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Nickel hydrogenation catalyst for tallow hydrogenation and for the selective hydrogenation of sunflower seed oil and soybean oil

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Abstract

The animal tallow, fats and vegetable edible oils hydrogenation is a very important operation in the chemical and food industry. A catalyst used in the industrial processes of the tallow and fat hydrogenation and in the vegetable oils selective hydrogenation, is a nickel catalyst deposited on a silicate support. A new nickel catalyst supported on a natural silicate – diatomite, for tallow hydrogenation and for the selective hydrogenation of sunflower seed oil and soybean oil, has been prepared by the precipitation method. Choice and chemical preparation of the nickel catalyst support, the process of depositing nickel and a promoter on the support, as well as the process of activating them, are all of vital importance for obtaining a highly active hydrogenation catalyst. The synthesis of a nickel catalyst supported on diatomite is a three-stage process: the precursor's synthesis, the dry precursor's reduction and the passivisation combined with impregnation. The final product contains between 20 and 22 wt.% of the reducted nickel within the catalyst mass, about 55 wt.% of the impregnate, while the rest of about 24 wt.% is the support. Checking of the catalyst's activity in the process of tallow and fat hydrogenation has been done with edible tallow at the lab level. The quantity of Ni-catalyst was 0.33 wt.%, which is corresponding to the industrial parameters. Results obtained from the synthesized catalyst samples, demonstrate the final iodine value (I.V.) being between 0.1 and 0.5, corresponding to the decrease of 399–404 units of the I.V. per 1 g of the nickel used. Testing of the synthesized catalyst's performance in a process of the sunflower oil and soybean oil selective hydrogenation, has been done in an industrial pilot and reactor plant. The experimentally obtained results show that the synthesized catalyst has good catalytic properties in a process of tallow and fat hydrogenation, while demonstrating a high selectivity during the sunflower and soybean oils hydrogenation process; i.e., C18:3 (linolenic)→C18:2 (linoleic); C18:2 (linoleic)→ C18:1 (oleic) and C18:1 (oleic)→C18:0 (stearic), respectively.

1. Introduction

The animal tallow, fats and edible oils hydrogenation is a very important operation in the industrial process of producing vegetable tallow, vegetable fats, margarines, and starting components for the cosmetic and chemical industry (emulgators, soaps, creams, pastes, and similar substances). The catalyst used in the industrial hydrogenation process, is a nickel catalyst deposited on a silicate natural support (diatomite) or on a silicate support obtained from aqueous glass [1–11]. The importance of obtaining a highly-active nickel hydrogenation catalyst is demonstrated by the fact that, even as early as 1976, *A Group for Catalysis* has been established at the European level, with an

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aim to standardize production of several exceptionally important strategic catalysts [12,13] within the EEC. One of those exceptionally important catalysts is EuroNi-1 catalyst, a Ni/SiO_2 hydrogenation catalyst with a nickel content of 25 wt.%.

The object of this research work has been to extract nickel from a spent Ni/hydrogenation catalyst; to synthesize a corresponding nickel salt through a feasible chemical treatment; to identify an adequate silicate support, as well as to synthesize a Ni-hydrogenation catalyst for a successful use in hydrogenating animal fats and in selective hydrogenation of the vegetable oils, as well.

2. Experimental

2.1. Nickel extraction and the Ni-salts synthesis

Nickel has been extracted from the exhausted industrial catalysts of the PRICAT 9904/9908/9910 (UNICHEMA) type. The extraction process goes through several stages depending on the kind of nickel salts obtained as a final product.

