Eurasian ChemTech Journal 9 (2007) 199-205

Optimizing of Cottonseed Oil Hydrogenation over Fixed Bed Catalyst with Use of Kinetic Simulation

Y.L. Sheludyakov[1]*, F.K. Khabibullin[2], K.A. Zhubanov[2],
A.G. Tomilov[3] and I.D. Gorlachev[4]

[1]Institute of organic catalysis and electrochemistry MOS RK,
142 Kunaev Street, Almaty, 050023, Kazakhstan

[2]Research Institute of New Chemical Technologies and Materials,
95-a Karasai Batyr Street, Almaty, 050012, Kazakhstan

[3]Combustion Problems Institute, 480012, Almaty, 172, Bogenbai Batyr str., Kazakhstan

[4]Institute of Nuclear Physics, 1 Ibragimov Street, Almaty, 050082, Kazakhstan

Abstract

Effect of temperature, hydrogen and oil flow rates on the quality of the products of cottonseed oil hydrogenation was investigated for different Ni-Al catalysts promoted with Ti, Cr, Mo, Cu, Fe. Fixed bed catalyst is used to exclude filtration stage from the technological flow sheet. Surface of the catalyst granules was preliminary leached to increase the area. Linear correlation between melting point and iodine value of the products was revealed, and correlation coefficients for different catalysts have been established. It was found out that minimum melting point and maximum hardness corresponds to the products with the following fatty acid composition: 5% of stearic acid, 45% of oleic acid and 20% linoleic acid. Comparison criteria for the catalysts with use of kinetic model were discussed, and 60% conversion of linoleic acid was selected as the optimum level for hydrogenation process to target products. Introduction of copper, iron and molybdenum in the Ni-Al-Cr-Ti alloy (Basic alloy) allows increasing activity and selectivity of the catalysts. In optimum conditions at 180°C the row of activity of the catalysts is as follows: Fe > Mo > Cu > Basic alloy and the row of selectivity: Cu > Fe > Bas > Mo.

Introduction

Hydrogenation of plant-seed oil is widely used in different countries for production of margarine, soap, stearine, glycerol, lubricants, *etc*. Difficulties of plant-seed oil hydrogenation are related to variation of raw material composition and tough requirements to the obtained products. Consumption of plant-seed oils for nutrient and industrial purposes is growing.

Balanced content of poly-unsaturated acids, absence of cholesterol and presence of vitamins makes margarine one of the most popular products in developing and developed countries. Lubricants produced from renewable raw material (plant-seed oil) also have promising future. Use of such easy degradable substances is important in the spheres where risk of spillage is high, for example is hydraulic systems. Such lubricants can replace many of presently used mineral lubricants. They are less stable at high temperatures and against oxidation, but could be improved via chemical modification [1,2].

Majority of processes of catalytic hydrogenation proceed in heterogeneous systems including complex combination of physical and chemical effects like mass and heat transfer, solution, crystallization, complex formation, adsorption and chemical reactions. Attempts to obtain products with required properties force to use complex multi-component catalysts and complex reactors like three phase catalytic membrane reactor [3].

In industry slurry reactor with suspended catalyst is used usually for hydrogenation of plant-seed oil. The lack of the method is related to hindrance of mass transfer in viscous medium and necessity to filter out suspended catalyst from the product. Regeneration

---

*corresponding authors. E-mail: shelud@nursat.kz of the catalyst is also a problem. Fixed bed catalyst and flow system is a good alternative. The product needs no filtration, the system provides better option for growth of selectivity due to better mass transfer [4]. However, activity of the catalyst and hardness of the product is lower. To increase surface area of the catalyst and subsequently its productivity the alloy is crushed into pieces of optimum size and surface of the particles is leached.

Majority of catalysts which are used in laboratories and in industry for plant seed oil hydrogenation are multi-component catalysts. They include modified Ni-Rhenium catalysts, metals supported on inorganic oxides [2] or alloy catalysts promoted with different additives [5-7]. They have high activity (because of big surface area of the powders), high selectivity, but could be used only once.

