas unrefined
1	Melting temperature [°C]	33.5	48
2	Mass concentration of nickel [mg/kg]	0.49	2.645
3	Acid number [mg KOH/g]	0.2	0.62
4	Mass concentration of moisture and volatile	0.1	0.14
5	substances [%]	2.83	0.001
6	Peroxide value [1/2 $O^{mmol}/_{kg}$]	80	82
7	Iodine number [g I_2/100g]	1.4542	1.4545
8	Refractive index [n_D^{60}]	0.0162	0.0181
9	Epoxy oxygen content [%]	0.21	0.318
10	Content of oxidation products insoluble in	0.644	4.059
11	petroleum ether [%]	0.17	0.367
12	Mass concentration of iron [mg/kg]	0.0033	-
13	Mass concentration of copper [mg/kg]	-	0.04
14	Mass concentration of lead [mg/kg]	5.93	8.24
	Mass concentration of zinc [mg/kg]		
	Content of carbonyl compounds [µmol/g]		

To determine the degree of hydrolysis of acylglycerols (salomas) under various heating methods, the acid number was determined in selected samples. To characterize the oxidation processes, the following indicators were determined: the content of carbonyl compounds, refractive index, iodine value, peroxide value, oxirane oxygen content, content of oxidation products insoluble in petroleum ether.

Considering the presence of a low-frequency electromagnetic field during the induction heating method, the question of the behavior of metals contained in fat is important. The content of iron, copper and zinc was determined in oil, and nickel, iron, copper and zinc in lard.

The physical parameters of oil heating are shown in Figure 2, physical characteristics of heating at the time of sampling - in Figure 4.

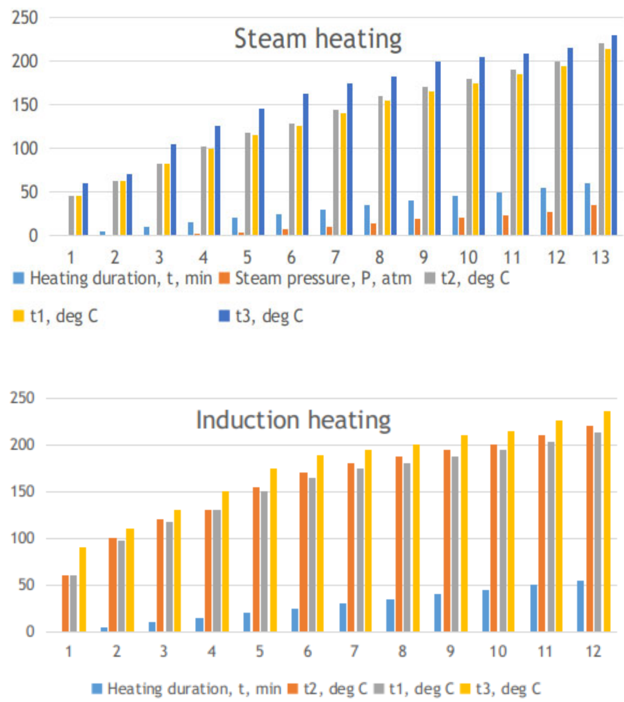

Fig. 2. Physical parameters of self-mass heating.

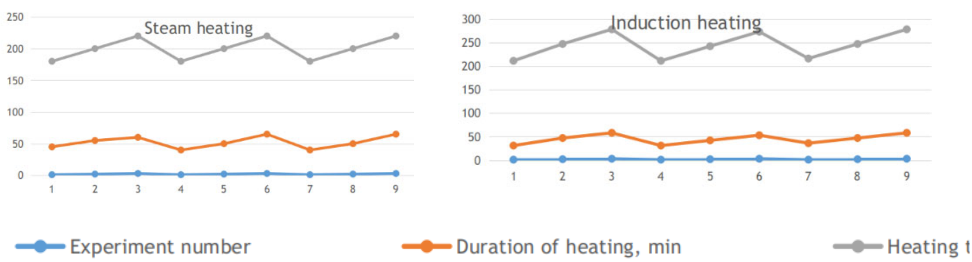

Fig. 3. Physical characteristics of oil heating at the time of sampling.

Average temperature change data are presented in Table 2, where Δtav is the average temperature difference between the heating wall and the lubricant at the outlet of the heater, dt/dτ is the average rate of temperature change (heating temperature).