The extraction of fats for impregnating the catalyst (highly hydrogenated fat with iodine number [I.V.] lower than 2, and partial or complete elimination of the hydrogenated industrial fat are done in the first stage. The average nickel content in this waste material ranges from 12–18 wt.%, depending on the type of hydrogenation and the efficiency of the industrial presses. Concentration of nickel in a fresh catalyst ranges from 20–22 wt.%. The most efficient performance of the first stage is with overheated steam, on the sieves. The residue, representing nickel deposited on a support, is treated with a corresponding mineral acid. A probable fat residue after the treatment with overheated steam is separated in the form of a hardened fatty cake on the surface, and it can be mechanically removed. In the course of this research work, the Ni-nitrate, Ni-sulfate, Ni-acetate and Ni-formiate have been synthesized. For the catalyst's synthesis, a solvent Ni-nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] has been chosen.

2.2. Choice and activation of the support

In an attempt to synthesize a catalyst from the domestic crude materials, being the main object of this research work, a diatomite from the Barosevac Site of the Kolubara Coal Basin [14] has been chosen to serve as a natural crude material for obtaining an adequate support of Ni-catalyst for fats and oils hydrogenation. Crude and ground diatomite has been calcinated and chemically treated in order to obtain an activated support which is vital in the Ni-catalyst synthesis.

An appropriate quantity of crude diatomite, previously dried at 150°C, has been measured up and ground in a ball grinder. A multiple volume of the HCl aqueous solution is added to diatomite, and this mixture is continuously stirred for 2 h while gradually heated up to the temperature of over 60°C.

Upon completion of the reaction, the mixture is filtered while being rinsed with de-ionized water. The precipitate is dried for 2 h in a drier at 150°C, and the so-treated diatomite is calcinated in a furnace at the temperature of 800°C. The obtained product is an activated diatomite ready for synthesizing a precursor with the following physico–chemical characteristics: specific surface of 17.6 m^2/g and the bulk density of 1.85 g/cm^3, and of the following chemical composition: SiO_2 (91.15%), Fe_2O_3 (0.55%), Al_2O_3 (3.79%), CaO (0.58%), MgO (0.78%), Na_2O (0.05%) and K_2O (0.55%). Considering the fact that a catalyst must also demonstrate a satisfying level of filterability, our diatomite activated support has been subjected to the granulometric analysis. The particle size distribution is given in Fig. 1.

Chemically treated and calcinated at 800°C diatomite contains the grain fractions of 0.005 mm, 0.002 mm, and 0.001 mm in almost equal percentages (about 30% each, see Fig. 1), while the fractions of somewhat larger grains (of 0.010 mm and 0.050 mm) are considerably less represented. A parallel comparison of these data with the data pertaining to the commercial supports extracted from the Ni-hydrogenation catalysts of the same type [G-70 (GIRDLER); PRICAT 9904 (UNICHEMA)] that as a domineering fraction have the grains of 0.001 mm, less grain fractions of 0.005 mm and 0.010 mm and even fewer grain fractions of 0.002 mm and 0.050 mm, points to the fact that the granulometric composition of commercial supports and of the lab-activated support of domestic origin is different. It is however, possible to obtain fractions with domineering grain size of less than 0.001 mm by applying

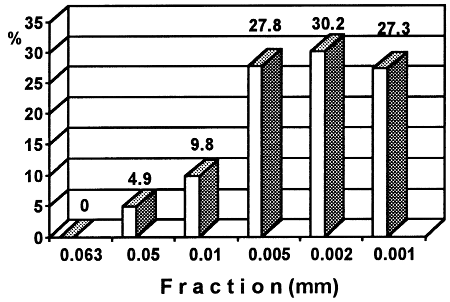

Fig. 1. Particle size distribution for activated catalyst support.

multiple grounding of crude diatomite in the special grinders.

Due to the physico–chemical characteristics and good distribution of the grain size which enables a good filterability of the catalyst after hydrogenation, a domestic activated support can be used for the catalyst's synthesis.

