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HYDROGENATION TECHNOLOGY AND CHEMISTRY OF COTTONSEED OIL AND FATS

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SUMMARY

The presented research describes the hydrogenation technology and the chemistry of vegetable oils and fats using powder and stationary catalysts. The hydrogenation technology process includes various equipment and materials, i.e., equipment for hydrogenation, laboratory flow reactor, autoclave for hydrogenation on powder nickel-copper catalyst, hydrogenation catalysts, and selection of alloy stationary catalysts and their structure. The hydrogenation process includes selecting alloy nickel-aluminum catalyst promoters, measuring the viscosity of hydrogenated fat, using static catalysts as forcontacts, kinetic regularities of cotton oil hydrogenation with new modifications of nickel-copper-aluminum alloy promoted catalysts, and reception of food hydrogenated fat by consecutive hydrogenation of cotton oil on powder and stationary catalysts. Modifying immobile nickel-copper-aluminum alloy catalysts also evolved with the addition of vanadium, rhodium, and palladium in the hydrogenation process. The cotton oil pre-contact hydrogenation on stationary and powder nickel-copper catalysts is a novel development. It ensures an increase in the physiological and nutritional value of margarine products based on hydrogenated food fat. Studying the influence of technological regimes of cotton oil hydrogenation on new modifications of stationary nickel-copper-aluminum promoted catalysts commenced. The obtained results established the technological parameters for acquiring food and confectionery salons by combining stationary and suspended catalysts. Likewise, a combination of stationary and suspended catalysts has instituted the industrial parameters for the production of food and confectionery salons based on the effects of technological regimes (temperature, pressure, oil, and hydrogen supply rates) of cottonseed oil hydrogenation on new modifications of stationary nickel-copper-aluminum promoted catalysts.

Keywords: Cottonseed oil, hydrogenation and recertification, chemistry of vegetable oil, powder and stationary catalysts, triacylglycerides, linoleic acid, ethylene

Key findings: The latest continuous technology of pre-contact hydrogenation of cottonseed oil with stationary and powder nickel-copper catalysts helped increase margarine products' nutritional and physiological values based on edible hydrogenated fat.

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INTRODUCTION

The oil and fat industry pursues creating a new and improved technology for processing vegetable oils and fats, significantly increasing the productivity of technological equipment and quality food products. In this regard, the exceptional focus is on producing oil hardening (Abdurakhimov, 1975). Nowadays, catalytic hydrogenation is the industrial process of vegetable oils and fats modified to obtain hydrogenated fats for margarine and confectionery products. Therefore, it is imperative to improve the technology of fats hydrogenation using stationary and dispersed nickel-copper catalysts (Majidov *et al.*, 1990; Sattarov *et al.*, 2007a, b; Mazhidov *et al.*, 2019).

The chemical and physical properties of vegetable oils and animal fats depend upon their fatty acid composition and distribution in a mixture of triglycerides. There are two types of chemical modification of fats, i.e., hydrogenation and reheating. However, both processes are catalytic, which requires a catalyst to lessen the energy barrier of the desired chemical reaction (Abdurakhimov, 1993). The essence of the hydrogenation process consists of targeted changes in the fatty acid composition of oils and fats by hydrogen addition to unsaturated acyl groups of glycerides and chemical transformations that occur in the presence of a catalyst simultaneously with the prime reaction. Changes in fatty acid composition lead to corresponding modifications in triglyceride composition and oils and fats properties, i.e., its hardness, melting point, plasticity, and increased resistance to oxidative and thermal effects (Ginzburg, 1991).

The partial hydrogenation process of vegetable oils and fats adheres to produce modified fats for margarine and other food products. The actual hydrogenation consists of hydrogen joining to double (ethylene) bonds in unsaturated acyl radical glycerides. However, at the same time, the degree of unsaturated fats decreases until turning into fully saturated compounds (Majidov *et al.*, 1990). The hydrogenation reaction of the acyl radical of linoleic acid to the oleic acid radical is as follows:

$$CH3—(CH2)4—CH = CH—CH2—CH = CH—(CH2)—CO— + H2 \rightarrow$$
$$\rightarrow CH3—(CH2)7—CH = (CH2)7—CO—$$

From the chemical point of view, the industrial hydrogenation of fats is significantly more complex than the given reaction of hydrogen addition. Given the catalysts used in this process can accelerate other chemical transformations, among which the most important in practical terms are:

- Displacement of ethylene bonds along the carbon chain of molecules (positional isomerization).
- Formation of hydrogenated oils (geometric isomerization).
- Hydrolysis of triglycerides with the gradual removal of fatty acids and formation of di-, mono-glycerides, and glycerin (at complete hydrolysis).
- Interaction of free fatty acids with nickel and other metals (formation of metal soaps).
- Pyrolytic cleavage (thermodestruction) of glycerides and fatty acids with the formation of aldehydes, ketones, oxy compounds, hydrocarbons, and other compounds.