Table 2. Average data on changes in oil temperature.

Salomas			
Δt_{av}, °C		**d*t*/dτ, °C/min**	
steam	induction	steam	induction
20.1	28.6	2.6	3.0

As can be seen from Table 4, Δt_{av} for induction heating is slightly larger than for steam heating, i.e. During induction heating, salomas comes into contact with a slightly more highly heated heat-transferring wall, but on the other hand, the heating rate with the induction method is slightly higher than with the steam method, i.e. It takes less time to heat up to the same temperature, in other words, the contact of salomas with the heated wall is shorter.

The acid number of lard for the heating methods studied is presented in Table 3, moisture content and volatile substances - Table 4.

Table 3. Acid number changes [mg KOH/g].

Heating temperature [°C]	**Salomas**	
	Steam heating	**Induction heating**
180	0.236±0.031	0.276±0.016
200	0.253±0.025	0.284±0.003
220	0.264±0.017	0.292±0.012

Table 4. Changes in moisture content and volatile matter [%].

Heating temperature [°C]	**Salomas**	
	Steam heating	**Induction heating**
180	0.09±0.026	0.09±0.019
200	0.06±0.012	0.08±0.009
220	0.06±0.015	0.07±0.009

As can be seen from Table 3 and fig. 4, when heated, the acid number for lard increases slightly compared to the initial value, but no significant difference between one heating method and another is observed. The small increase in acid number is obviously due to the insignificance of hydrolytic processes under conditions of low humidity and a relatively short heating duration. As the salomas heats up, the moisture and volatile matter content decreases slightly, both during induction heating and when heated with high-pressure steam (Table 4).

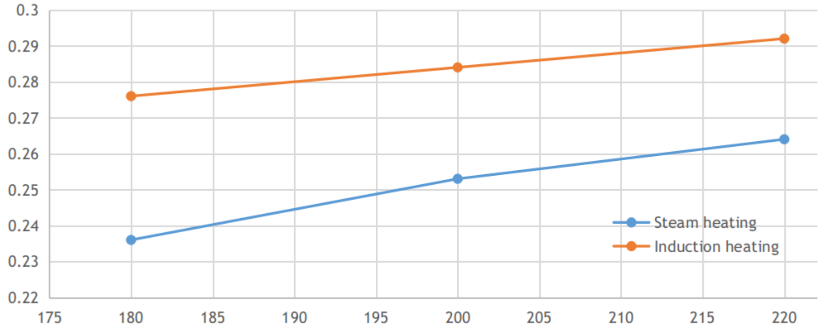

Fig. 4. Increase in the acid number of lard during continuous heating to 220 °C.

3 Results of experiment

It should be noted that the oxidation of salomas under experimental conditions is carried out due to intramolecular oxygen and oxygen dissolved in fat. Salomas are heated continuously to high temperatures (180-220 °C) for a relatively short time (55-75 minutes). Thermal transformations of fats under the influence of oxygen are caused mainly by two interrelated processes - thermal oxidation and thermopolymerization.

The composition of oxidation products can be divided into three groups [5]:

1. products of oxidative destruction, breakdown, mainly of acyl unsaturated fatty acids;
2. oxidation products of acylglycerols, containing the same number of atoms as in the original acylglycerols, but differing in the content of additional functional groups containing oxygen;
3. oxidation products containing polymerized or condensed fatty acids, which may also contain new oxygen-containing functional groups.

As already noted, the thermal oxidation process includes all stages of autoxidation, but is characterized by a sharp increase in the reaction rate. Autoxidation usually occurs via a free radical mechanism. According to modern concepts, a radical chain process includes the stages of nucleation, continuation, degenerate branching and chain termination [7]:

At the stage of chain nucleation, the formation of a primary free radical occurs due to the cleavage of the C-H bond in the CH_2 groups located in the α-position to the double bonds. At the stage of chain continuation, the formation of peroxide and new free radicals occurs. At this stage, the formation of hydroperoxides (primary oxidation products) also occurs. The resulting hydroperoxides are the first valence-saturated products of the oxidation of acylglycerols, but they are unstable and decompose at the O-O bond. The decomposition of hydroperoxides when the oil is heated can be traced by the change in the peroxide number with different heating methods (Table 5). Degenerate chain branching decomposition of hydroperoxides occurs both with the formation of free radicals, one of which is the oxide radical, and with the formation of molecular products [6-7].