The advantage of alloy catalysts (as compared to supported catalysts) is possibility to regenerate them to original activity and selectivity in case of poisoning, which is inevitable [8] using surface leaching for many times.

The aim of the work is optimizing the cottonseed oil hydrogenation over Ni-Al alloy catalysts with additives of chromium, titanium, copper, *etc.* in different combinations into the products with required properties. Kinetic model was used for optimizing the process.

Experimental

The process was carried out in a flow system. Fixed bed reactor with electric heating of 16 mm diameter and 500 mm length made of stainless steel was used for hydrogenation [4]. Commercial purified cottonseed oil was used in the experiments. The cottonseed oil is fed by dosed high pressure pump to the mixer where it is heated and mixed with hydrogen from a steel cylinder. Then the mixture is pumped to the reactor under the catalyst bed. Passing through the catalyst bed the product is transferred to the collector where it is separated from excess of hydrogen. Sampling of the products is carried out in 3-5 hours of work in the stationary regime depending on volume flow rate of the oil. The stationary regime is monitored every hour via determination of melting point and refraction index of the product. The hydrogenation flow unit is a small analogue of industrial hydrogenation units.

Characteristics of the obtained products were determined according to the methods approved by VNIIZ (Head research institute of fat industry of Russia) [9]. The set of standard methods for determination of fat quality includes: iodine number (I.N.), melting point (MP), hardness, acid number (A.N.), fatty acid composition (GC method) percentage of trans-isomers (IR-spectroscopy). Activity of the catalyst was estimated on the basis of volume flow rate to the same rate of conversion of linoleic acid. Selectivity of the hydrogenation process was determined on the basis of the ratio of linoleic and stearic acids in the product.

The alloys were prepared in a graphite vessel in SP-1 shaft furnace from nickel, aluminum and other modified additives (Mo, Cu, Cr, Ti, Fe). Composition and structure of the alloys analyzed with the following physico-chemical methods: XRF, ICP MS, RBS and PIXE are presented in Table 1. The promoters were selected on the basis of literature data and tried in different combinations. They do not provide harmful impact on health when present in the product being important microelements.

Catalyst modules were prepared from pieces of the alloy with optimum size [10] after leaching of the surface of the pieces.

In order to optimize the process the following technological parameters were varied for each catalyst: flow rate of hydrogen and cottonseed oil, pressure and temperature. Kinetic simulation was used to facilitate selection of optimum conditions.

Standard error for experiments on hydrogenation taking into account Student criterion ($P = 0.95$) was 2.9%.

Results and Discussion

Typical results obtained for Ni-Al alloy catalyst promoted with Cr and Ti, are shown in Table 2.

The dynamics of change of fatty acid composition and other parameters of the cottonseed oil during hydrogenation process are seen from the Table 2. It is seen that hydrolysis is very low as compared to the original oil. Maximum value at highest temperature (240°C) is about 1.7% (mol). Iodine value is declining together with increase of contact time on the catalyst. Concentration of linoleic acid during the hydrogenation process is declining, stearic acid is increasing and oleic acid is coming through the maximum. Similar results were obtained for the other catalyst promoted additionally with Cu, Fe, Mo.

Physical parameters of the hydrogenation products are changing as follows: melting point is grow-

Table 1

Element composition of the catalysts on the basis of Ni-Al alloy with addition of alloying elements

Sample	Al, %	Ni, %	Ti, %	Cr, %	Fe, %	Cu, %	Mo, mkg/g	Zn, mkg/g	Ca, mkg/g
Bulk composition									
Basic	59.7	35.4	2.93	1.75	0.14	< 0.03	< 7	98	260
Cu	59.0	35.6	2.86	1.68	0.04	0.92	70	18	580
Mo	60.4	34.9	2.64	1.63	0.07	< 0.08	8900	30	350
Fe	56.8	36.3	3.00	1.94	1.68	< 0.07	12	50	710
Method	ICP, PIXE	ICP, PIXE XRF	XRF	ICP, PIXE, XRF	XRF, HAA	ICP, PIXE XRF	XRF, HAA	XRF, HAA	PIXE
Surface composition									
–	63.6	31.7	3.12	1.47	0.028	< 0.05	n.d.*	n.d.	610
Cu	61.3	33.7	3.02	1.03	0.002	0.88	n.d.	n.d.	500
Mo	63.4	32.3	2.58	1.58	0.014	0.036	n.d.	n.d.	440
Fe	66.3	28.6	2.71	1.52	0.87	0.045	n.d.	n.d.	400

