Obtaining technologically and physiologically functional special-purposes of fat products

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Abstract. The possibilities of obtaining special fat products for baking and confectionery products based on two-stage hydrogenation, both on stationary promoted and dispersed catalysts, are investigated. At the same time, at the first stage, non-selective partial hydrogenation was carried out to obtain liquid baking fats characterized by a sufficient amount of solid glycerides, and at the second stage, this partially hydrogenated fat was subjected to final selective hydrogenation to obtain high-solid confectionery fat. In order to enrich the obtained fats with polyunsaturated fatty acids of the group ω-3, it was first proposed to mix these fats with non-fat flaxseed flour to obtain functional fat-flour compositions.

1. Introduction
The main trends in the development of fat production for margarine, bakery, confectionery and other food industries are to ensure a balanced fat composition with a minimum content of trans-isomers. This is achieved by combining traditional methods of processing oils and fats, such as hydrogenation fractionation, transesterification, as well as their combination.

In food technologies, the range of use of solid fats, usually animal fats, is limited by their low reproducibility, high saturation and high melting points. Therefore, the above-mentioned technologies for modifying oils and fats are widely used.

The classic method of modifying vegetable oils is their hydrogenation to obtain the product of the required degree of unsaturation and hardness. The disadvantage of the technology is to reduce the content of essential fatty acids (due to their saturation) during hydrogenation and their partial isomerization. The resulting trans-isomerized acids have unfavorable physiological properties, which limits the introduction of hydrogenated fats into food products.

Acyllic migration (transesterification) allows the modification of mixtures of fats of different fatty acid composition by rearranging fatty acids in triacylglycerides under the influence of alkaline catalysts. This method makes it possible to obtain modified fats with a high content of linoleic acid (20...40 %), in which the structuring glycerides are saturated acids.

Prospects for transesterification are associated with the possibility of a general increase in the biological value of margarine products and ensuring its optimal fatty acid composition for certain age groups of the population. However, the production of highly solid modified fats from liquid vegetable oils by transesterification alone is problematic, so in the case of further increasing the biological requirements for the chemical composition of fat bases, the combination of hydrogenation and transesterification seems to be a very promising way.
Fractionation is one of the ways to modify fats without affecting their structure. It allows the fat to be divided into fractions by tempering (in the melt) at different temperatures or by recrystallization from a solvent. In this case, fat fractions of various degrees of saturation, hardness and melting point are obtained.

Fractionation in the melt is used in the processing of oils and fats with a high initial content of high-melting triacylglycerides (at least 30%). The method gives positive results with a significant difference in the crystallization and melting temperature of the target and by-products.

The latest trend in the oil and fat industry is the creation of various combined fat and lipid-protein products that meet the modern requirements of nutrition science. Deep fundamental studies of the dependence of lipid metabolism in the body on the composition and ratio of fatty acids of various degrees of unsaturation, the structure of triacylglycerides and other biologically active components allowed us to establish the basic requirements for fat products for general, therapeutic, preventive and special purposes.

The creation of dietary fats, including special-purpose fats, with optimal physical and chemical parameters, with a minimum level of trans-isomerized acids, and with the preservation of the main biologically important components in the native state is an urgent problem from the point of view of nutrition physiology.

At the same time, an important task is also the development of methods for obtaining, organizing industrial production and application of dietary fats using local raw materials [1].

The aim of this study is to obtain technologically and physiologically functional baking and confectionery fats by combining non-selective and selective two-stage hydrogenation, followed by mixing them with flaxseed flour for enrichment with polyunsaturated fatty acids of the group ω-3.

2. Methods and materials
Partial and deeper hydrogenation of cottonseed oil was carried out both with the use of new modifications of stationary alloy catalysts, and with the use of a dispersed nickel-copper catalyst obtained from nickel and copper sulfite salts with reverse precipitation in soda solution (Ni:Cu=1 ratio:1).

For the hydrogenation of the oil, electrolytic hydrogen was used (H content=99.8 %).

For exploratory studies of the hydrogenation of cottonseed oil under flow conditions in the presence of stationary alloy catalysts, an installation with column-type reactors was used. Hydrogenation of raw materials was carried out sequentially in two hydrogenation reactors, including non-selective and selective stages. Non-selective partial hydrogenation (the first stage) of cottonseed oil was carried out in the first reactor of the plant at a feed rate of 1.5...5.5 h⁻¹ through a layer of the most effective nickel-copper-rhodium-aluminum stationary catalyst with germanium and vanadium additives. At the same time, the selectivity of the hydrogenation process ranged from 44 to 63%.