2.3. *Synthesis of the catalyst*

Synthesis of the nickel catalyst supported on a natural silicate support (diatomite) is a three-stage process: the precursor's synthesis, reduction, and passivisation with impregnation. During the catalyst's synthesis, the following chemicals has been used: $Ni(NO_3)_2{\cdot}6H_2O$ (I.Ch.T.M. production from a spent catalyst); Na_2CO_3 ('ZORKA', Sabac, Yu.); $Mg(NO_3)_2{\cdot}6H_2O$ (I.Ch.T.M. production), an activated diatomite (I.Ch.T.M. production) and an impregnate – a hydrogenated fat (I.V.<2.0) (I.Ch.T.M. production and the Henkel Riviera Industry, Kotor, Yugoslavia).

2.3.1. *Synthesis of the precursor*

Synthesis of the precursor [15–17] is based on several previously established assumptions. The final product, i.e., the catalyst, should contain between 20 and 22 wt.% of reducted nickel in the catalyst's mass. The impregnate content should be about 55 wt.% with about 24 wt.% being a support.

For the catalyst's synthesis, nickel has been chosen in the form of a solvating synthesized $Ni(NO_3)_2{\cdot}6H_2O$, with a concentration of magnesium, serving as a promoter, being in the molar ratio Mg/Ni=0.1. The alkaline precipitation agent is a nonaqueous Na_2CO_3, p.a., in a 10 wt.% concentration which is optimal for precipitation. Precipitation of a nickel ion and the promotor's ion (Mg) with an alkaline agent, has been done at an elevated temperature (90°C) with strictly defined pH values (pH=9.2). A support – an activated domestic diatomite, is added to the reaction mixture in the form of an aqueous suspension of the concentration satisfying molar ratio of SiO_2/Ni=1.0. Upon completion of the precipitation process, the filtered and rinsed precipitate is transferred to the oven for drying at a temperature of 120–140°C. After drying, the homogenous mass is minced and ground for further homogenization. The obtained greenish powder is the catalyst's precursor ready for further treatment – reduction.

2.3.2. *Reduction of the precursor*

Reduction of the precursor represents one of the most important operations in the course of synthesizing a catalyst. Depending on the quantity of initial precursor, the construction of a reactor, heating rate during the reduction process, the hydrogen flow, the final reduction temperature, duration of the reduction and the reducted mixture cooling process, the different catalyst's forms of the variable catalytic activity, are obtained. Reduction parameters are chosen in a manner appropriate for obtaining the catalyst with high hydrogenation activity. The catalyst precursor's reduction parameters in a quartz reactor of one's own make [18] have been as follows: the reduction gas – the H_2/N_2 (1 : 1) mixture; the reduction gas flow: 10 l/h; heating rate: 1.0°C/min; the reduction temperature: 430°C; reduction time: depending on the precursor's mass; and the cooling rate: equaling the heating rate.

2.3.3. *Passivisation and impregnation*

In order to reduce an exceptional pyrophority of the reducted metal nickel, it is necessary to perform a partial passivisation of nickel during the process, so handling of the reducted catalyst in course of its impregnation is facilitated. Passivisation has been done with a specially prepared mixture of 350 ppm O_2 in nitrogen at room temperature over the time required for reducing the catalyst's pyrophority down to the level desirable for preventing self-ignition of the reducted nickel.

Having achieved a satisfactory level of the catalyst's passiveness, the active catalyst's mass impregnation is commenced. Impregnation is done with a highly hydrogenated fat (I.V.<2.0) inside a specially prepared container with intensive stirring at an elevated temperature. After completing impregnation, pouring out the mixture into the molds and cooling of the mixture, the final product – a nickel catalyst for the fats and edible oils hydrogenation is obtained.

3. Results and discussion

3.1. *Testing activity of a synthesized catalyst in the process of tallow's hydrogenation*

Testing of the synthesized catalyst's activity (the catalyst service name is: NICAT-2000) in the total hydrogenation of animal fats process, has been done at a lab level at the premises of I.Ch.T.M. (Institute for Chemistry, Technology and Metallurgy), at the Institute for Catalysis and Chemical Engineering, Belgrade, Yugoslavia [19].