The deep cleaning of hydrogenated raw material from phosphatides, free fatty acids, pigments, moisture, and catalytic poisons require hydrogen drying to restrain the undesirable side chemical reactions (splitting of glycerides, soaping of metal soaps). The properties and qualities of hydrogenated fats have the following factors determining them: the chemical composition of hydrogenated raw material and the degree of its purification, including catalytic poisons, the ratio of various chemical transformations in the hydrogenation process, and the degree of chemical transformation of raw material (Glushenkova, 1971).

Research relevance

Edible fats are an essential food commodity, and per physiological norms requirement in the human diet, the recommended fat content is 30%–33%, which is the total energy value of food. The world progressively focuses more on the research about catalytic modification of vegetable oils and fats to improve the quality and ensure food safety of target fats. Generating a new generation of catalytic converters for producing target edible fats is imperative. In this area, research and development work to improve the properties of target edible fats, optimizing their composition, and technological processes are advancing significantly. Problems with quality and safe food fats and their processed products are the priority directions in realizing the concept of state policy in the field of healthy nutrition for the population of the Republic of Uzbekistan (Majidov *et al.*, 1990).

The action plan 2017–2021 for further development of the Republic of Uzbekistan specifies the tasks, i.e., the development of production sectors, modernization and diversification of industry, application of resource and energy-saving methods, ensuring food safety of the products, and production of competitive and export products for import substitution. Relatedly, the scientific research aimed at producing high-quality target edible fats using vegetable oils, particularly soybean, sunflower, safflower, and sesame oils, to prepare a wide range of food products of specific importance.

Therefore, the research on hydrogenated fats production from vegetable oil using new-generation catalysts, its establishment, and justification of scientific and practical bases of catalytic processes are of immense scientific and practical concern. Uzbekistan has sufficient raw materials and opportunities for organizing new technologies and producing catalysts for hydrogenated fats. Hence, conducting scientific and experimental research for developing hydrogenation technology of oils and fats with new-generation stimulants is vital, resulting in improved quality and food safety of the target food fats.

Managing the hydrogenation process to obtain fats with the specified properties comprises, i.e., the selection of raw material and catalyst for hydrogenation and the optimal process parameters (temperature, hydrogen pressure, duration of contact among the raw material, hydrogen, and reactant, and the ratio among the feed rate of raw material, hydrogen, and the catalyst in the reaction zone). The combination of controlled process parameters can produce hydrogenated fats with numerous properties. Industrial hydrogenation of oils and fats refers to heterogeneous catalytic processes carried out in three phases, i.e., gas-liquid-hard catalyst system. The hydrogenation process includes several physical and chemical stages, viz., hydrogen supply from the gas phase to liquid, supply of hydrogen molecules dissolved in the oils and fats liquid to the catalytic surface, supply of glycerides of oil or fat to the catalytic surface, chemisorption of hydrogen and triglycerides on the catalyst surface, chemical transformations on the catalyst surface, desorption of reaction product from the catalytic surface, and the removal of hydrogen molecules from the reaction zone to liquid phase volume.

MATERIALS AND METHODS

Uzbekistan uses hydrogenated fats for foodstuffs with characteristics specified in the Technical Conditions TU (Technical Requirements) 10-04-02-66-90 on the "Unpurified hydrogenated fat for the margarine industry." According to specifications, the required characteristics of hydrogenated fat for margarine and confectionery products are in Table 1.

Research objective

The study seeks to develop stage-wise hydrogenation of vegetable oils with new-generation catalysts for producing target edible fats. It pursues selecting highly efficient and scientifically grounded technologies and catalytic systems to ensure quality

Table 1. Characteristics of hydrogenated fats for margarine and confectionery products as per specifications.

Process	Margarine products	Confectionery fat
Melting points (°C)	31–36	35–37
Hardness, g/cm at 15 °C	160–320	550–750
Acid-degree value (g OH/g)	1.0	2.0
Mass fraction of solid triglycerides at 20 °C (%)	29–37	at least 45
Mass fraction of nickel (mg/kg)	10	15

Table 2. Connection of hydrogenated fats properties and the depth of their hydrogenation with stationary catalyst.