Deep hydrogenation (second stage) of partially saturated cottonseed oil (iodine number 68...82 % J₂) was carried out in the second reactor of the plant at a feed rate of 0.7...2.5 h⁻¹. Hydrogenation was carried out on a regenerated and trained stationary nickel-copper-rhodium-aluminum catalyst with rhenium and vanadium additives. The selectivity of hydrogenation at this stage of the process ranged from 88 to 98 %.

The hydrogenation properties of stationary and dispersed catalysts were evaluated under the conditions given in tables 1 and 2.

Table 1. Conditions for evaluating the hydrogenation properties of stationary alloy catalysts.

| Parameters                        | Continuous hydrogenation |
|-----------------------------------|--------------------------|
|                                   | at the first stage | at the second stage |
| Temperature, °C                   | 180                     | 200                     |
| Hydrogen pressure, kPa            | 100                     | 300                     |
| Feed rate of raw materials, h⁻¹   | 1.5-5.0                 | 0.7-2.5                 |
| Hydrogen feed rate, h⁻¹           | 60                      | 45-60                   |
Rhodium, germanium, rhenium, and vanadium were used as the promoting metals. The choice of these promotional supplements was not random, and it is based on deep and fundamental research [2-5]. In order to increase the efficiency of existing stationary catalysts and reduce the content of trans-isomerized fatty acids in hydrogenates, we have proposed new modifications of stationary promoted nickel-copper-aluminum-rhodium catalysts, where paired combinations of germanium with vanadium and rhenium with vanadium are used as promoting metals.

Table 2. Conditions for hydrogenation of raw materials on a dispersed nickel-copper catalyst.

| Parameters                              | Hydrogenation on the 1st autoclave | Hydrogenation on subsequent autoclaves |
|-----------------------------------------|------------------------------------|----------------------------------------|
| Temperature, °C                         | 195-200                             | 195-200                                |
| Pressure, kPa                           | 100-150                             | 250-300                                |
| Feed rate of raw materials, m³/h Supply | 5-7                                 | 8-10                                   |
| volume of hydrogen, m³/ton              | 45-50                               | 55-60                                  |
| Duration of hydrogenation, min.         | 7-10                                | 55-60                                  |
| Catalyst consumption in terms of Ni, kg/ton | 0.10-0.15                           | 0.25-030                               |

The method for producing fat-rich mixtures enriched with omega-3 fatty acids includes dosing the ingredients in accordance with their formulation (the temperature of the fats is 5.0...6.0°C higher than their melting temperature), mixing, tempering, supercooling and mechanical (plastic) processing [6-8]. At the same time, the oilseeds of flax used for the production of non-fat flaxseed flour corresponded to the interstate standard GOST 10582-76 “Oil flax-seed. Industrial raw material. Specifications”.

3. Results and discussion

For the practical implementation of the tasks of developing methods for the production, organization of industrial production and application of food fats using local raw materials, in some countries, factories for the production of specialized food fats have been built and operate. These are the plant in Alekseevka, Belgorod region "EFKO-Sloboda" (Russia) and the plant of ADM (Archer Daniels Midland Company) in Quincy, Illinois (USA). In turn, ADM works closely with Novozymes (Denmark) [9, 10].

For the Central Asian regions, the potential raw material for the oil and fat industry is cotton seeds, and the main type of vegetable oil is cottonseed oil. The physical and chemical properties of cottonseed oil, as well as other vegetable oils, can not promote their use as special prescription fat components for the production of high-quality bakery and confectionery products. Therefore, for these purposes in the Central Asian region, it is recommended to use hydrogenated or transesterified fat products based on cottonseed oil and its processed products.

