KH. I. ARESHIDZE
G. O. CHIVADZE
Z. V. KOBALADZE
Institute of Physical and Organic Chemistry
named after P. G. Melikishvili
Academy of Sciences of the Georgian SSR
Tbilisi
U. S. S. R.

HYDROGENATION OF LIQUID FATS BY THE FLOW METHOD ON THE STATIONARY CATALYST

HIDROGENAÇÃO CONTÍNUA DE ÓLEOS GORDOS SOBRE CATALISADOR ESTACIONÁRIO

The current method of hydrogenation of liquid fats to obtain the hydrogenated fat, requires separation from the catalyst on the filtering presses. Being exposed to the air, the catalyst loses its activity and becomes useless.

Our stationary Cu-Ni catalyst and the flow method of hydrogenation of the liquid fats enables to avoid the labour-consuming process of filtration, to reduce the size of the equipment and to improve the manufacturing process of the hydrogenated fat.

The flow method suggested in this work makes the hydrogenation process of the liquid fats a continuous one, the catalyst staying all the time in the hydrogen medium and thus resulting in an extreme increase of durability of the catalyst which saves the valuable metals.

The common method of hydrogenation of fats used nowadays by the hydrogenation plants in the Soviet Union and elsewhere employs a battery of hydrogenators and suspended catalysts. The resulting hydrogenated fat requires further filtration which inevitabely involves losses of the fat and the active metal.

The stationary catalyst and the flow method suggested in our work enables to eliminate the labour consuming process of filtration from the production line, to reduce the overall size of the equipment and to diminish thel losses of the fat and the metal. The manufacturing process can be made fully automatic, the quality of the hydrogenation products improving significantly.

One of the most important features of the stationary catalysts is their stability. Laboratory research data have shown that the life of the copper – nickel catalyst reached 800 hours during hydrogenation of oils. Additions of transition metals to the above catalyst increased its activity and stability.

In our earlier studies (1, 2) the oil's hydrogenation reaction was carried out on mixed catalysts at relatively high temperatures, 180 – 220 °C. Since the process of hydrogenation is usually accompanied by various side reactions, we used solvents which reduced the reaction's temperature, and thus avoided these side – effects.

The problem of the hydrogenation reaction in solvents seems to be actually important due to the growing interest towards their use in the process of extraction of oils from raw materials.

It was the purpose of this work to investigate the dynamic regularities of low-temperature hydrogenation of fats, to pick out and to study the active and stable nickel-copper catalysts on the carriers, to study the effect of small metal additions (Pt, Pd, Cr), of various solvents, and, finally, to seek for the conditions of obtaining eatable hydrogenated fats.

Experiments on hydrogenation of cotton oil were conducted on the flow-type equipment in the stainless-steel reactor with the inner diameter of 20 mm. The catalysts were prepared by the treatment of gumbrine (natural aluminium silicate) with salt solutions (see ref. 1). Table 1 presents the composition and characteristics of the catalysts that were used in the study of the hydrogenation process of cotton oil.

Table 1

Composition and properties of the catalysts

Catalyst	Content of the catalyst's active phase	Specific surface, sq.m/g	Mechanical strength, kg/sq.cm
1	Ni – 6%, Cu – 2%	78	125
2	Ni – 6%, Cu – 2%, Cr – 2%	71	120
3	Ni – 6%, Cu – 2%, Pd – 0.15%	76	125
4	Pd – 1%	80	115
5	Ni – 6%, Cu – 2%, Pt – 0.2%	76	120
6	Ni – 6%, Cu – 2%		

Catalysts 1 – 5 were prepared on gumbrine, while catalyst 6 on askanite clay.

Specific surface of the catalysts was determined chromatographically on argon (3) after reduction.

Hydrogenation was conducted on refined cotton oil with the iodine number 108 – 110 and pH 0.8, by means of electrolytic hydrogen. The iodine number, melting temperature, acid number, Kaminski hardness and fat-acid content characterizing the hydrogenated products were all estimated chromatographically, while the trans-isomers content was determined by the UR – 20 spectrometer.