*n.d. – not determined

Table 2

Characteristics of the salomases obtained in hydrogenation of cottonseed oil over Ni-Al catalyst promoted with Cr and Ti. P_{H_2} = 0.1 MPa, V_{H_2} = 120 h^{-1}

T, °C	V_{oil}, h^{-1}	I.N. % J_2	T_{melt}, °C	A.N. mg KOH	Hardness, g/cm	Fatty acid composition, %					S*, %
						$C_{18}^{2=}$	$C_{18}^{=}$	C_{18}°	C_{16}°	C_{14}°	
180	0.5	45.6	50.3	0.49	–	4.5	42.6	25.6	26.3	1.0	49.3
180	0.85	64.5	42.5	0.48	–	11.1	48.2	13.2	26.6	0.9	71.7
180	1.10	71.0	40.4	0.44	–	18.3	45.6	9.0	26.3	0.8	78.2
180	1.50	80.5	36.4	0.42	35	28.5	38.2	5.9	26.5	0.9	82.1
200	0.55	47.9	50.9	0.61	–	4.0	44.0	24.9	26.3	0.8	51.3
200	0.85	61.1	45.5	0.60	–	7.8	51.1	13.8	26.5	0.8	72.5
200	1.20	71.9	40.4	0.58	–	17.5	46.4	8.6	26.6	0.9	79.9
200	1.55	80.5	36.2	0.57	80	23.9	42.5	6.2	26.4	1.0	84.0
220	0.60	50.1	49.9	0.82	–	4.6	45.2	23.2	26.3	0.7	54.3
220	0.90	62.5	43.5	0.80	–	10.5	51.2	11.1	26.4	0.8	77.3
220	1.35	74.1	38.7	0.75	–	19.1	46.0	7.6	26.5	0.8	82.0
220	1.60	80.5	37.1	0.70	130	21.5	45.2	6.0	26.4	0.9	86.0
240	0.80	56.4	45.1	1.32	–	6.3	51.0	15.5	26.4	0.8	69.6
240	1.00	63.5	42.0	1.16	–	11.0	51.1	10.5	26.5	0.9	78.5
240	1.35	72.2	37.5	1.03	–	20.5	45.5	6.6	26.5	0.9	84.5
240	1.65	80.5	35.7	0.86	140	20.1	46.8	5.8	26.6	0.7	87.2
Original oil		106.4	–	0.39	–	51.4	19.5	1.8	26.5	0.8	–

*S – selectivity of hydrogenation on the basis of the ratio of linoleic and stearic acid $S = (\Delta C_{lin} - \Delta C_{stear})/\Delta C_{lin} \times 100\%$.

ing from 35.7°C to 50.9°C together with increase of contact time, hydrogen: oil ratio and temperature.

To determine correlations of hardness and melting point of products depending on hydrogenation parameters and catalyst composition all obtained data were systemized and analyzed for the four catalysts and the set of conditions.

It is known that hardness of the product is growing together with rate of hydrogenation, as well as melting point. Correlation of melting temperature and iodine number of the products obtained for Ni-Al-Cr-Ti-Mo catalyst is shown on Fig. 1.

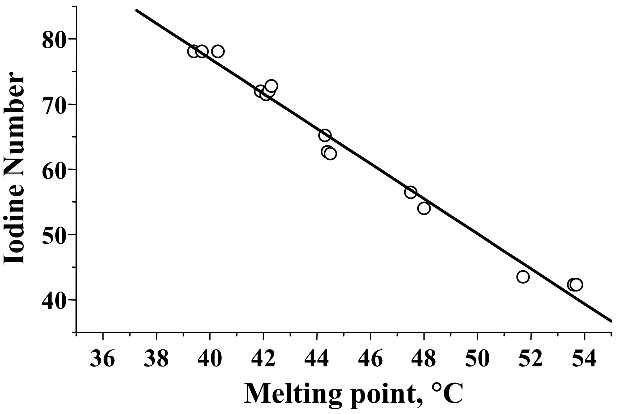

Fig. 1. Dependency between melting points and iodine numbers of the product obtained during hydrogenation of cottonseed oil on the catalyst promoted with molybdenum.