Activity of the several identically synthesized samples of a Ni-hydrogenation catalyst and of the one synthesized 'scale-up' sample, has been tested. [In synthesizing the 'scale-up' sample (5 g), the final catalyst (500 g) weight ratio has been 100:1]. For the sake of comparison and under the same conditions, activity of the commercially available catalyst PRICAT 9904 (UNICHEMA) used by the Henkel Riviera Industry, Kotor, Yugoslavia, has been tested.

The hydrogenation parameters have been chosen so that they should stimulate the hydrogenation process conditions at the plant of the Henkel Riviera Industry in Kotor. The tallow hydrogenation process (edible tallow of Russian origin, provided by the Henkel Riviera Industry, Kotor, Yugoslavia) has been conducted in a reactor and under the following working conditions: total volume of the reactor: 2000 cm^3; the fat's (tallow's) mass: 150 g (in a glass inset); the catalyst's mass: 0.33 mass% ; stirring rate: 300 rpm; the hydrogen pressure: 1.5 MPa; system: closed, with permanent H_2 pressure being maintained; final hydrogenation temperature: 195–200°C; process duration time: 180 min.

After hydrogenation is completed, the reaction mixture is filtered. A filtrate is cooled and its iodine number is determined so that the catalyst's activity could be computed. At the same time residual nickel was checking by AAS (Shimadzu, model AA-6601). The tallow's iodine number, as well as the iodine numbers of the hydrogenated tallow samples, have been determined by a classic titer method with sodium thiosulfate solution and according to the Henkel Riviera Industry's, Kotor methodology – method No. MA-5. The catalyst's activity is expressed as a number of the grams of fat (tallow) that has been hydrogenated down to the obtained iodine number (I.V.<2.0) according to 1 wt g of Ni, i.e., as a ratio of the iodine number change related to the quantity of nickel used. The obtained filtered-out precipitate contains a partially inactive (spent) catalyst mixed with the hydrogenated fat. Such mixture, with an addition of a fresh catalyst, may be re-used in the hydrogenation process (which is in principle being done in industry) or its components: nickel, promotor, support and an impregnate, could be subjected to a recuperation process.

After determining the iodine values, the following results have been obtained: The initial I.V. of edible tallow has been 44.0. After considerable experimenting with the hydrogenation processes, the obtained results ranged from 0.1–0.5, which demonstrates a decrease of over 400 I.V. units per one gram of the catalyst's nickel. Checking of the residual nickel in the solid filtrate demonstrated a negative reaction according to the nickel content food standard. For comparison, and under identical working conditions, a test of the commercial catalyst's, PRICAT 9904 (UNICHEMA) performance, has been run. Value of the iodine number of the hydrogenated-down fat has ranged from 0.4–0.9, meaning that a synthesized catalyst NICAT-2000 and the commercial one are in the same class.

3.2. *Testing activity of a synthesized catalyst in the process of hydrogenation of vegetable oils (soybean and sunflower oil)*

Industrial testing of the synthesized NICAT-2000 catalyst's activity has been done in the factory of edible oils and fats, VITAL, Vrbas. Testing of the catalyst's performance has been conducted in a pilot plant in an industrial reactor under the following conditions (Table 1.)

The soybean and sunflower oil used in the hydrogenation process have had the following physico–chemical characteristics (Table 2).