It was shown in (4) that, as the excess hydrogen yield grows from 50 to 200 ml/min, the rate of reaction of hydrogenation of cotton oil increases, but further growth of the hydrogen output doesn't practically affect the reaction's rate. Therefore, the hydrogen rate 200 ml/min was kept constant in this work.

Hydrogenation was carried out in the presence of the following solvents – ethanol, acetone, n-hexane, cyclohexane, mixtures of n-alkanes of the $C_5 - C_8$ – content and a concentrate of naphthenes with isoparaffins with the boiling temperature 30 – 85 °C. The n-alkanes mixture was obtained by denormalization of low-octane benzine (5), while the naphthenes concentrate – by thiourea treatment (6).

The relation of the hydrogen saturation degree of cotton oil to the time of contact with the catalyst at 90 °C, at 2 atm. pressure and the ethanol-oil ratio 1 : 1 (fig. 1), was studied in order to find the most active catalyst. As fig. 1 shows, the catalysts'activity was almost the same, the most active ones being catalysts 3 and 4.

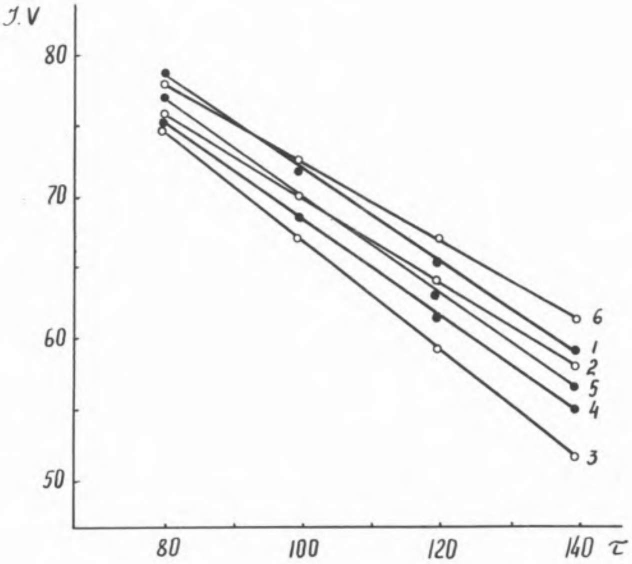

Fig. 1

Relation of the iodine number (i. v.) of hydrogenated fat to the contact time ($T = 90$ °C, $PH_2 = 2$ atm).
Numbers 1 - 6 refer to the catalysts numbers in table 1

Catalyst 3 was used to study the influence of the temperature on the velocity of hydrogenation. The velocity (K) was calculated as in (7). The results are presented in fig. 2.

The data have proved that as the hydrogenation reaction temperature increases, the rate of reaction also grows up to a certain limit, then it decreases slightly. The study of the temperature dependence of the reaction's velocity has shown that each solvent has a certain temperature at which the hydrogenation rate reaches its maximum and this seems to be caused by the partial pressure of the solvent's vapours.

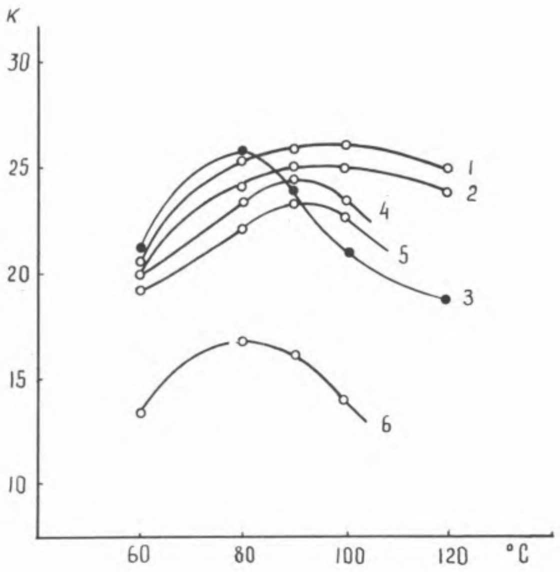

Fig. 2

Relation of hydrogenation rate of cotton oil to temperature on catalyst 3. The solvents used – (1) n-alkanes, (2) naphthenes, (3) n-hexane, (4) ethanol, (5) cyclohexane, (6) acetone.

