

Research of chemical transformations in the technology of hydrogenation of vegetable oils

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Abstract. Chemical transformations in the technology of hydrogenation of vegetable oils have been studied. The equations describing the saturation of fatty acids in hydrogenation technology have been established. The diffusion coefficients of hydrogen and triglycerides in oils and fats have been determined. It has been shown that the observed rate of hydrogenation does not depend on the amount of catalyst and the degree of unsaturation of the fat. The high quality and food safety of catalytically hydrogenated edible fats have the required content and ratio of solid and liquid fractions of fatty acids in fat triglycerides, maintain the quantitative content of biologically important components in the composition of the initial raw material. The selection of the additive and its use in the composition of catalytic systems allows establishing and regulating the hydrogenating properties of hydrogenated edible fats with high indicators of quality and food safety. Methods for optimizing technological regimes made it possible to increase the food safety of margarine products and expand its range. The scientific and experimental results have allowed expanding and supplementing the theoretical provisions on improving the quality and food safety of catalytically hydrogenated edible fats based on cottonseed oil using various types of catalytic systems.

1 Introduction

The chemical transformations in hydrogenation of fats occur on the surface of the catalyst, which, together with the reactants, forms “gas-liquid-solid” three-phase system [1-3]. The purpose of the research is to study the chemical transformations of fatty acids in the technology of hydrogenation of oils and fats.

2 Methods of research

The essential stages of this heterogeneous process are the following physical processes [4-8]:

- dissolution of gaseous hydrogen at the gas-liquid interfacial area;
- transfer of hydrogen from the gas-liquid interface into the volume of the liquid phase;

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- transfer of dissolved hydrogen and hydrogenated molecules from the volume of the liquid phase to the boundary layer of the liquid surrounding the catalyst particles;
- molecular diffusion of hydrogen and hydrogenated molecules from the liquid-solid boundary layer to the outer surface of the catalyst;
- diffusion of molecules into the pore volume and to the inner surface of the catalyst;
- diffusion of reaction products from the catalyst surface into the boundary layer of the liquid;
- transfer of reaction products from the liquid-solid boundary layer into the volume of the liquid phase;
- equalization of temperature differences caused by the thermal effects of reactions on the catalyst surface (heat transfer).

In case when the reaction rate on the catalyst surface is significantly less than the rate of supply of reagents and removal of reaction products under the given conditions (which can be observed in the hydrogenation of fats only at sufficiently low temperatures and low concentrations of a moderately active catalyst), then the resulting (observed) rate of the process is equal to the rate of the chemical reaction itself. The process is not limited by the stages of mass transfer and proceeds in the so-called kinetic area for all reaction components. Under these conditions, the hydrogenation rate proportionally increases with an increase in the amount of catalyst and hydrogen pressure, increases exponentially with an increase in temperature, but depends little (theoretically does not depend) on the intensity of hydrogen stirring and bubbling [9-12].

In order to conduct experiments and analyze the results obtained, modern physical, chemical and physical-chemical methods (IR, GLC, TLC), as well as methods of mathematical processing and modeling of the research results processes have been used.

3 Results of research

Due to the high reactivity of glycerides of linoleic and more unsaturated acids, the kinetic range of hydrogenation is practically unattainable in modern hydrogenation reactors and at temperatures that are necessary for the required process rate.

Generally, the rate of hydrogenation reaction on the catalyst surface is more or less substantially greater than the rate of mass transfer and is largely dependent on it.

If the rate of mass transfer of any component of the reaction is significantly less than the potential rate of the reaction under certain conditions, then the process proceeds in the diffusion region for this component.

Since the solubility of hydrogen in oils and fats, as well as the diffusion rates of hydrogen and triglycerides, increase more slowly with increasing temperature than the rate of a chemical reaction, the diffusion inhibition of the hydrogenation process increases more with increasing temperature. The rate of hydrogenation increasingly depends on the intensity of mixing of the gas-liquid-catalyst system, which is carried out using a mixing device and hydrogen bubbling. The resulting turbulence increases the gas-liquid interface, reduces the thickness of the boundary (diffusion) liquid layer around the catalyst particles, more evenly distributes the reaction components in the liquid phase, and thereby accelerates mass transfer processes.

Under the steady state of the process, the rate of supply of reagents, the rate of reaction on the catalyst surface, and the rate of removal of reaction products into the volume become equal to each other: in the kinetic area, the reaction rate increases to the rate of supply of reagents, and in the diffusion area, it decreases to the rate of supply of reagents.

Under the conditions of industrial hydrogenation of fats, especially when processing glycerides of linoleic and more unsaturated acids, the rate of the process is limited by the

supply of hydrogen to the reaction zone due to its low solubility in fats and insufficiently efficient dispersion of gaseous hydrogen in the liquid phase.