Table 1
Working conditions of pilot and industrial reactor vessels in the process of oil hydrogenation

	Pilot reactor	Industrial reactor
Type of the reactor	D.D. VITAL	Krupp-d404s
Capacity (kg)	5.0	5000
Mass of the oil (kg)	5.0	4000
H_2 pressure (init.) (MPa)	0.08	0.05
H_2 pressure (end) (MPa)	0.12	0.20
Temperature (init.) (°C)	150	165
Temperature (end) (°C)	167	195/200
Catalyst (wt. %)	0.10	0.10
Nickel (wt. %)	0.022	0.022
Agitation (rpm)	720	1425

The iodine and saponification number values have been determined by titration, a relative density measured with an aerometer at 20°C, while the refraction index at 20°C (and at 60°C) has been determined with refractometer according to Abbe. In all the Figures, only the last three figures of the refraction index following the values above 1.4, have been shown. The gas-chromatography measurements of the fatty acid methyl esters in the examined oils and hydrogenated products, have been performed on the model HP5890, series Plus (Hewlett Packard). The solid components content percentage (dilatometric number) at 20°C, 30°C and 35°C, has been determined by the pulse-NMR method [20] on the Bruker instrument; the hydrogenated product's melting point has been determined by the standard capillary method [21], while the total *trans*-fatty acids content in the hydrogenated product has been measured on FTIR (Perkin Elmer, model 1725X) [22].

Table 2
Physico–chemical characteristics of soybean and sunflower oils

	Soybean oil	Sunflower oil
Iodine value (g I_2/100 g)	128	130
Saponification value (mg KOH/g)	189	190
Non-saponification residue (g/kg)	up to 15	up to 12
Relative density (g/cm^3)	0.919–0.925	0.920–0.927
Index of refraction (n_D^{20})	1.470–1.476	1.474–1.476
Fatty acid composition in mass %		
C16:0 – palmitic acid	10.12	6.51
C18:0 – stearic acid	4.13	3.92
C18:1 – oleic acid	21.15	21.26
C18:2 – linoleic acid	50.78	65.76
C18:3 – linolenic acid	7.23	0.18
C20:0 – arachidic acid	0.22	0.19

The soybean and sunflower oil hydrogenation process course in a pilot plant and one of the soybean oil in an industrial reactor, have been monitored by taking and analyzing samples every 10 min from the pilot plant, and after 30, 40, 75, 85, 95, 105 and 115 min from the industrial reactor, respectively. Although this hydrogenation reaction (soybean oil) includes a series of side processes (like the geometrical and position isomerization reactions), the first approximation indicate that the basis of this mechanism is composed of a series of consecutive stages:

$$\mathrm{C3} \xrightarrow{k_3} \mathrm{C2} \xrightarrow{k_2} \mathrm{C1} \xrightarrow{k_1} \mathrm{C0}$$

with C3, C2, C1 and C0 being the concentrations of linolenic, linoleic, oleic and stearic acids, and k_1, k_2 and k_3 being the corresponding rate constants. These rate constant values are used for determining the selectivity relations SLn (k_3/k_2) and SLo (k_2/k_1).

Results of the fatty acids content changes as a function of the time lapse during the soybean and sunflower oil hydrogenation reaction in the pilot plant are presented in the Fig. 2 and Fig. 3; changes of the refraction index as a function of the I.V. change are given in the Fig. 4, while the changes of the melting point values as a function of the iodine number are

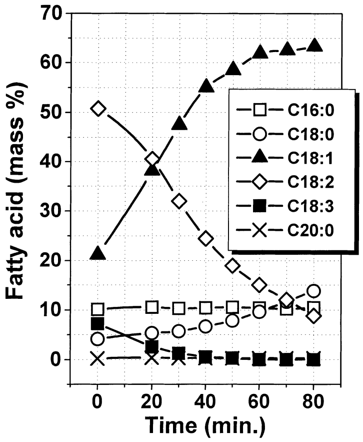

Fig. 2. Fatty acids concentration (soybean oil) vs. time – pilot plant reactor.

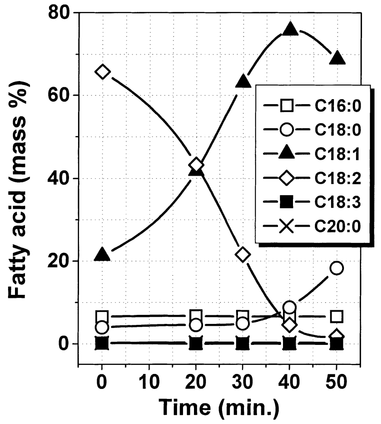

Fig. 3. Fatty acids concentration (sunflower oil) vs. time – pilot plant reactor.