Table 5. Changes in peroxide value [1/2 $O^{mmol}/_{kg}$].

Heating temperature [°C]	Salomas	
	Steam heating	Induction heating
180	0.46±0.09	0.77±0.053
200	0.43±0.05	0.40±0.017
220	0.40±0.082	0.23±0.056

The continuation of chains involving peroxide and oxide radicals leads to the formation of secondary oxidation products that contain alcohol, aldehyde and ketone groups. Data on changes in the content of carbonyl compounds during induction heating and heating with high pressure steam are presented in Table 6.

Table 6. Changes in the content of carbonyl compounds [µmol/g].

Heating temperature [°C]	Salomas	
	Steam heating	Induction heating
180	10.24±0.61	10.16±0.62
200	11.13±0.72	10.6±0.21
220	11.75±1.1	11.23±0.67

The increase in the content of secondary oxidation products is confirmed by IR spectroscopy data [8]. The spectra of sunflower oil and lard show all the bands of stretching ν and bending δ vibrations characteristic of fats (Table 7).

Table 7. Absorption bands in IR spectra.

Band assignment	Oil frequency [cm^{-1}]
-(CH_2)- skeletal	729
$^{\delta}$C-H in trans connection -CH=CH-	970
$^{\nu}$C-O ester linkage of triacylglycerols	1169
$^{\delta}$C-H in group CH_2	1469
$^{\nu}$C-O (esters)	1750

When analyzing the IR spectra, it was found that on the short-frequency arm of the base of the $^{\nu}$C-O band 1748-1750 cm^{-1} in the spectra of lard there is an expansion, which indicates the presence of secondary oxidation products of carbonyl compounds in fats. The expansion is formed due to bands (bends) at 1690 cm^{-1} - $^{\nu}$C-O in unsaturated conjugated structures and 1714 cm^{-1} $^{\nu}$C=O in saturated aldehydes and ketones.

In the IR spectra of lard, compared to vegetable oil, the highest intensity is the band at 970 cm^{-1}, which corresponds to bending vibrations $^{\delta}$C-H in the isolated transethylene bond CH=CH-.

The width of the $^{\nu}$C-O d15 band characterizes the level of accumulation of secondary oxidation products in lard. The value of d_{15} was measured at a distance T=15 from the base line xx^1 of the $^{\nu}$C=O band.

With a relatively short continuous heating of lard to 220 °C by induction and high-pressure steam, the overall absorption in the IR spectra increases, especially in the region of 700-1760 cm^{-1}, but the bands of the main vibrations of triacylglycerols are slightly affected: skeletal vibrations - (CH_2) n-, $^{\nu}$C-O ester group $^{\delta}$C-H in the CH_2 group.

When the oil is heated, the base of the vC-O band at 1748-1750 cm_{-1} expands. This indicates the accumulation of carbonyl compounds in lard. The d_{15} values for vegetable oil depend on the heating method. The original oil has d_{15} = 33.3 cm^{-1}. For oil heated using high pressure steam, d_{15} = 40 cm^{-1}, induction d^{15} = 46 cm^{-1}. The original lard has d^{15} =40 cm^{-1}, heated in various ways - d^{15} =46.7 cm^{-1}.

The data obtained are in accordance with the values of the content of carbonyl compounds determined by the spectrophotometric method (Table 7).

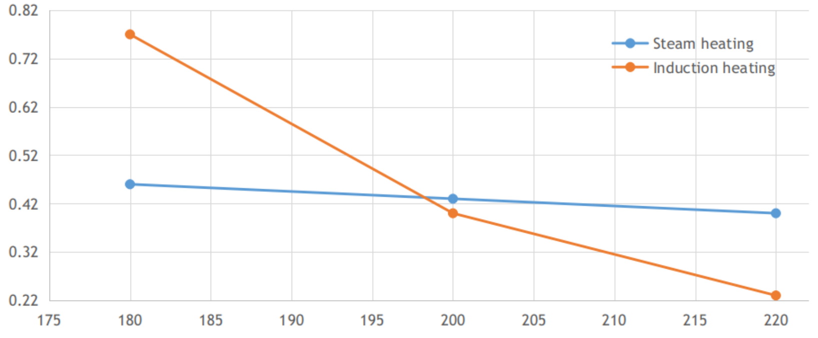

Fig. 5. Decrease in the peroxide number of lard during continuous heating to 220 °C.