The production of special fats for the baking and confectionery industry through the use of highly solid hydrogenated, transesterified fats, palm stearin and animal fats is limited for a number of reasons, the main of which are the complexity and high cost of technological modification processes, the lack of transesterification catalysts, the use of imported palm stearin. Therefore, the production and use of such fats for the baking and confectionery industry has not yet found a proper wide distribution in many regions. The use of dispersed selective catalysts in hydrogenation technology is associated with the complexity of separating the catalyst from the finished product and the cost of filtration, as well as the content of a large amount of trans-isomerized fatty acids in hydrogenates.
Obtaining food fats with the desired properties from oils by hydrogenation on stationary catalysts is somewhat difficult for a number of reasons. However, the process of obtaining liquid fats with a certain ratio of the solid and liquid phase by partial hydrogenation (subhydrogenation) on stationary catalysts can be more efficient. Moreover, in contrast to the fat bases of margarine and solid confectionary fats, for which the selectivity of hydrogenation, and therefore their uniformity is very important, the simultaneous content of solid and liquid glycerides in non-selectively hydrogenated fats is a desirable property for their use in baking. That is, the non-selective subhydrogenation of cottonseed oil on active alloy polyfunctional catalysts at the first stage of the proposed two-stage saturation has its own technological (ratio of solid and liquid fractions), economic (productivity) and social (reduction of the content of trans-isomers of fatty acids) justification. In this regard, we have investigated and developed a two-stage continuous technology (figure 1) for the hydrogenation of cottonseed oil using series-connected column-type reactors in the presence of a stationary alloy promoted nickel-copper-rhodium-aluminum catalyst.

Hydrogenated cottonseed oil with IN (iodine number) =109.1 %, AN (acid number) 0.2 mg KOH/g, color 11 r. u.(red units). Fatty acid composition of raw materials, %: the sum of saturated-27.0, monoenic -19.9, diene-53.1.

![Figure 1. Technological scheme of two-stage hydrogenation of cottonseed oil on stationary catalysts.](image)

In the conducted studies, it was interesting to obtain liquid and high-solid food fats used for the production of bread products and confectionery products.

Taking into account the efficiency of the technology of sequential hydrogenation of cottonseed oil in column reactors and ensuring the production of fats of increased nutritional value, the saturation of raw materials was carried out in two separate stages:

- The first is the partial hydrogenation of raw materials on a stationary nickel-copper-rhodium-aluminum catalyst promoted by germanium+vanadium to produce liquid hydrogenated edible fats for baking;
- The second is the hydrogenation of partially hydrogenated raw materials on a stationary trained nickel-copper-rhodium-aluminum catalyst, promoted by rhenium+vanadium, in order to obtain high-solid food fats for margarine and confectionery products.

Partial hydrogenation of cottonseed oil (stage 1) was carried out at 180°C, a pressure of 100 kPa and a volumetric hydrogen supply rate of 45h⁻¹. The volume feed rate of the raw material was set in order to obtain liquid fats with a relatively minimal (5...13 %) content of trans-isomerized fatty acids. At the same time, partially hydrogenated fats with a melting point of 17...21 °C were obtained, the content of
fatty acids in triacylglycerides were: diene – 42.0...52.7; monoene – 22.8...27.8 and saturated-24.5...30.2.

The resulting partially hydrogenated oils are further subjected to deep saturation in the second stage of hydrogenation of the raw material. The studies were carried out at 200°C, a pressure of 300 kPa and a volumetric hydrogen supply rate of 60 h\(^{-1}\). The volume feed rate of the raw material was varied in order to obtain high-solid food fats. In this case, dietary fats with a melting point of 31.0...36.1°C, a hardness of 200...550 g/cm and a content of fatty acids in triacylglycerides, % were obtained: dienoic – 11.2...30.3; monoenic – 44.2...56.7 and saturated-25.5...32.1.

Based on the conducted research and development, a technology for producing liquid and high-solid food fats for the production of bread products and confectionery products has been created.

In the course of studying the technology of two-stage hydrogenation of cottonseed oil at the first stage of the technological process, a relative decrease in selectivity and ensuring the necessary content of the solid phase in the composition of liquid fat is observed. By adjusting the volumetric speed of the oil supply, the required content of high-melting glycerides is achieved at a temperature of 35°C, which is very important in the production technology of liquid baking fats (table 3).

