

Technology for obtaining a domestic catalyst for hydrogenation of vegetable oils

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Abstract. Vegetable oils are obtained from oil-containing sunflower seeds, burdock, flax, rapeseed, corn, soybeans, etc. The composition of vegetable oils contains esters (triglycerides) of fatty acids with varying degrees of unsaturation. One of the main processes of vegetable oil processing is the hydrogenation process. Hydrogenation of vegetable oils is a widespread technological process of obtaining raw materials for the production of confectionery fats, detergents, soaps, stearin and other products. It is the hydrogenation of vegetable oils that is of great importance, because it increases the volume of food production. Catalysts for hydrogenation of vegetable oils are not produced in Russia. The volume of the import market is about 250 tons per year. The development and production of domestic catalysts is a priority task in solving import substitution problems. The paper suggests the most environmentally friendly and economical way to obtain catalysts of various chemical compositions is the method through an ammonia-carbonate complex. The results of reserve tests of the developed samples of nickel catalyst for hydrogenation of vegetable oils, as well as the conclusion of potential consumers are presented.

1 Introduction

The fat and oil industry in Russia today is one of the dynamically developing areas of industry. Russia continues to increase the processing of oilseeds. In July 2023, more than 2 million tons of the main oilseeds were processed, which is a third higher than last year. This growth stimulates the export of oilseeds. The main buyers are China, India, Turkey, the Middle East and North Africa.

Hydrogenation of vegetable oils is of particular interest in the process of modification of edible fats and oils. The main purpose of this process is the transformation of ordinary liquid oil into a semi-solid product - salomas of the desired consistency in a certain temperature range. The second method is to reduce the content of dienes and trienes in the product to a minimum, thereby contributing to the resistance of the product to oxidative rancidity [1-3]. Nickel, copper, copper-chromite, platinum and palladium are the most common metals used as active components in heterogeneous catalysts for partial hydrogenation of polyunsaturated triglycerides [4,5].

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In addition to nickel, palladium-based catalysts can be used as catalysts for hydrogenation of vegetable oils. Nefis Cosmetics JSC has proposed a method for hydrogenation of vegetable oils and distilled fatty acids, characterized in that hydrogenation is carried out on a stationary catalyst layer, which is crystallites of catalytically active palladium deposited on the surface of a carbon material, a mesoporous graphite-like material is used as a carbon material. A fibrous catalyst with silicon oxide as a carrier is known, consisting of segments of amorphous fibers or filaments with a catalytically active metal such as Ni, Pd, Pt, Cu, Cr, Co in an amount of 0.001 - 1.0 wt.%. The content of the catalytically active metal with respect to the hydrogenated oil is 0.001 - 0.05 wt. %. The process is carried out by pumping oil through a fixed layer of a fibrous catalyst or by mixing oil with a fibrous catalyst [6].

The use of monolithic catalysts in the hydrogenation of edible oils as an alternative to suspension systems has been of increasing interest over the past decade [8]. However, in industry, hydrogenation is carried out mainly using nickel catalysts, mainly due to the availability, low cost and inertia of the metal in relation to oil. A typical catalytic system for hydrogenation of edible oils is reduced nickel in an average concentration of 22 wt.%, deposited on a suitable substrate and dispersed in the absence of air into highly hydrogenated fat to stabilize it. It is known that the choice and chemical preparation of the carrier, the nickel and promoter deposition technology, particle size, pore size and pore size distribution of the precursor, as well as the activation procedure are important for the activity and selectivity of the catalyst. Kieselgur (diatomaceous earth), clay, silica, silicium, bentonite and palygorskite, as well as zeolites of the LTA type were used as carriers of nickel catalysts [7]. Nickel deposited on kieselguhr is the most widely used catalyst in the process of industrial hydrogenation.

The main industrial methods for the preparation of nickel hydrogenation catalysts are the deposition of components from aqueous solutions and suspensions and impregnation with aqueous solutions of active metals of a formed and specially prepared carrier.

Obtaining catalysts is a complex process that requires high temperatures for activation in a hydrogen current. In the reduced form, the nickel catalyst is pyrophoric, and for safe operation it is passivated in an oxygen-containing flow medium. Before direct use, the catalyst is reactivated in a hydrogen current.

2 Materials and methods

Today, under the conditions of sanctions and the necessary import substitution, many enterprises are looking for an opportunity to optimize the process of preparing nickel catalysts for hydrogenation of vegetable oils.

In this regard, an urgent task is to create a domestic technology for obtaining nickel catalysts for hydrogenation of vegetable oils without additional stages of its preparation before use.

In order to develop a technology for obtaining domestic hydrogenation catalysts that are not inferior to imported analogues, at the first stage we analyzed three samples of imported catalysts from Pricat and Nysosel companies used in the fat and oil industry of Russia. The studied samples of active nickel catalysts based on silicon coated with cured fat on top as protection.

The method of determining nickel.

A 0.5 g powder weight, taken with an error of 0.0002 g, is placed in a glass with a capacity of 150 cm³, 20 cm³ of "royal vodka" is poured, the glass is covered with a watch glass and gently boiled for 15 minutes.

Then about 50 cm³ of distilled water is added to the glass, heated to a temperature of 70-80 °C and filtered through a "white ribbon" filter into a measuring flask with a capacity of 250 cm³. The filter is washed into the same flask with several portions of hot distilled water.

The remainder with the filter is discarded. The volume of the solution in the flask is brought to the mark with water and thoroughly mixed.