In the saturated acids that make up acylglycerols, the weakest is the C-H bond of the carbon atom located in position α to the carboxyl group. When an alkyl radical is formed, it quickly turns into a peroxide radical and then into a hydroperoxy acid. Hydroperoxy acids can be formed by attacking C-H bonds that are more distant from the carboxyl group (the most reactive are the C-H bonds of the 3rd and 4th atoms). The resulting hydroperoxy acids are unstable and can turn into aldehydes, hydroxy and keto acids (secondary oxidation products).

When chains break, radical electrons join together (radical recombination) and fatty acid chains are "cross-linked" by C-C, C-O-C bonds, both within fat molecules and intermolecularly. During thermopolymerization of fat, as a result of the recombination of free radicals of fat molecules and the formation of new bonds (C-C, C-O-O-C, C-O-C), oxypolymers are formed, which contain various oxygen-containing groups in the fatty acid chains. The resulting oxypolymers are capable of hydrolyzing to form monomeric, di- and trimeric oxidized fatty acids.

At a certain stage of thermopolymerization, double bonds in fatty acid chains are destroyed, as a result of which the iodine number decreases [8].

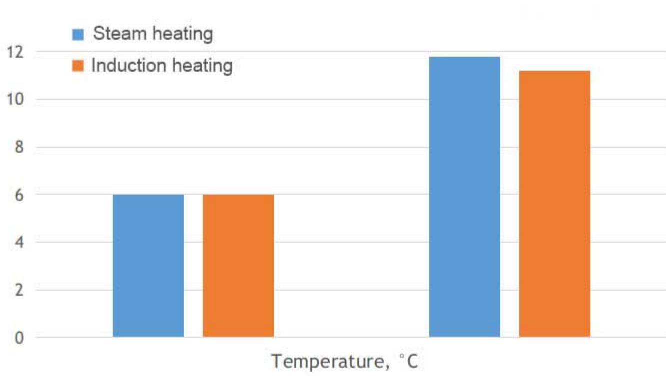

Fig. 6. Changes in the content of carbonyl compounds in lard during continuous heating to 220 °C.

Thermopolymerization of fat is accelerated due to the formation of conjugated polyene systems. These systems are formed by isomerization of isolated structures $-CH=CH-CH_2-CH=CH-$ linoleic and arachidonic acids that are part of sunflower oil. The increase in the number of conjugated dienes can be observed in the UV spectra of single samples of salomas. The change in the specific absorption value for various methods of heating salomas at a wavelength of 232 nm (diene conjugated structures) and 268 nm (triene conjugated structures) is presented in Table 8.

The depth of thermal oxidation and thermal polymerization can be judged by changes in indicators such as iodine number, refractive index, and the content of oxidation products insoluble in petroleum ether (Table 9).

It has already been noted that peroxide radicals are capable of oxidizing an isolated double bond to oxirane structures (epoxides). This product is thermophilic and at high temperatures with relatively short heating it decomposes to form other compounds. Data on changes in the content of oxirane oxygen are presented in Table 11. It should be noted that with longer periodic heating of fats (from 2 to 10 hours), a continuous increase in the content of oxirane oxygen was observed.

Table 8. Changes in specific absorption [$\mathring{A}^{1\%}_{1\tilde{n}\grave{i}}$].

Raw material name	Salomas			
	Steam heating		Induction heating	
	$\mathring{A}^{1\%}_{1\tilde{n}\grave{i}}$ 232 nm	$\mathring{A}^{1\%}_{1\tilde{n}\grave{i}}$ 268 nm	$\mathring{A}^{1\%}_{1\tilde{n}\grave{i}}$ 232 nm	$\mathring{A}^{1\%}_{1\tilde{n}\grave{i}}$ 268 nm
Raw materials	3.1	0.16	3.1	0.16
Warmed up to 220 °C	3.4	0.2	3.3	0.22

Table 9. Iodine number values [mg I_2/100g].

Heating temperature [°C]	Salomas	
	Steam heating	Induction heating
180	78+0.50	78±0.64
200	79+0.63	78±0.54
220	78±0.59	78±0.38

Table 10. Refractive index values.