Autoclave oil flow rate (t/h)	Volumetric oil flow rate (h^{-1})	Hydrogenated fat (% J_2)	T-melt (°C)	Hardness (g/cm)	Selective ability (%)	Trans-isomer content (%)
Disperse catalyst						
6.0	–	69	34.4	320	86	23
6.2	–	71	32.0	280	92	25
6.4	–	74	31.6	220	94	28
Fixed-bed catalyst						
–	1.0	65	44	400	74.5	25
–	1.5	71	42	320	79.7	29
–	2.0	77	38	160	84.3	37

improvement and food safety of target edible fats. In Uzbekistan, the chief raw material for hydrogenated fat production is refined cottonseed oil produced locally.

For this reason, the research task was to obtain the above-hydrogenated fat from cottonseed oil. The hydration of cottonseed oil was with nickel-copper carbonate catalyst produced in Uzbekistan, which is restored directly in the hydrogenation process, then used repeatedly. In reusing the stimulant, its activity gradually decreases; however, the selectivity of action increases. The second stage of hydrogenation used was the "spent" nickel-copper catalyst produced by Tashkent oil and fat plant.

RESULTS AND DISCUSSION

A typical pattern of industrial hydrogenation of cotton oil with a "spent nickel-copper powder catalyst" has an autoclave battery capacity of approximately 6 t/h (Table 2). As reflected in Table 2, it contains hydrogenated fat with iodine number (69–74), obtained at a hydrogenation temperature of 160 °C–180 °C, with 23%–28% trans-isomers of monounsaturated acids (chromatographic method of analysis), having a hardness of 220–320 g/cm. The selectivity of the hydrogenation process to iodine number (71–74) remained at 92%–94%. At the Tashkent MZhK (an electrical substation), the tests at the pilot plant also showed that the new hydrogenation scheme makes it possible to use a low-activity nickel catalyst and, thereby, significantly reduces its consumption while increasing the plant productivity (Mazhidov *et al*., 2019).

For comparison, Table 2 also showed the hydrogenation results of the same cottonseed oil on a trained stationary nickel-copper-aluminum catalyst promoted with rhodium. In this case, hydrogenated fat with almost the same iodine number (65–75) contained about the same amount of trans-isomers and had sufficient hardness. However, the selectivity of hydrogenation lessened; thus, hydrogenated fat had an unsatisfactory hardness and high melting point. Studies on the regularities of the continuous technology of

hydrogenation of cottonseed oil had advanced, establishing at the beginning of the process the mechanism and kinetics of the process of non-selective hydrogenation of unsaturated fatty acids on a stationary catalyst (Sattarov *et al*., 2007a, b).

The connection between the hydrogenation depth on a stationary catalyst and the process selectivity appears in Table 3. Expectedly, from the previous data, a fresh stationary catalyst preserved the high selectivity only if hydrogenated fat has an iodine number of about 100. Similarly, hydrogenated fat has a low melting point and a low content of trans-isomers. Acquiring principally diverse findings revealed partial hydrogenation of cottonseed oil with a stationary catalyst, promoted by rhodium and vanadium, performed at 180 °C–200 °C, with a pressure of 200–300 kPa, and volume hydrogen barbotage rate of 65 ± 5 h^{-1} (Table 4). The volumetric speed of the oil supply, chosen slightly higher (3–4 h^{-1}), obtained unfrozen hydrogenated fat with low trans-isomer content. Such conditions made it possible to reduce the quantitative content of trans-isomerized monounsaturated fatty acids (Sattarov *et al*., 2007a; Mazhidov *et al*., 2019).

Hydrogenated fat with iodine numbers 85–100, containing no more than 8% of trans-mono-unsaturated fatty acids, resulted from this catalyst (Table 3). Then one hydrogenated fat (No. 2) with an iodine number 95 gained hydrogenation using a nickel-copper catalyst at the designed oil supply speed in an autoclave 7.4–8.7 t/h. Running hydration was at a nickel concentration of 0.05%–0.1% in oil, temperature (170 °C–200 °C), and close to atmospheric hydrogen pressure. Under these conditions, the selectivity of the process ensured at 96% ± 3% had the accumulation of trans-isomers at 11% ± 3% (Table 4). Based on the resulting fats, kinds of margarine with high-quality indicators came about (Ginzburg, 1991; Abdurakhimov, 1993; Sattarov *et al*., 2007a, b).