All obtained data well fit to linear dependency with the parameters shown in Table 3.

Similar linear dependencies were obtained for the other catalysts, but parameters of linear equations for them are different (Table 3) as well as fatty acid composition of the products. Typical dependency of melting point of the product depending on fatty acid composition for Ni-Al-Cr-Ti-Mo catalyst is shown on Fig. 2.

Table 3

Dependency of melting point of the product on the iodine number for different catalysts (I.N. = A + B×MP)

Catalyst	A coefficient	B coefficient	Correlation coefficient
Basic alloy	161.9	-2.27	0.983
+ Cu	151.4	-2.08	0.985
+ Mo	184.4	-2.68	0.993
+ Fe	172.1	-2.48	0.996

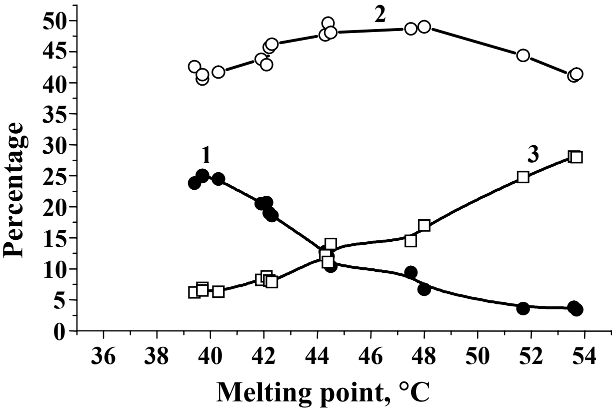

Fig. 2. Dependency of melting points of the product (salomas) on its fatty acid composition for the catalyst promoted with molybdenum. 1 – linoleic acid; 2 – oleic acid; 3 – stearic acid.

On the catalyst promoted with molybdenum were obtained products with melting point from 40 to 54°C. It is seen from the figure that concentration of stearic acid is growing, linoleic acid is declining and oleic acid is going through the maximum.

Fats with melting point above 35°C cannot be used as components of food products. Therefore, the obtained data were analyzed to find dependency of hardness of the products with melting point at 35°C depending on the composition and other factors.

It was established that there is no correlation between hardness and iodine number for the products with low melting point. However, there is a correlation between hardness of the product and fatty acid composition (Fig. 3).

It is seen from Figure 3 that hardness of the product is growing together with increase of concentra-

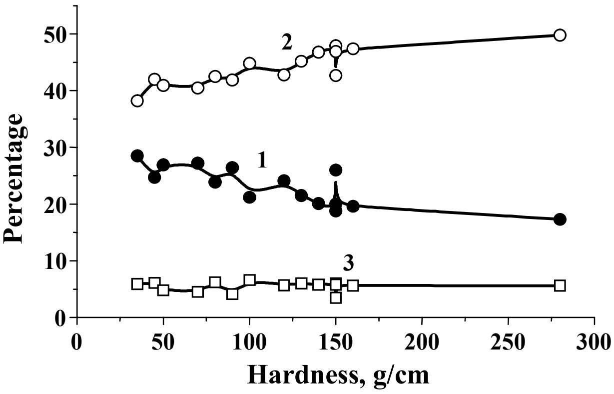

Fig. 3. Dependency of hardness of the products of hydrogenation of cottonseed oil on fatty acid composition of the products. 1 – linoleic acid; 2 – oleic acid; 3 – stearic acid (for all catalysts).

tion of oleic acid in fatty acid composition of the product (together with simultaneous decrease of concentration of linoleic acid). Concentration of stearic acid at the same time should be constant and at the level of 5% approximately. This means that product with higher hardness could be obtained over more selective catalyst when original linoleic acid (2 double bonds) during hydrogenation process is transformed into oleic acid (one double bond) with minimum formation of saturated stearic acid. Rate of hydrogenation of linoleic acid should be higher as much as possible than rate of hydrogenation of oleic acid. It was established that the products with low melting point and hardness over 100 g/cm could be obtained at approximately 50% conversion of original linoleic acid (Fig. 3). The products with low melting point and hardness of ~150 g/cm could be obtained at 60% conversion of original linoleic acid. That is why values of activity and selectivity of the catalysts should be compared not for the same (arbitrary taken) iodine number, but for the rate of conversion of linoleic acid when best quality products are obtained.