The above assumption was justified by experiments conducted in the presence of catalyst 3 with the temperature range of 70 – 110 °C and volumetric speed 0,70 hr^{-1}, taking into consideration ethanol's partial pressure (table 2).

The obtained results show that as the temperature increases, the hydrogenated oil's iodine number reduces from 83.4 to 50.2 and the melting point grows from 29.6 to 42.5 °C.

Table 2

Dependence of the oil saturation rate on the temperature, considering the partial pressure of the solvent – ethanol

Temperature of experiment °C	Volumetric speed of micelle, hr^{-1}	Hydrogen pressure, atm	Hydrogenated oil's iodine number	Hydrogenated oil's melting temperature, °C
70	0.7	1.5	83.4	29.6
80	0.7	2.0	75.6	32.3
90	0.7	2.6	70.0	34.2
100	0.7	3.5	63.6	37.9
110	0.7	4.5	50.2	42.5

As table 2 shows, the hydrogenation temperature grows in proportion to the decrease of the iodine number, suggesting that the maximum of the hydrogenation speed is connected with the solvent's partial pressure (fig. 2).

The differences in the hydrogenation speed of cotton oil with different catalysts seems to be caused by the different solubility and adsorbing ability of the solvent of the catalyst's surface, and this may affect the binding energy of the reactants.

The relation of the cotton oil hydrogenation depth to the time of its contact with the catalyst (fig. 1) reveals a linear dependence of the iodine number on the contact time, indicating that the oil's saturation process can be described by a kinetic equation of zero order for unsaturated compounds (7).

A linear characteristics was also found for the relation of the reaction's rate logarithm to the inverse temperature at 1 atm pressure within the temperature range of 60 – 90 °C (fig. 3). Therefore, the apparent activation energy was calculated graphically. The apparent energy of activation for the cotton oil hydrogenation in the n-alkanes mixture was 3.2 – 5.0 kcal/mol, depending on the catalyst used.

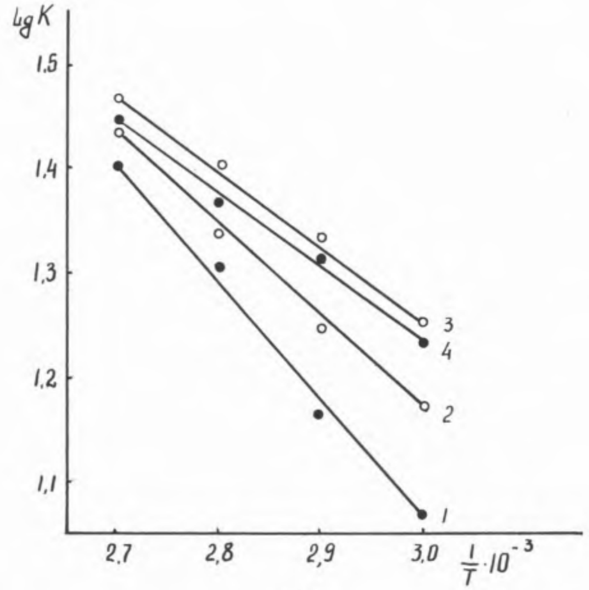

Fig. 3

Relation of logarithm of the reaction rate to the reverse temperature. Numbers 1 - 4 correspond to the catalysts numbers

The influence of the hydrogen pressure of the process of hydrogenation of oil was studied in the range of 1 – 6 atm, with the n-alkanes mixture as the solvent (table 3).

Table 3 shows that in the same conditions of the process the selectivity index goes up to 0.92 when the hydrogen pressure increases to 4 atm., while when the hydrogen pressure reaches 6 atm, the oil saturation depth increases and the rate of the reaction grows in proportion to the hydrogen pressure increase (fig. 4).

The linear characteristic of the reaction velocity to the pressure growth (fig. 4) seems to indicate the first order of the reaction for hydrogen. These results imply that the hydrogen pressure growth causes the increase of its concentration in the liquid phase and the acceleration of the hydrogen diffusion through the liquid layer up to the surface of the catalyst (7).