**Table 3.** Physical and chemical characteristics and fatty acid composition of liquid edible fat obtained at the first stage of sequential hydrogenation technology.

| Sample, N | Volumetric oil feed rate, h\(^{-1}\) | Iodine number (IN),% | Acid number (AN), mg KOH/g | Content | Composition of fatty acids, % |
|-----------|-----------------------------------|------------------|----------------------------|---------|-----------------------------|
|           |                                   |                  |                            | Acid trans-isomers, % | High melting glycerides, melting point \(35^\circ\)C | 16:0+18:0 | 18:1 | 18:2 | Selectivity, % | Fat fluidity at \(0^\circ\)C |         |
| 1         | 1.5                               | 79.8             | 0.5                        | 17.2                | 12.8                        | 30.2 | 27.8 | 42.0 | 63          | non-flowing         |
| 2         | 1.8                               | 85.5             | 0.4                        | 13.0                | 9.6                         | 29.5 | 26.5 | 44.0 | 61          | non-flowing         |
| 3         | 2.4                               | 92.7             | 0.4                        | 10.2                | 7.3                         | 28.5 | 25.7 | 45.0 | 60          | non-flowing         |
| 4         | 2.8                               | 94.0             | 0.3                        | 8.6                 | 6.2                         | 28.0 | 25.6 | 46.4 | 58          | ointment            |
| 5         | 3.2                               | 96.1             | 0.3                        | 6.0                 | 5.5                         | 27.4 | 24.8 | 47.8 | 57          | Fluid              |
| 6         | 4.0                               | 101.1            | 0.3                        | 5.9                 | 5.3                         | 27.1 | 24.4 | 48.5 | 56          | Fluid              |
| 7         | 4.5                               | 103.6            | 0.3                        | 5.4                 | 5.1                         | 26.8 | 23.2 | 50.0 | 52          | Fluid              |
| 8         | 5.0                               | 104.9            | 0.2                        | 5.1                 | 4.8                         | 25.7 | 23.0 | 51.3 | 48          | Fluid              |
| 9         | 5.5                               | 107.0            | 0.2                        | 5.0                 | 4.6                         | 24.5 | 22.8 | 52.7 | 44          | Fluid              |

The evaluation of the hydrogenability of the oil at this first stage shows that under the selected modes, the process proceeds non-selectively and in the direction of accumulation of both high-melting and liquid glycerides at the same time. This means that the resulting hydrogenates meet the requirements of special liquid baking fats.

With further saturation of the selected 4th sample at the second stage of hydrogenation, salomas were obtained that meet the requirements for use in the production of confectionery products in terms of hardness and melting point. The relatively low content of trans-isomerized fatty acids with a high degree of hydrogenation selectivity is important (table 4).

However, despite the fact that stationary alloy catalysts are undoubtedly promising in the technology of hydrogenation of oils and fats, in the industrial practice of domestic and foreign hydrogenation production, dispersed powdered catalysts are still mainly used. In this regard, research has also been conducted on the development of a consistent technology for the hydrogenation of cottonseed oil using a dispersed nickel-copper catalyst.
Table 4. Physical and chemical characteristics and fatty acid composition of hydrogenated fat obtained at the second stage of sequential hydrogenation technology.

| Sample, № | Volumetric oil feed rate, h⁻¹ | IN, % J₂ | AN, mg KOH/g | Selectivity, % | Acid trans isomer content, % | Fatty acid composition, % | Melting point, °C | Salomas hardness, g/sm |
|-----------|-------------------------------|-----------|---------------|----------------|-----------------------------|---------------------------|-------------------|------------------------|
| 4-1       | 0.7                           | 67.8      | 0.75          | 88.1           | 20.1                        | 16:0+18:0 18:1 18:2      | 32.1             | 56.7 11.2 36.1         | 550                    |
| 4-2       | 1.0                           | 71.1      | 0.80          | 87.0           | 18.7                        | 31.4 55.5 13.1          | 500               |                        |                        |
| 4-3       | 1.5                           | 78.9      | 0.73          | 93.4           | 15.3                        | 28.2 52.0 19.8          | 360               |                        |                        |
| 4-4       | 2.0                           | 80.8      | 0.60          | 96.5           | 12.8                        | 26.7 51.1 22.3          | 250               |                        |                        |
| 4-5       | 2.5                           | 81.6      | 0.55          | 98.7           | 11.4                        | 25.5 44.2 30.3          | 200               |                        |                        |

Hydrogenation of raw materials (IN =109.1% J₂, AN= 0.3 mg KOH/g, composition of fatty acids, %; saturated – 27.0; monoene-19.9; diene-53.1) was carried out in a battery consisting of 3 series-connected autoclaves. Partial hydrogenation of the oil was carried out in the first autoclave at 200°C and a pressure of 300 kPa. As a dispersed catalyst, a freshly prepared powder obtained from nickel and copper sulfate salts with reverse precipitation in a soda solution was used. The amount of the catalyst used and the volumetric feed rate of the raw material are set taking into account the production of liquid baking fat. The results of the study are shown in table 5.