Upon contact of gaseous hydrogen with fat in the boundary layer of a liquid, which is in direct contact with the surface of a gas bubble (in a liquid film), saturation equilibrium is quickly established:

$$C_0 = a \cdot P_H \tag{1}$$

where C_0 is the concentration of hydrogen at the gas-liquid interface; a is the coefficient of hydrogen solubility in liquid; P_H is the pressure of hydrogen in the gas phase.

The solubility of hydrogen in fats and oils is negligible. Calculations show that at a normal fat hydrogenation temperature (180–200 °C) and close to atmospheric pressure, the hydrogen concentration at the gas-liquid interface does not exceed 6 mole/m³.

The flow rate of hydrogen through the boundary layer of a liquid of thickness X can be represented by the equation

$$V_{GL} = \frac{D_H}{X} \cdot (C_0 - C_H) \cdot S \tag{2}$$

where V_{gl} is the rate of hydrogen transfer from the gas phase to the liquid; D_H is the diffusion coefficient of hydrogen; C_H is the concentration of hydrogen in the liquid phase; S is the surface area of the gas-liquid interface.

The following relation expresses the effective thickness of the boundary layer, in which the diffusion transfer of matter takes place:

$$X \approx D^{1/6} \cdot \eta^{1/6} \cdot \gamma^{1/6} \cdot w^{1/6} \tag{3}$$

where D is the coefficient of molecular diffusion; η is the kinematic viscosity of the liquid; γ is the linear coordinate of the gas bubble in the liquid flow; w is the flow rate.

The thickness of the diffusion layer is inversely proportional to the square root of the relative speed of the fluid, which essentially depends on the intensity of mixing.

The intensity of mixing also determines the size of the gas-liquid interface, therefore the rate of hydrogen flow into the liquid phase will be the higher, the better the dispersion of gaseous hydrogen in the fat, which is achieved by mechanical mixing of the gas-liquid system and gas bubbling through the liquid.

Coefficients of molecular diffusion of hydrogen and triglycerides at temperatures of 120–200°C are compared in Table 1.

Table 1. Coefficients of molecular diffusion of hydrogen and triglycerides in oils and fats.

Coefficients of diffusion	Temperature, °C				
	120	140	160	180	200
Coefficients of diffusion of hydrogen $D_H \cdot 10^5, \text{ cm}^2/\text{s}$	13	15	17	22	29
Coefficients of diffusion of triglycerides $D_T \cdot 10^5, \text{ cm}^2/\text{s}$	0.14	0.21	0.26	0.31	0.36

At temperatures of industrial hydrogenation of fats, the coefficient of molecular diffusion of hydrogen is 80 times greater than the coefficient of diffusion of triglycerides. However, in such oils as sunflower, soybean, and cottonseed oils, the concentration of unsaturated triglycerides is about 1000 mole/m³, i.e., 170 times higher than the maximum possible concentration of hydrogen dissolved in the oil. In fact, at industrial hydrogenation temperatures, the reaction rate on the catalyst surface is very high, the hydrogen concentration on the catalyst surface (C_H) is close to zero, and the concentration of dissolved hydrogen in the liquid (C_H) is significantly less than the solubility limit. In this regard, at high temperatures, when using a sufficiently active catalyst and at high concentrations of unsaturated triglycerides, the flow rate of triglycerides to the catalyst surface is higher than

the flow rate of hydrogen. The process is limited not by the transport of glycerides to the catalyst surface, but only by the transport of hydrogen.

4 Discussion

The hydrogenation rate K is proportional to the concentrations of unsaturated triglycerides (C_{ut}) and hydrogen (C_H) on the catalyst surface:

$$R = k_p \cdot C_K \cdot C_{ut} \cdot C_H \quad (4)$$

where, k_s is constant of the reaction rate on the catalyst surface;

C_c is the catalyst concentration.

Since in the case under consideration the process is not limited by the diffusion of hydrogenated molecules, there is an equilibrium between their concentration in the volume (C_{ut}) and on the catalyst surface (C_{ut}), which can be represented by the approximate equation:

$$c_{ut} = b_{ut} \cdot C_{ut} \quad (5)$$

where, b_{ut} is the adsorption coefficient of hydrogenated unsaturated triglycerides.

On the other hand, the concentration of unsaturated compounds in the liquid phase determines the overall unsaturation of such a solution. This allows the reaction rate equation to be expressed in terms of iodine number of the hydrogenated fat:

$$R = k \cdot c_H \cdot C_K \cdot I.N. \quad (6)$$

In the steady state of the hydrogenation process

$$V_H = V_{ut} = R \quad (7)$$

where, V_H is hydrogen flow rate;

V_{ut} is the flow rate of triglycerides to the catalyst surface.