As the hydrogen pressure grows, the trans-acids content in the hydrogenated oil drops from 31.6 to 26.6 and at the same time the hydrogenated oil's hardness reduces from 180 to 140 (table 3).

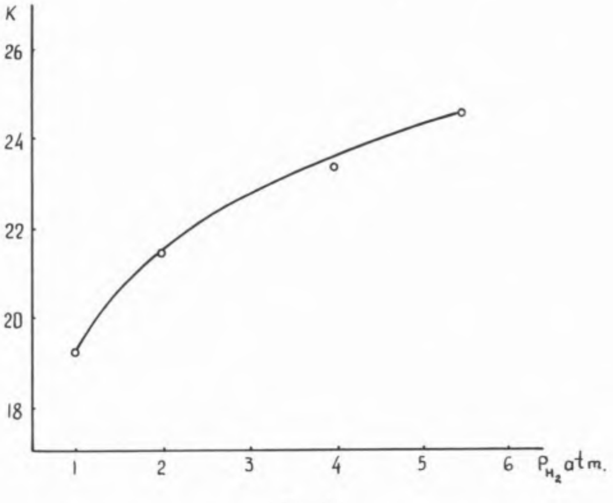

Fig. 4

Relation of hydrogenation rate to hydrogen pressure on catalyst 3. $V = 0.75\ hr^{-1}$, $T = 100\ ^\circ C$

Dependence of the cotton oil saturation depth on the volumetric speed of micelle supply was studied with n-alkanes mixture used as the solvent. The selectivity of the process was found to grow slightly at the constant temperature (100 °C) and at the hydrogen pressure 1 atm with an incrèased supply speed (table 3).

Table 3

Hydrogenation of cotton oil on catalyst 3. The oil-to-solution (n-alkanes mixture) ratio is 1 : 1

Temperature of experiment, °C	Volumetric speed, hr^{-1}	Hydrogen pressure, atm.	Iodine number	Melting temper. °C	Acid number	Hardness	Fat-acid content, %			Selectivity index	Transacids content	K
							L	oe	S			
60	0.75	1	83.5	28.5	0.8	120	31.8	35.6	34.6	0.83	26.1	14.7
70	»	1	79.0	29.3	0.8	140	27.1	38.9	34.0	0.86	26.9	17.2
80	»	1	77.3	31.5	1.1	160	25.4	42.0	32.6	0.86	27.8	18.1
90	»	1	76.6	32.6	1.2	180	22.2	43.5	34.3	0.91	30.0	18.5
100	»	1	76.2	33.0	1.3	180	20.2	44.8	35.0	0.87	31.6	18.7
120	»	1	77.4	33.8	1.4	190	20.9	45.0	35.1	0.86	44.2	18.1
100	0.95	1	81.2	31.2	1.1	160	21.8	45.5	33.7	0.92	30.9	21.6
100	1.20	1	86.6	30.3	1.0	130	20.3	45.1	34.6	0.92	29.6	21.9
100	1.52	1	91.3	29.2	1.0	90	22.0	43.7	34.3	0.95	28.4	22.5
100	0.75	2	71.4	34.5	1.2	180	19.0	45.2	35.7	0.89	29.6	21.5
100	»	4	68.0	36.0	1.1	160	16.8	45.7	37.5	0.92	28.1	23.3
100	»	6	65.8	36.8	1.3	140	15.5	45.0	37.6	0.87	26.6	24.5

Studies were also carried out on the effect of the oil and solvent ratio on the speed of the reaction and the process's selectivity. Table 4 of the experimental results shows that while the oil content grows up to 50 % the speed of the reaction increases, but the further growth of the oil content decreases the reaction speed.

The fat-acid content depends on the oil content in micelle – the glyceride content of the linolic acid reduces while the glyceride content of the oleic acid increases (both acids are designed in the tables as Ω and 0 Ω respectively). The glyceride content of the saturated acids (H) in the hydrogenated oils grows, but insignificantly.