Table 5. The first stage of sequential hydrogenation of cottonseed oil on a dispersed nickel-copper catalyst (Ni:Cu=1:1).

| Sample, № | Iodine number, % J₂ | Acid number, mg KOH/g | Fatty acid composition 16:0+18:0 18:1 18:2 | Content of transacids, % | Melting point, °C | Hardness, g/sm |
|-----------|----------------------|-----------------------|------------------------------------------|----------------------------|------------------|----------------|
| 1         | 86.5                 | 0.6                   | 29.7 26.2 44.1                           | 25.1                       | 25.3             | Ointment       |
| 2         | 95.1                 | 0.5                   | 28.3 24.2 47.5                           | 16.5                       | 19.3             | Ointment       |
| 3         | 101.5                | 0.4                   | 27.5 24.0 48.5                           | 15.7                       | -                | -              |

As can be seen from the above data, the use of a dispersed catalyst also achieved the production of liquid dietary fats with increased nutritional value.

In the future, the selected 2-sample of the experimental liquid fat is subjected to final hydrogenation in subsequent autoclaves. The studies were carried out under similar conditions using a reused regenerated dispersed nickel-copper catalyst. The results obtained are presented in table 6.

Table 6. The second stage of sequential hydrogenation of cottonseed oil on a dispersed nickel-copper catalyst (Ni:Cu=1:1).

| Sample, № | Iodine number, % J₂ | Acid number, mg KOH/g | Fatty acid composition 16:0+18:0 18:1 18:2 | Content of transacids, % | Melting point, °C | Hardness, g/sm |
|-----------|----------------------|-----------------------|------------------------------------------|----------------------------|------------------|----------------|
| 2-1       | 67.5                 | 0.9                   | 31.2 55.4 13.4                           | 26.7                       | 36.1             | 550            |
| 2-2       | 71.3                 | 0.7                   | 29.6 52.6 17.8                           | 23.1                       | 33.2             | 420            |
| 2-3       | 74.2                 | 0.6                   | 28.1 52.3 19.6                           | 20.6                       | 31.8             | 280            |

These data indicate that the final hydrogenation of raw materials produced high-solid edible fats that meet the standard indicators of margarine and confectionery production.
One of the important aspects of the functionality of fat products is to provide them with the required ratio of polyunsaturated fatty acids (PUFAs) of the groups ω-6: ω-3. Hydrogenated fats, being the fat base of many dietary fats, practically do not contain PUFAs of the group ω-3. Therefore, when obtaining special-purpose dietary fats, vegetable oils rich in PUFAs of the ω-3 group, such as flaxseed, soy, wheat germ oil, and others, are usually added to the food salomas. However, if the production of some of these oils, for example, linseed, is associated with the difficulties of their protection from oxidative changes, then the production of oils such as wheat germ oil—the difficulties of the extraction process by pressing, since the wheat germ is a low-oil raw material.

In this regard, we have proposed a method for obtaining functional fat-flour mixtures of the target purpose enriched with PUFAs of the group ω-3 by mixing the obtained salomas and flaxseed finely dispersed unfat flour. When calculating on a computer program, the fatty acid composition of the components was taken into account. As a result of the calculations, it was found that in order to achieve the optimal ratio of ω-6: ω-3, equal to approximately 10, the components should be selected in the ratios:

- Partially hydrogenated hydrogenate – 80-84%
- Unfat flaxseed flour – 16-20%

And in the case of using high-hard salomas obtained after the 2-stage hydrogenation:

- Salomas – 90-93%
- Unfat flaxseed flour – 7-10%

4. Conclusion

Thus, both technologically and physiologically functional food fat products for baking and confectionery products were obtained. If the functionality from the technological point of view is explained by the necessary ratio of liquid and solid glycerides in fat products, then the functionality from the physiological point of view is due to their chemical composition, in particular, the minimum amount of trans-acids and the necessary content of PUFA group ω-3.

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