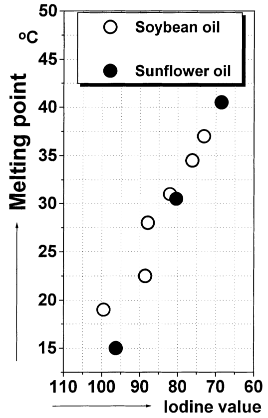

Fig. 5. Melting point vs. I.V. – pilot plant reactor.

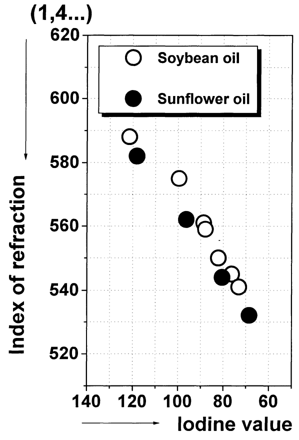

Fig. 4. Index of refraction vs. I.V. – pilot plant reactor.

presented in the Fig. 5 for both oil types. The final dilatation values for soybean and sunflower oils are: 37.04 (20°C), 16.25 (30°C) and 7.56 (35°C), i.e. 57.61 (20°C), 29.76 (30°C) and 15.50 (35°C), respectively.

The Figs. 2 and 3 clearly demonstrate that the hydrogenation process is moving into the targeted direction with the catalyst demonstrating good activity and selectivity (for soybean oil: SLn=2.5; SLo=59.4; for sunflower oil: SLo=67.1) in regard to the mono and poly unsaturated fatty acids hydrogenation. In both experiments (Fig. 4), a change of the refraction index (n_D^{60}), i.e., its declining with hydrogenation time lapsing, and a decrease of the hydrogenated product's iodine value, respectively, has been recorded.

Analogously, with a change of the refraction index, an increase of the product's melting point accompanied with a decline of the iodine number (Fig. 5) takes place due to the hydrogenated product's fatty acids composition change (which is also the consequence of geometric and positional isometric occurrence in the C18:2, and even more in C18:1 fatty acid [23]); a mono unsaturated oleic fatty acid (C18:1) is dominant in both *cis*- and *trans*- forms (55 *cis*- : 45 *trans*- at the end-point for both oil types) and the stearic fatty acid (C18:0).

Applying the results obtained in the pilot plant, the soybean oil hydrogenation (95% production of margarine in Yugoslavia is obtained from a partially hydrogenated soybean oil) has been done in an industrial reactor (Krupp, type D404S) of the operating capacity of 5.000 kg, at the hydrator plant of the factory of edible oils and fats, 'VITAL', Vrbas (hydrogenation parameters given in the Table 1). The results obtained are presented in the Table 3, and the fatty acids composition changes (C18:3, C18:2, C18:1, C18:0) and the total *trans*- fatty acids' content changes related to the iodine value, are given in Fig. 6.

The refraction index (n_D^{60}) and melting point changes – due to the iodine value change and the reaction duration, are presented in Figs. 7 and 8, while the selectivities are: SLn=2.7 and SLo=53.3

Table 3
Industrial reactor vessel results (soybean oil)

Time of reaction [min]	30	40	60	75	85	95	105	115
H_2 pressure (MPa)	0.05	0.05	0.08	0.09	0.09	0.10	0.14	0.20
Reaction temp. (°C)	190	195	195	195	195	195	190	195
Iodine value (gJ_2/100 g)	115.9	112.5	101.0	96.7	91.8	87.4	81.8	76.5
% solids (at 20°C)	0.54	1.19	2.97	5.16	8.57	15.41	23.84	36.25
% solids (at 30°C)	0.19	0.35	0.22	0.57	0.68	1.77	4.98	10.90
% solids (at 35°C)	0.36	0.27	0.18	0.07	0.36	0.15	0.64	3.59