It should be pointed out that elaidic acid (trans-isomer of oleic acid) has great impact on hardness of the product. According to our data the share of elaidic acid could vary from 24% for Mo promoted catalyst to 40% for Cu promoted catalyst in the mixture of oileic acid isomers. Probably, this is the reason of high hardness of the products obtained for copper promoted catalyst and big distortions on the curves (Fig. 3). Unfortunately, we have insufficient amount of data on trans-isomers for a correlation.

Selectivity of the catalyst is greatly depends on the rate of conversion (contact time, flow rate) even for the same catalyst composition. Selectivity has maximum value at low rate of conversion and is reduced considerably at high rate of conversion (see Table 2).

For visualization of stages and whole hydrogenation process simplified kinetic model based on mechanisms of homogeneous hydrogenation and isomerization (stages 1-7 below) was used [11]. Mechanisms of homogeneous hydrogenation do not contradict mechanisms of heterogeneous hydrogenation [12], in particular, mechanism of Horiuti-Polanyi, but better investigated, well proven and understood. For this purpose each surface atom of solid catalyst (or active site at the surface) could be assumed as metal complex where crystal lattice plays role of one or more ligands.

1. $2M + H_2 = 2MH$
2. $MH + RC_4H_6R' = MRC_4H_7R'$
3. $MRC_4H_7R' + H_2 = MH + RC_4H_8R'$
4. $MH + RC_4H_8R' = MRC_4H_9R'$
5. $MRC_4H_9R' + H_2 = MH + RC_4H_{10}R'$
6. $MRC_4H_9R' = MH + RC_4H_8R'$-trans
7. $MRC_4H_9R' = MH + RC_4H_8R'$-position

Hydride MH is assumed as original active form of the catalyst. It is formed in-situ during the hydrogenation process or before the process during leaching of Ni-Al alloy and drying of the catalyst in hydrogen atmosphere. This hydride form of the catalyst interacts with unsaturated compounds (with double bonds) forming sigma complex (via pi complex). Once sigma complex is formed, double bond is transformed into a single bond providing the possibility of rotation of molecule parts around the axis of the bond. Equilibrium decomposition of the sigma complex yields both original molecule and molecule with displaced double bond and also trans-isomer of the original molecule (natural plant seed oils contain only cis-isomers of unsaturated acids in their composition). Interaction of the sigma complex with hydrogen molecule gives the product with a single bond and regenerates the original hydride form of the catalyst.

The following assumptions were used for the model: in complex ether of glycerol (cottonseed oil) each double bond reacts independently of the others; each accessible Ni atom is an active site; Number of active sites is proportional to the catalyst mass. The ratio of the reagents were determined on the basis of the ratios of their flow rates in the experiments. Contact times of oil with the catalyst was determined on the basis of their relative flow rates.

It was calculated in the experiments (Table 2) that hydrogen: cottonseed oil ratio is in the range of 3.2-10. This means that amount of hydrogen is sufficient for complete hydrogenation of all double bonds in the oil if contact time would be long enough.

Since majority of the reactions are reactions with equilibrium initial values of relative rate constants were set on the basis of thermodynamic data [13]. According to thermodynamic information the most probable direction is complete hydrogenation. For migration of double bond probabilities are close for both position isomers as well as for cis- trans- isomerization.

The stages of the model (reactions 1-7) were transformed into the system of differential kinetic equations. The system of differential equations was solved with numerical Gere's method. Finally were obtained kinetic curves for initial, final and intermediary substances from the very beginning to the very end of the hydrogenation process (Fig. 4).

