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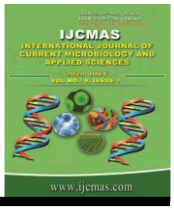

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Assessment of Process Selectivity at Hydrogenation of Vegetable Oils

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ABSTRACT

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Effect of conditions of oil hydrogenation on the selectivity of the process has been studied. Process parameters ensuring high degree of selectivity have been determined.

Introduction

Several substances or mixtures of substances capable of various conversions are involved in chemical processes of oil and fat hydrogenation. Selectivity means the preferred course of only one of possible reactions, conversion in one of possible directions, or consumption of only one of substances (Arutyunyan *et al.*, 1999; Tovbin, *et al.*, 1982).

Unsaturated triglycerides of most vegetable oils and animal fats are formed by di-unsaturated linoleic acid (L) and monounsaturated oleic acid (Ol) (Sattarov *et al.*, 2007; Tovbin *et al.*, 1982; Tyutyunnikov *et al.*, 1992; Akramov *et al.*, 2006; Allen, 1980). The selectivity of hydrogenation of such oils and fats is expressed primarily in the following:

- preferential hydrogenation of glycerides of linoleic acid in mixtures with glycerides of monounsaturated acids (oleic acid and its isomers);

- significantly higher rate of hydrogenation of glycerides of linoleic acid compared to the rate of hydrogenation of glycerides of oleic and other monounsaturated acids;

- hydrogenation of only one double bond in linoleic acid;

- significantly higher rate of hydrogenation of glycerides of cis-isomers of unsaturated fatty acids mixed with their trans-isomers;

- significantly higher hydrogenation rate of glycerides of di-unsaturated fatty acids with conjugate double bonds in comparison with their isomers with isolated double bonds.

Purpose of researches aimed at studying the effect of conditions of oil hydrogenation on the process selectivity when using catalysts of the new modification.

Materials and Methods

Hydrogenation of vegetable oils was carried out on flowing-type hydrogenation installations (Arutyunyan, 1979; Melamud, 1982). Modern methods of physical-chemical research were used for the quality assessment of raw materials and products of hydrogenation (Coenen, 1978; Cray 1979; Stopsky *et al.,* 1992).

Results and Discussion

It was experimentally established that, during the separate hydrogenation of glycerides of linoleic and oleic acids, depending on the process conditions the saturation rate of linoleic acid acyls is 2-10 times higher than the rate of saturation of oleic acid acyls (Majidova *et al.,* 2009). Under the same conditions, the relative rates of simultaneous hydrogenation of acyls of linolenic, linoleic and oleic acids on nickel catalysts are characterized by the values:

oleic acid 1
linoleic acid 20–50
linolenic acid 30–100

Selective hydrogenation of mixtures of triglycerides of linoleic and oleic acid can be shown by scheme, in which the letter C denotes stearic acid (Arutyunyan, 1979).

$$Л \xrightarrow{K_{Л}} Ол$$

$$Ол \xrightarrow{K_{Ол}} C$$

In this scheme $k_{Л}$ is specific rate of hydrogenation of linoleic acid in mixtures of glycerides of linoleic and oleic acids (reaction rate constant of hydrogenation of linoleic acid). Designation $k_{Ол}$ refers to the specific rate of oleic acid hydrogenation and denotes the rate constant of the oleic acid hydrogenation reaction.

In absolutely selective process, the hydrogenation of oleic acid and its formed isomers begins only after the hydrogenation of linoleic acid in triglycerides is completed. The process proceeds strictly according to a consistent scheme, and $k_{Ол} = 0$ until linoleic acid glycerides are present in the hydrogenated feed:

$$Л \rightarrow Ол \rightarrow C$$

Under industrial conditions, with the exception of special cases, hydrogenation does not pass completely selectively – both reactions proceed in parallel with one or another rate (Table 1). The higher the hydrogenation selectivity, the lower the reaction rate constant for the conversion of oleic acid, which is part of the glycerides, to stearic acid.

A measure of the selectivity of the process is a coefficient numerically equal to the ratio of constants $k_{Л} = k_{Ол}$. The higher the selectivity of the process, the greater the value of this coefficient.