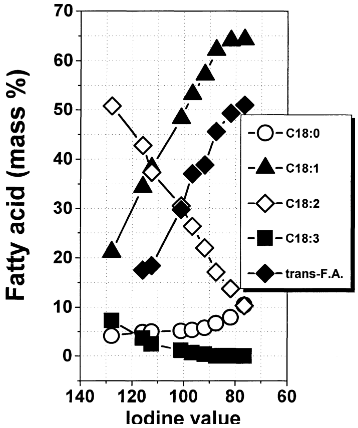

Fig. 6. Fatty acids and total *trans*-fatty acids concentration vs. I.V. (soybean oil) – industrial 5-ton reactor.

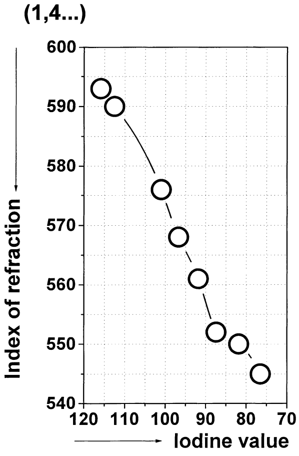

Fig. 7. Index of refraction vs. I.V. (soybean oil) – industrial 5-ton reactor.

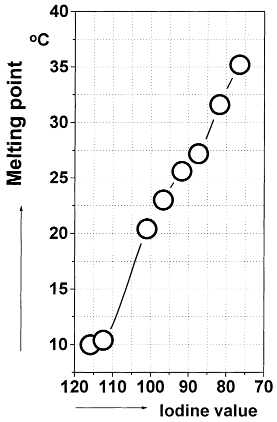

Fig. 8. Melting point vs. iodine value (soybean oil) – industrial 5-ton reactor.

4. Conclusion

The experimental results obtained at the lab and industrial level, have led to the following conclusions:

- With this technology a nickel's recuperation from an exhausted hydrogenation catalyst has been done, and a palette of the nickel salts has been synthesized;
- a technology of activating diatomite of the characteristics feasible for application in synthesis of a nickel hydrogenation catalyst, has been mastered;
- a technology of the nickel hydrogenation catalyst's synthesis has been mastered. The performed synthesis of a 'scale-up' catalyst has confirmed a high reproductivity of the synthesis' methodology, as well as the good catalytic performances of the laboratory-level synthesized catalyst;
- a synthesized catalyst in the total tallow hydrogenation process has demonstrated a good perfor-

mance and it is proved to be in the class of the corresponding commercially available catalysts;

- results obtained in the edible vegetable oils' (soybean and sunflower oil) hydrogenation process, in a pilot plant and in an industrial 5-ton reactor, do indisputably demonstrate that a synthesized catalyst NICAT-2000 possesses all the properties of the other modern catalysts of the same type. The parameters tested, such as: the hydrogenation duration-related change of the fatty acids concentration; a good selectivity of the catalyst; change of the refraction index and the hydrogenated mass' melting point relative to the I.V. change; change and content of the total *trans*-fatty acids; dilatation changes; good filterability of the catalyst and a negative reaction to a residual nickel that may be present in the product after primary filtration, are all pointing to the fact that a NICAT-2000 catalyst may be successfully applied in the food-production industry's vegetable oils hydrogenation processes.

For confirmation of all the above research results, the Factory of Edible Oils and Fats 'VITAL', Vrbas, has issued a certificate to the I.Ch.T.M. – Institute for Catalysis and Chemical Engineering, Belgrade, Yugoslavia verifying that a synthesized NICAT-2000 catalyst is successfully applicable in the industrial soybean oil, sunflower oil, palm oil and the palm-kernels oil hydrogenation process.

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