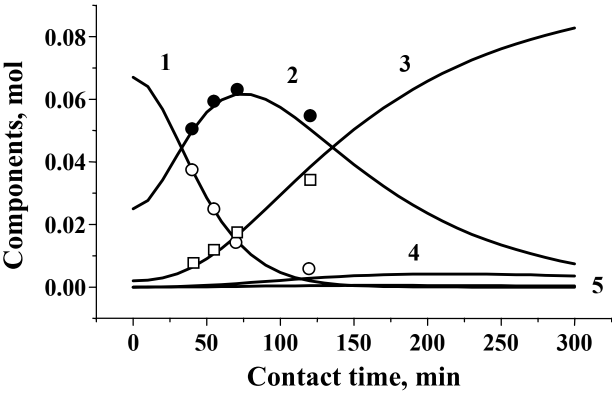

Fig. 4. Kinetic curves of cottonseed oil hydrogenation. H_2 = 120 h^{-1}, T = 180°C. The curves obtained according to the kinetic model. The points on the curves correspond to different contact times (oil flow rate) according to Table 1. 1 – linoleic acid; 2 – oleic acid; 3 – stearic acid, 4 – trans isomers, 5 – position isomers.

One experiment in a flow system gives only one set of points on the kinetic curves for single contact time with the catalyst. Therefore for each temperature were carried out four experiments with different contact times. The experimental data (Table 2) were compared with the model data. New constants for the model were calculated to minimize sum of square deviations between the model data and the experimental data (Fig. 4).

The following set of equilibrium and kinetic constant were obtained for the model: $k_1 = 0.7090$; $k_2 = 3.410$; $k_3 = 694000$; $k_4 = 0.7100$; $k_5 = 351.5$; $k_6 = 1.579$; $k_7 = 8.059$.

On Figure 4 kinetic curves of the model that fit to the experimental data are presented. Experimental points on the figure were taken from Table 2 for different contact times (flow rates of oil). The model adequately describes the hydrogenation process (according to Fisher criterion) for temperature 180°C and different oil flow rates.

Similar sets of kinetic curves were obtained for other temperatures and other catalysts.

Since we had little data on concentration of elaidic acid (trans-isomer) and no data on position isomers relevant values of the constants in the model were minimized and concentration of oleic acid represents, in fact, sum of concentrations of cis- trans- and position isomers of this acid.

According to the Figure 4, concentration of linoleic acid is decreasing, stearic acid is increasing and oleic acid is going through the maximum with reaction time increase. For different temperatures for the same catalyst and for different catalysts at the same temperature location of maximum on oleic acid curve is different both in time and in amplitude (concentration). It is seen from the Figure 4 that stearic acid is the main product when contact time is long. Increase of hydrogen pressure is a favorable factor for stearic acid formation. It is obvious that selectivity in the sequence of the hydrogenation reactions will have maximum value at the beginning of the process [14]. However, the product at this time will be liquid. Using the model one can intentionally select compromise conditions taking into account required melting point and hardness of the products. It is seen from Figure 4 that in case of complete conversion of linoleic acid the product contains almost equal concentrations of oleic and stearic acids. The obtained product has high hardness and high melting point. If contact time corresponds to maximum concentration of oleic acid in the oil conversion of linoleic acid is about 80%, but the product contains up to 20% of stearic acid. Such product has high melting point and also cannot be used for food purposes. Of course, activity and selectivity of the catalysts could be compared at the point of oleic acid maximum. When rate of conversion of linoleic acid is 50% the product has low melting point, but low hardness. According to our opinion, 60% conversion of linoleic acid is better. In this conditions rate of formation of oleic acid is greater than that for stearic acid in spite of the fact that concentration of oleic acid does not reach its maximum. Concentration of stearic acid at this time is low (5-10%). For most selective catalysts (Ni-Al-Cr-Ti-Cu) concentration of stearic acid at 60% conversion is about 5% and product on its properties is close to salomases for food purposes, however, concentration of trans-isomers in the product can be up to 40%.

Increase of the temperature increases rate of all the reaction and lets to increase volume flow rate of the reagents, performance of the catalyst keeping high selectivity value.