More visual method for assessing the selectivity of hydrogenation is the ratio of the increase in the content of monounsaturated acids in glycerides of hydrogenated fat ($\Delta[\text{Ол}] = [\text{Ол}]_{\text{кон}} - [\text{Ол}]_0$) to the value characterizing the decrease in the content of diunsaturated acids ($\Delta[\text{Л}] = [\text{Л}]_0 - [\text{Л}]_{\text{кон}}$):

$$K_{Л} = \frac{\Delta[Ол]}{\Delta[Л]} \bullet 100$$

where $\Delta[\text{Ол}]$ – difference between the final and initial content of oleic acid in the glycerides of the hydrogenated raw material ($[\text{Ол}]_{\text{кон}}$ and $[\text{Ол}]_0$ accordingly); $\Delta[\text{Л}]$ – difference between the initial and final content of linoleic acid ($[\text{Л}]_0$ and $[\text{Л}]_{\text{кон}}$ accordingly).

There is a dependence between the kinetic coefficient of selectivity $k_{\text{Л}} = k_{\text{Ол}}$ and the concentration coefficient of selectivity $K_{\text{Л}}$, presented in Table 2.

Decrease in the selectivity of hydrogenation to a level of 85–90% leads to significant increase of stearic acid in glycerides of oil-and-fat mixtures at high residual content of linoleic acid. The following features are characteristic of such oil-and-fat mixtures:

non-uniform crystallization at cooling to room temperature;
delamination into liquid and soft hardened fractions during storage;
increased melting temperature at relatively low hardness;
oily aftertaste of frozen fat and others.

It is necessary to distinguish between the selectivity of the process and the selectivity of the chemical reaction on the catalyst (selectivity of the catalyst). The selectivity of the catalyst is determined by its porous structure and chemical composition.

Increase in hydrogen pressure and intensity of mixing, decrease in the temperature of the reaction medium, decrease in the concentration of glycerides of linoleic acid, as well as some other factors reduce the selectivity of the process even when using highly selective hydrogenation catalysts.

Process selectivity is subject to the number of laws (Coenen, 1978):

linoleic acid, which is part of the glycerides, is saturated much more than oleic in the first stages of the hydrogenation process;
when hydrogenating glycerides of linoleic acid it is preferable to saturate the double bond in position Δ12 as compared to the double bond in position Δ9;
when hydrogenating glycerides of dienoic acids with isolated and conjugate double bonds, acids with conjugate double bonds are preferable to hydrogenate, therefore, despite the continuous formation of conjugate isolinoleic acids during hydrogenation, their amount in hydrogenates rarely exceeds 2-3%;
cis-isomers are more saturated than trans isomers during the hydrogenation of spatial isomers.

Selectivity of hydrogenation of various compounds in mixtures is explained by differences in their adsorption capacity. In particular, the adsorption capacity decreases as the number of ethylene bonds in the acid molecule decreases. As a result, acyls of linolenic acid displace acyls of linoleic acid etc. from the catalytic surface (competing adsorption). Acyls of linoleic and polyunsaturated acids can displace chemisorbed hydrogen from the surface of the catalyst, which also promotes selective hydrogenation due to the lack of chemisorbed hydrogen on the catalyst.

Selectivity of hydrogenation is also affected by technological factors. At the main stage of the process, when hydrogenation proceeds in the kinetic region with respect to glycerides of di-unsaturated acids (diffusion zone with respect to hydrogen), it is possible to increase the selectivity of hydrogenation due to increase in temperature, increase in the amount and increase in catalyst activity, decrease in hydrogen pressure and mixing intensity. In the zone of low concentrations of glycerides of diunsaturated acids, i.e. under conditions when hydrogenation rate is limited by the diffusion of these triglycerides (the diffusion zone with respect to glycerides of di-unsaturated acids), selectivity of hydrogenation decreases with increasing temperature (since the surface reaction rate increases more than the diffusion rate), it increases with mixing intensity, decreases with increasing hydrogen pressure and catalyst activity.

Qualitative characteristic of effect of technological factors on the selectivity of hydrogenation of linoleic acid acyls is given in Table 3. Sign (+) indicates increase, and sign (-) indicates decrease in the selectivity of the process as this process parameter increases.

Therefore, the selectivity of the hydrogenation is enhanced by carrying out the process under conditions where hydrogenation is carried out in the kinetic zone through the glycerides of the di-unsaturated acids and is limited by the transfer of hydrogen to the reaction zone. However, since improving the hydrodynamic modes of the reactors is necessary to increase the efficiency of the hydrogenation plants, the desired selectivity of hydrogenation is ensured by selecting the catalyst, its amount and the process temperature.