Heating temperature [°C]	Salomas	
	Steam heating	Induction heating
180	1.4541±0.5*10^{-4}	1.4541±0.94*10^{-4}
200	1.4541±0.72*10^{-4}	1.4541±0.72*10^{-4}
220	1.4541±0.86*10^{-4}	1.4541±0.61*10^{-4}

Table 11. Changes in oxirane oxygen content [%].

Heating temperature [°C]	Salomas	
	Steam heating	Induction heating
180	0.0109±8.4*10^{-4}	1.0113±9.1*10^{-4}
200	0.0104±7.9*10^{-4}	1.0106±8.5*10^{-4}
220	0.0097±7.6*10^{-4}	1.0096±8.1*10^{-4}

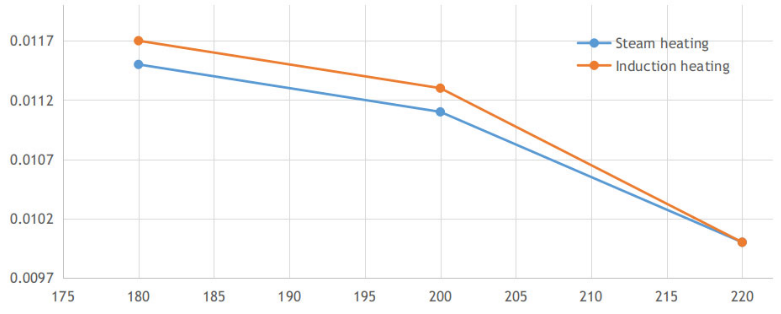

Fig. 7. Reduction of oxirane oxygen content in lard during continuous heating to 220 °C.

Table 12. Change in the content of secondary oxidation products insoluble in petroleum ether [%].

Heating temperature [°C]	Salomas	
	Steam heating	Induction heating
180	0.261±6.9*10^{-3}	0.258±9.2*10^{-3}
200	0.265±9.2*10^{-3}	0.262±8.9*10^{-3}
220	0.268±12.7*10^{-3}	0.264±11.1*10^{-3}

4 Discussion

Thus, with continuous heating of dalomas by induction and high-pressure steam, hydroperoxides decompose and secondary oxidation products form. The peroxide number of oil on average decreases when heated with high-pressure steam during induction heating, lard by 90% and 91%, respectively (Table 5, Figure 5). The rate of decomposition of salomas hydroperoxides under different heating methods does not differ significantly. With both heating methods, an increase in carbonyl compounds is observed (Table 5, Figure 6). This indicator when heated to 200 °C with both methods increases heating on average by 2 times.

As a result of heating, the content of epoxides decreases (Table 11, Figure 6-7), which, like hydroperoxides, are unstable products and decompose under the influence of high temperatures. The content of epoxy oxygen in lard decreased by 40% (steam heating), by 41% (induction heating).

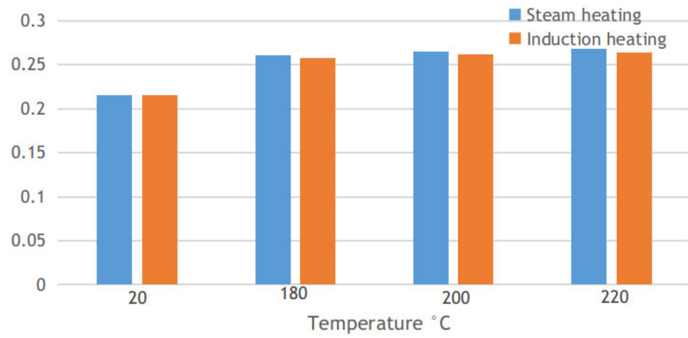

Fig. 8. Increase in the content of secondary oxidation products, insoluble in petroleum ether, in lard during continuous heating to 220 °C.

Compared to the original oil (saloma), an increase in secondary oxidation products insoluble in petroleum ether is observed (Table 12, Figure 8). For lard, with both heating methods, the content of secondary oxidation products increased on average by 1.3 times.

The iodine numbers of salomas do not change noticeably during the heating process, either compared to the initial value or depending on the heating method (Table 9).