Additional introduction of copper, iron and molybdenum in the Ni-Al-Cr-Ti alloy (Basic alloy) lets to increase activity and selectivity of the catalysts. In optimum conditions at 180°C the row of activity of the catalysts is as follows: Fe > Mo > Cu > Basic alloy. However, the row selectivity is different: Cu > Fe > Bas > Mo.

According to the data of physico-chemical analysis, the obtained alloys contain in average 60% of aluminum, 35% of nickel, and 5% of alloying components (Table 1). Alkaline treatment of the surface of the catalysts increases not only surface area of the catalysts, but also concentration of nickel and the additives on the surface.

Phase composition of the catalysts is similar. The difference is low. The alloys mainly contain $Al_{1.1}Ni_{0.9.}$ phase. Besides, the alloys probably contain also phases Ni_2Al_3, and Al_4Ni_3. One may believe that active sites are formed from the main phase after leaching of part of the aluminum. Promoters provide soft activation effect because of similar electronegativity and geometry of their atoms.

Conclusions

Effect of composition of the fixed bed catalyst with leached surface prepared from Ni-Al alloy with additions of Ti, Cr, Mo, Cu, Fe, and technological parameters of hydrogenation of cottonseed oil to quality of the obtained products have been investigated.

It is shown that at melting point of about 35°C maximum hardness has the product with 5% of stearic acid, 45% of oleic acid (with admixture of trans-isomer) and 20% of linoleic acid. Taking this into account and on the basis of the kinetic model it was established that optimum rate of conversion of linoleic acid in order to get maximum selectivity is 60%.

In these conditions the row of activity of the tested catalysts is as follows: Fe > Mo > Cu > Basic alloy. The row of selectivity shows another sequence: Cu > Fe > Bas > Mo. Only for the copper promoted catalyst (having the highest selectivity) the obtained products on their melting point and hardness meet requirements for salomases for food purposes, however concentration of trans-isomer of oleic acid is high.

Ni-Al-Cr-Ti-Fe catalyst was found the best taking into account its activity and selectivity values as compared to the others tried catalysts. The catalyst is stable, its regeneration in the reactor is easy and only trace amount of Ni could be found in the product.

We believe that use of flow system with fixed bed catalyst has promising future, however activity and selectivity of the catalyst should be increased.

Acknowledgement

The work carried out in the Research Institute of New Chemical Technological and Materials was supported by ISTC (Grant K-197).

References

1. Wagner H., Luther R., Mang T., Applied Catalysis A: General 221:1-2:429 (2001).
2. Ravasio N., Zaccheria F., Gargano M., *et al.*, Applied Catalysis A:General, 233:1-2:1(2002).
3. Veldsink J.W., J. Amer. Oil Chem. Soc. 78:5:443 (2001).
4. Zhubanov K.A., Khabibullin F.K., *et al.*, Oil and fat industry (Rus), No 10:17 (1986).
5. Sokolsky D.V., Zhubanov K.A., *et al.*, Deposited KazNIINTI No 1543 (1987)
6. Nalibaev T.N., Fasman A.B., *et al.*, J. Phys. Chem. (Rus) 48:4:889 (1974).
7. Fasman A.B., Raiskina F.I., J. Phys. Chem. (Rus) 50:7:889 (1976).
8. Edvarsson, J.; Irandoust, S., J. Am. Oil Chem. Soc. 70:1149 (1993).
9. Manual on research methods and technological control of production in oil and fat industry. VNIIZ, L., 1964, Vol. 4, p. 495.
10. Ginzburg M.A., Khabibullin F.K., *et al.*, J. Prikl. Khim (Rus), No 9:2149 (1988).
11. Masters K., Homogeneous transition metal catalysis M. "Mir" 1983, p. 47.
12. Marangozis, J., Keramidas, O., *et al.*, Ind. Eng. Chem., Process Des. Dev. 16:361 (1977).
13. Stull D., Westrum E., Sinke G., Chemical thermodynamics of organic compounds. Mir, M., 1971, p. 807.
14. Niklasson, C., Andersson, B., Schöön, N.-H., Ind. Eng. Chem. Res. 26:1459 (1987).

Received 11 May 2006.