Table 4

Effect of oil content in micelle on saturation.
Solution – n-alkanes mixture, Catalyst 3.
Volumetric speed of micelle – 0.65 hr^{-1}, $PH_2 = 2$ atm

Temperature of experiment, °C	Oil concentrat. in micelle	Iodine number of hydrog. oil	Melting temper. of hydrog. oil °C	Fat-acid %			Selectivity	K
				L	oe	S		
100	80	79.9	30.5	36.0	35.5	28.5	0.73	20.0
100	70	76.8	31.8	29.6	41.0	29.4	0.76	23.5
100	60	72.6	32.0	19.9	46.4	33.7	0.81	24.9
100	50	70.1	34.6	17.7	47.7	34.6	0.86	26.6
100	40	72.2	32.6	18.8	44.0	37.2	0.79	25.2
100	30	73.0	31.8	19.5	42.5	38.0	0.71	24.6
100	20	75.4	31.0	21.3	38.9	39.8	0.68	23.1

The selectivity of the process changes according to oil content in the micelle. If the oil content exceeds 50 % the selectivity reduces, and it reaches maximum (0.86) when the oil and n-alkanes ratio becomes 1 : 1. Reduction of the oil concentration also affects the selectivity. The best catalyst appeared to be the nickel-copper-palladium catalyst. Maximum speed of reaction of cotton oil hydrogenation is achieved when the n-alkanes mixture is used as the solvent.

The obtained results enabled to develop optimal conditions of hydrogenation of cotton oil (reaction's temperature 90 – 100 °C, micelle's supply speed 0.60 – 0.65 hr^{-1}, hydrogen pressure 2 – 3 kg/sq.cm). The eatable hydrogenated fat obtained in these conditions has the following characteristics: iodine number 69 – 72, melting temperature 30 – 33 °C, hardness 180 – 220 g/cm, hard trigliceriдes content 30 – 33 %, transacids content 27 – 30.8 %.

The obtained catalysts were tested in big laboratory plants of Tbilisi oil mill. It has been proved that the process can be fully simulated with the reactor's size enlarged 100 times.

BIBLIOGRAPHY

1. ARESHIDZE KH. I., CHIVADZE G. O., BALAKHISHVILI L. I., KHAKHNELIDZE V. V., CHKHEIDZE L. Z., KOBALADZE Z. V., Trans. of Academy of Sciences of Georgian SSR, 68, 1, 73 (1972).
2. ARESHIDZE KH. I., CHIVADZE G. O., KOBALADZE Z. V., SOKOLSKI D. V., ORLOV V. K., Fat and Oil Industry, 3, 20 (1973).
3. BUYANOVA N. S., GUDKOVA G. B., KARNAUKHOV A. P., Kinetics and Catalysis, 6, 1085 (1965).
4. NECHAEV N. A., GOLDOV F. G., SOKOLSKI D. V., ADENOV K. A., CHIVADZE G. O., Chemistry and Chemical Technology. Min. of High and Secondary Special Educ. Kaz. SSR, 6, 47 (1967).
5. ARESHIDZE KH. I., CHIVADZE G. O., Trans. of Jass Politechnical Institute (Rumania), 3-4, 269 (1968).
6. ARESHIDZE KH. I., CHIVADZE G. O., Neftekhimia, 4, 518 (1963).
7. SOKOLSKI D. V., Hydrogenation in Solutions. Alma-Ata, Kaz. Ac. Sc. (1962).

RESUMO

O método corrente de hidrogenação de óleos gordos para obter gorduras hidrogenadas requer separação do catalisador em filtros prensas. Sendo exposto ao ar, o catalisador perde a sua actividade e inutiliza-se.

O método contínuo de hidrogenação catalítica de óleos gordos em leito estacionário permite evitar o processo de filtração, oneroso quanto a necessidades de mão-de-obra, reduzir o tamanho de equipamento e melhorar o processo de fabricação de óleo hidrogenado.

O processo sugerido neste trabalho faz com que o processo de hidrogenação de óleos líquidos passe a ser contínuo, permanecendo sempre o catalisador num meio contendo hidrogénio, o que dá lugar a um aumento da vida do catalisador, poupando metais valiosos.