Analyzing the data obtained, it should be noted that with continuous heating to 220 °C for a relatively short time, very deep changes associated with thermal oxidation and thermopolymerization do not occur in lard. According to the accepted theory of oxidation, the decomposition of hydroperoxides and epoxides and the accumulation of secondary oxidation products containing a carbonyl group are observed. High heating temperatures contribute to a slight increase in the content of secondary oxidation products insoluble in petroleum ether (polyhydroxy acids, condensation products of oxidized fatty acids).

When heated, conjugated diene and triene systems accumulate in lard, which is confirmed by an increase in the specific absorption values at 232 and 268 nm (Table 8) and the UV spectra of lard. The accumulation of conjugated diene and triene structures occurs especially intensively.

A slight change in the iodine numbers of salomas indicates that polymerization processes using double bonds occur to a very small extent. For such indicators as iodine number, refractive index, peroxide number, no significant differences are observed with the heating methods under consideration.

Vegetable oils contain natural antioxidants: tocopherols, sterols [1]. The most powerful antioxidant is tocopherol, which belongs to the class of phenols. σ-tocopherol exhibits especially strong antioxidant properties. Many authors argue that carotenoids increase the resistance of dietary fats to oxidation. However, the refining process involves removing carotenoids from vegetable oils. A small part of them is removed during hydration and 80% during bleaching [9].

Metals get into oils both naturally (from seeds) and artificially (during the production process at a high acid number, metals can transfer from the equipment material). About 3% of the metals contained in the seeds pass into the oil. A significant proportion of oil metals is part of phospholipids (55%), and the rest can be in the form of fatty acid salts [10].

Some of the metals contained in the oil are removed at various stages of refining. On average, after hydration and refining, the metal content is reduced by 5-10 times, depending on the technological processing mode [1]. In this work, an attempt was made to determine the effect of different heating methods used in continuous deodorization on changes in the metal content of lard. The content of the mass fraction of metals was determined in lard, heated continuously by various methods to 220 ° C, the data is placed in Table 13. Analyzing the data in Table 13, it should be noted that when the lard was heated, the content of all metals (except Ni) increased compared to the initial data (Table 1). At the same time, the content of the mass fraction of metals of the same name for different heating methods does not differ significantly, with the exception of iron. The observed increase can be explained by the ingress of metal ions into the oil from the material of the installation equipment. It should be noted that stainless steel grade 12X18H10T includes iron and nickel, and brass grade L70, from which stop valves are made, contains copper, zinc and small amounts of lead. In the literature there are similar data on the increase in the content of metals (Fe) in oil during periodic heating to 170 °C for 10 hours in a container made of steel grade 18M-9T [12].

Table 13. Content of mass fraction of metals [mg/kg].

Object of study	Metals	Steam heating	Induction heating
Salomas	Ni	0.5±0.02	0.47±0.04
	Fe	1.51±0.08	1.84±0.06
	Cu	0.48+0.03	0.53±0.04
	Pb	0.083±0.006	0.071±0.005

The observed growth of metals makes it difficult to draw a final conclusion about any influence of the electromagnetic field on the content of metals in lard. Taking into account the data obtained, we can say that the heating method does not have a significant effect on the content of the mass fraction of metals in lard.

5 Conclusion

With the induction heating method, the average temperature difference between the heating wall and the oil at the outlet of the heater is 5.9 °C higher than when heating with high-pressure steam, for lard oil by 8.5 °C. At the same time, the heating rate with the induction method is higher by 0.1 degrees/min (oil) and 0.4 degrees/min (salomas).

Analysis of the quality indicators of lard heated continuously by induction using high-pressure steam showed that there are no differences between heating methods.

Analyzing the content of the mass fraction of metals in fat under different heating methods in comparison with the initial values, it should be concluded that the increase in the metal content does not depend on the heating method.

The spectra of lard continuously heated in various ways, taken in the visible region (500-800 nm) and the spectra of 1% solutions of oil in hexane, oil taken in the UV region, as well as the IR spectra of oil solutions in CCI4, confirm a slight tendency towards an increase in oxidative processes during induction heating of oil compared to steam.

The higher temperature difference between the heating wall and the heated lard during continuous induction heating compared to steam heating does not affect the quality of the latter. Therefore, for lard, these heating methods are equivalent.

Thus, with the induction heating method, the degree of hydrolysis of lard does not change compared to traditional steam heating, which allows us to speak not only about the effectiveness, but also about the safety of this heating method.

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