To determine nickel, 50 cm³ of the resulting solution is pipetted into a conical flask with a capacity of 250 cm³ and a dilute ammonia solution (1:1) is gradually added until an ammonia nickel complex is formed, which is judged by the appearance of a blue color of the solution. Then 0.2-0.4 g of an indicator mixture prepared by carefully rubbing 0.1 g of murexide with 10 g of sodium chloride is added to this solution.

The contents of the flask are diluted with distilled water to a volume of about 100 cm³, then titrated with a solution of trilon B until the orange-red color turns purple.

The mass fraction of nickel as a percentage (%) is determined by the formula:

$$Ni = \frac{V \cdot F \cdot 2,935 \cdot 10^{-3} \cdot 100 \cdot 250}{50 \cdot g}$$

where 2.935 · 10⁻³ is the amount of nickel corresponding to 1 cm³ exactly 0.05 mol/dm³ of the trilon B solution, g;

V is the volume of the trilon B solution consumed for titration, cm³;

F is the molarity coefficient of the trilon B solution;

250 is the volume of the measuring flask, cm³;

50- the volume of the sample taken for titration, cm³;

g is the sample sample of the catalyst, g.

The samples were examined according to well-known methods in Table 1.

Table 1. Composition of European samples of active nickel catalysts based on silicon, coated on top with cured fat as protection.

Compositions of catalysts	Sample		
	№1	№2	№3
Oil, % mass%.	64.66	58.38	72.29
Ni, % mass%.	22.90	20.93	18.31
Carrier+Ni, mass%.	35.34	41.62	27.71

It was found that all the samples under study are flattened drops of black or gray color, diameter 5-8mm, the protective medium is refractory fat, the proportion of nickel and its derivatives in terms of nickel is 19-20%, specific surface area, 140-160 m²/g.

The study of samples without refractory fat by dissolving it in a solvent (chloroform) showed that foreign companies use silicon oxide, natural diatomaceous earth as a carrier. The catalyst is produced in the active phase and sulfidated with a nickel content of 50-65%.

At the second stage of research, knowing the content of imported catalyst analogs, a technological scheme for their production was proposed.

3 Results and discussion

The technology consists of the following stages: Preparation of an ammonia-carbonate solution, formation of an ammonia-carbonate complex, its decomposition, deposition of metal ions on a carrier (capture of waste gases CO₂ and NH₃), grinding (sieving), tableting.

The preparation of an ammonia-carbonate solution consists in mixing solutions of transition metal carbonates with ammonia water and ammonium bicarbonate and heating. The decomposition of the ammonia-carbonate complex leads to the formation of CO₂ and NH₃ and the deposition of metal ions.

Samples of catalysts obtained under laboratory conditions using the technology proposed above were studied for their catalytic properties in the hydrogenation reaction of rapeseed oil.

Determination of the solid fat content (TSH) in the resulting hydrogenation product (salomas) by pulsed nuclear magnetic resonance was carried out according to GOST 31757-2012 (method 1D).

The burning temperature of the obtained salomas was determined according to GOST 32189-2013. The studies were carried out in the temperature range from 20 °C to 50 °C.

The iodine number was determined according to the interstate standard GOST ISO 3961-2020 Animal and vegetable fats and oils.

The results of the analyses are given in Table 2.

Table 2. Test results of samples of developed analogues of nickel catalysts for hydrogenation of vegetable oils.

Sample of the catalyst	Temperature, °C	Hydrogenation time	Requirements for the finished product					
			TTG				Iodine number	trans fats
			10	20	30	35		
			95-99	90-97	42-52	max 4	<0.5	<0.7
The standard	150-195	6h	96.70	95.20	44.50	2.00	0.44	0
Sample 1	195	9h	96.60	94.90	40.40	3.20	0.99	0
		6h	96.60	95.00	42.00	2.20	0.10	0
Sample 2	195	9h	96.70	95.00	40.20	2.4	0.15	0
		6h	95.9	94.4	39.9	2.3	0.1	0
Sample 3	195	9h	96.5	94.8	38.1	1.8	0.2	0
		9h	95.6	94.5	41.2	2.1	0.1	0
	150	9h	95.0	92.1	34.6	0.1	4.1	1.1

The results of the accumulated salomas on the obtained samples of the nickel hydrogenation catalyst are comparable with the results on the reference sample (a sample of an imported catalyst from Pricat). Sample No. 1 catalyzes the hydrogenation reaction most well. It should be noted that when using sample No. 3, a greater amount of trans fats is formed in the product of hydrogenation of rapeseed oil. Taking into account the restriction on the content of trans fats in fat-and-oil products up to 2% effective from January 1, 2018 in the Russian Federation, it can be noted that all the samples of hydrogenation products obtained by us do not exceed this indicator and comply with the technical regulations of the Customs Union for fat-and-oil products and comply with the recommendations of the World Health Organization.

4 Conclusion

The arithmetic mean of two definitions of this indicator for one sample sample is taken as the result of the analysis. In this paper, a method for obtaining a highly efficient precipitated nickel catalyst for hydrogenation of vegetable oils is proposed. The results of a comparative study of the hydrogenation of vegetable oil of two nickel catalysts imported by the company and obtained.

Thus, based on the results of the conducted research, a new method for obtaining a highly efficient deposited nickel catalyst for hydrogenation of vegetable oils is proposed. This technology is promising and can be implemented in the production of fat and oil products.

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