Selectivity of the catalyst N-800 (Basf, Germany) at different temperatures of hydrogenation shown in Table 4, and selectivity of the same catalyst at different hydrogen bubbling rates shown in Table 5.

Data of Table 4 and Table 5 show that high selectivity of hydrogenation even under intensive mixing and moderate temperatures of process characterize the catalyst N-800.

Table.1 Change in the fatty acid composition of cottonseed oil during selective hydrogenation on the nickel-copper catalyst

Iodine number, g I_2/100g	Fatty acid composition, %				Note
	18:2	18:1	18:0	16:0	
116.8	54.6	20.9	4.2	6.3	Selective hydrogenation of glycerides of linoleic acid
104.8	32.4	55.6	4.6	6.4	
85.6	12.9	73.6	7.1	6.4	
77.2	5.6	78.5	9.5	6.4	Transitional area of hydrogenation
72.6	3.2	78.0	12.4	6.4	
65.6	1.8	72.7	19.1	6.4	Hydrogenation of oleic acid glycerides and its isomers
57.3	0	66.6	27.1	6.3	
51.4	–	59.8	33.8	6.4	
46.1	–	53.6.	40.0	6.4	
41.5	–	48.2	46.4	6.4	

Table.2 Relation between kinetic and concentration coefficients of selectivity of hydrogenation

Coefficient	Coefficient value					
$k_{Л} = k_{Ол}$, %	10	15	20	30	40	50
$K_{Л}$, %	85	90	92	95	96	97

Table.3 The influence of technological factors with increasing parameter on the selectivity of hydrogenation

Influencing process parameter	Change in the selectivity of hydrogenation in the diffusion zone	
	by hydrogen	by glycerides of linoleic acid
Temperature	+	–
Hydrogen pressure	–	–
Intensity of mixing	–	+
Activity of catalyst	+	–
Concentration of catalyst in raw material	+	+

Table.4 Selectivity of catalyst “Nisosel-800” (N-800) at different temperatures of hydrogenation (cottonseed oil, 0.05% nickel, intensity of hydrogen bubbling 180 m^3/h per ton of oil)

Indicator	Indicator value				
Temperature, °C	120	140	160	180	200
Iodine number of oil-and-fat mixture, g I_2/100 g	86	81	79	81	77
Selectivity:					
$K_{Л}$, %	90	90	92	93	95
$k_{Л} / k_{Ол}$	15	15	17	20	30

Table.5 Selectivity of catalyst N-800 at different intensity of hydrogen bubbling (cotton oil, nickel 0.05%, 200 ° C)

Indicator	Indicator value				
Hydrogen bubbling, m^3/h per ton of oil	15	30	60	120	180
Iodine number of oil-and-fat mixture, g I_2/100 g	81	80	84	79	77
Selectivity:					
$K_{Л}$, %	97	97	96	96	95
$k_{Л} / k_{Ол}$	50	50	40	40	30

Table.6 Hydrogenation of cottonseed oils on spent catalyst N-800 (200 °C, 0.1% nickel in oil)

Indicator	Indicator value			
Iodine number of hydrogenate, g I_2/100 g	99	95	89	80
Selectivity of hydrogenation, $A_л$, %	99	97	96	95
Increase in content of stearic acid, %	0	0	3	3
Residual content of linoleic acid, %	24	18	12	6

At 180-220 °C and overpressure of hydrogen up to 0.2 MPa, modern nickel industrial catalysts have a selectivity of Кл = 92-98% in the field of high and medium concentrations of diunsaturated acids in glycerides. Selectivity of hydrogenation is within 70-80% at concentration of linoleic acid below 15-17%

It is necessary to create catalysts with wide pores, i.e. diameter of more than 2.5 nm in order to increase the selectivity of hydrogenation. A common technique for increasing selectivity of hydrogenation is to modify the catalyst by reusing it. Table 6 shows the results of the hydrogenation of cotton oils on the spent catalyst N-800.

Analysis of quantitative indicators of the selectivity of hydrogenation of fats allows making the following conclusion: the higher selectivity of the process, the lower increase in the content of acyls of stearic acid in triglycerides of oil-and-fat mixture at the given depth of saturation of raw materials.

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