Theoretically, with a decrease in the iodine number of oil with 25–34 units, the trans-isomer content should increase to 7%–22%. However, in the presented study, trans-isomers growth was less, as explained by not achieving the equilibrium formation of trans-isomers at such a high hydrogenation speed. Nevertheless, the resulting hydrogenated fat at a melting point of 33 °C–34 °C had a superb hardness (320–480 g/cm), and hydrogenated fat with a melting point of 38 °C in hardness met the requirements of confectionery production. A series of similar sequential hydrogenation experiments transpired using a stationary catalyst promoted with vanadium and palladium as a pre-contact. At the same time, acquiring fully hydrogenated fats met the requirements of the margarine and confectionery industries. Results revealed the establishment of technological parameters for producing food and confectionery lards by combining stationary and suspended catalysts (Glushenkova, 1971; Abdurakhimov, 1975; Sattarov *et al*., 2007b).

Attempts have also occurred to use a stationary catalyst instead of a powder catalyst. In other words, acquiring hydrogenated food fat is sequentially hydrogenating cottonseed oil first on an active stationary catalyst and then on an exhaust, very inactive immobile catalyst. Typical hydrogenation at a high rate of an iodine number 95 ran on a fresh catalyst promoted by rhodium and vanadium, and the final stage of hydrogenation followed at a lower rate of 1.5–2.0 times on a trained stationary stimulant promoted by palladium and vanadium (Table 5). In this way, it was possible to obtain food lard with a melting point of 31 °C–36 °C and a hardness of 280–550 g/cm^3, with a process selectivity of about 98% (Majidov *et al*., 1990; Sattarov *et al.*, 2007b; Mazhidov *et al*., 2019).

Hydrogenated food fats with a melting point of 31 °C–36 °C and hardness of 280–550 g/cm resulted in a process selectivity of about 98% (Table 4). However, the study emphasizes that selecting the second catalyst is exceptionally difficult and the technology of stationary catalyst training is yet for implementation. In other words, choosing the catalyst was random, and the most promising one was the proposed scheme of sequential hydrogenation with stationary and disperse catalysts.

Table 3. Relationship between the hydrogenated fats properties and the depth of their hydrogenation with a stationary catalyst.

U_m, h^{-1}	P^{60}_d	Fatty acid content, %				Selective ability (%)	AV (mg)	T-melt (°C)	Hardness (g/cm)	Trans-isomer content (%)
		C^0_{14-18}	$C^{1=}_{18}$	$C^{2=}_{18}$	Hydrogenated fat (% J_2)					
0.5	1.4522	54.4	34.2	12.4	50.9	68.5	0.7	53.7	753	43
1.0	1.4545	41.8	31.8	26.4	73.0	70.8	0.5	44.4	246	31
1.5	1.4568	30.4	27.5	42.1	96.5	82.2	0.3	36.5	180	17
2.0	1.4575	29.5	26.5	44.0	100.6	85.5	0.3	26.5	Salve	8

Table 4. Sequential hydrogenation of cotton oil with stationary (rhodium- and vanadium-promoted) and disperse catalysts under chamber conditions.

Volumetric oil flow rate (h^{-1})	Autoclave oil flow rate (t/h)	Hydrogenated fat (% J_2)	Selective ability (%)	Trans-isomer increase (%)	T-melt (°C)	Hardness (g/cm)
Fixed-bed catalyst						
4.0 (№1)	–	100	–	5.6	–	–
3.6 (№2)	–	95	–	6.9	–	salve
3.2 (№3)	–	85	–	8.3	27	80
Disperse catalyst (hydrogenated fat No.2)						
–	7.4	66	94	15	38	550
–	8.1	70	96	11	34	480
–	8.7	72	99	8	33	320

Table 5. Continuous hydrogenation of cottonseed oil with two stationary catalysts.

Volumetric oil flow rate (h^{-1})	Hydrogenated fat (% J_2)	T-melt (°C)	Hardness (g/cm)	Selective ability (%)	Trans-isomer increase (%)
Fresh rhodium- and vanadium-promoted catalytic converter					
3.6 (No. 2)	35	–	Salve	–	6.9
Trained catalyst promoted with palladium and vanadium					
1.8	67	34	550	96	8.3
2.2	71	32	420	98	14.3
2.8	74	31	280	98	16

CONCLUSIONS

Pioneeringly, a continuous technology of pre-contact hydrogenation of cottonseed oil with stationary and powder nickel-copper catalysts has become available. New modifications of stationary nickel-copper-aluminum alloy catalysts with addition of vanadium (0.5%–2.5%), rhodium (0.5%), and palladium (0.05%) have advanced. At the same time, in hydrogenated fats, the lowest content of trans-isomerized acids attained was with a vanadium content of 1.5%. The recommended technology can significantly enhance the oil hydrogenation production of plants and reduce the content of trans-isomerized fatty acids in the hydrogenated fats. It also improves margarine products' physiological and nutritional values based on edible hydrogenated fats.

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