This allows expressing the dependence of the rate of the hydrogenation process on the size of the gas-liquid interface, hydrogen mass transfer coefficients, catalyst concentration, hydrogen pressure, and the degree of unsaturation of the hydrogenated fat:

$$R = -\frac{d \cdot I.N.}{d \cdot \tau} = \frac{k \cdot k_1 \cdot k_2 \cdot C_K \cdot P_H \cdot I.N.}{k_1 \cdot k_2 \cdot C_K \cdot I.N. + k_1 \cdot k_2 \cdot S \cdot I.N. + k_1 \cdot k_2 \cdot S} \quad (8)$$

where: k_1 is the hydrogen mass transfer coefficient in the gas-liquid boundary layer;

k_2 is the hydrogen mass transfer coefficient in the liquid-catalyst boundary layer;

P_H is the pressure of hydrogen.

Let us consider special cases of this dependence. Due to the insufficient intensity of hydrogen bubbling, the gas-liquid interface is small and the mass transfer coefficient k_1 is low.

Therefore, in the denominator of the general equation of the process rate, small values of the second and third terms can be neglected:

$$-\frac{d \cdot I.N.}{d \cdot \tau} = \frac{k \cdot k_1 \cdot k_2 \cdot C_K \cdot P_H \cdot I.N.}{k_1 \cdot k_2 \cdot C_K \cdot I.N.} = k_1 \cdot C_K \cdot P_H \quad (9)$$

Summarizing the research results with a catalyst promoted by vanadium, we concluded that this catalyst allows obtaining selectively hydrogenated oils with a low content of trans-isomers at temperatures of 180-200 °C and a hydrogen pressure of up to 300 kPa.

Similar research was carried out on a catalyst with the addition of vanadium-rhodium promoters. The results of the study are shown in Table 1.

Table 1. Technological modes and quality of oil-and-fat mixtures during catalytic hydrogenation of cottonseed oil.

Conditions of catalytic hydrogenation					Quality of the oil-and-fat mixtures (Tmelt=32 °C, solidity 220 g/cm)		
Temperature, °C	Pressure, kPa	Hydrogen volumetric feed rate, h ⁻¹	Oil volumetric feed rate, h ⁻¹	Duration, min.	Chromaticity, All-Union scientific and research institute of fats	Acid number, mg-KOH/g	Content of trans-isomers, %
Stationar catalyst							
200	300	60	1.0	40	4	0.30	27
200	300	60	1.2	45	4	0.27	21
200	300	60	1.5	50	5	0.25	16
200	300	60	2.0	60	5	0.23	15
Powder catalyst "Nisosel-800"							
160	200	45*	3.5*	90	2	0.17	23
160	200	60*	2.0*	45	3	0.13	18
180	100	45*	3.5*	90	2	0.09	11
180	100	60*	2.0*	45	3	0.07	8
180	100	60*	1.7*	40	3	0.05	7
180	100	60*	1.5*	40	3	0.05	5

*- volume flow rate in these cases, m³/h.

Research of the effect of the oil supply rate on the rate of its saturation in the presence of catalyst No. 5 showed that at supply rates oil of the order of 1.5-2.5 h⁻¹, hydrogenation products with an iodine number of food lard are obtained. At the same time, the selectivity of hydrogenation of cottonseed oil on a vanadium-containing catalyst, also promoted by rhodium, is quite high and ensures the accumulation of no more than 5–7% of trans-isomerized acids in the hydrogenation product.

Catalytic hydrogenation on catalyst No. 15 after its repeated leaching was studied in a similar way. The data obtained at an oil flow rate of 1 h⁻¹, and a hydrogen pressure of 300 kPa on the spent catalyst No. 15 indicate that the high selectivity of hydrogenation on this catalyst is maintained at temperatures from 140 to 220 °C.

The data obtained show that the rhodium-promoted catalyst has a high selectivity and a relatively low isomerization ability, which change relatively little even with a significant increase in pressure.

The stability of the stationary catalyst was studied in the mode of obtaining hydrogenates that meet the requirements of the standard for edible tallow (TPL=32-34 °C, I.n.=68–75% J2, solidity is 180–260 g/cm). The studies were carried out at 200°C, a pressure of 300 kPa, a hydrogen feed rate of 60 h h⁻¹, and an oil feed rate of about 1 h-1.

It has been established that hydrogenation of cottonseed oil, stable in terms of iodine number and selectivity, on a stabilized catalyst lasts approximately 23-25 days (Table 1).

5 Conclusions

In industrial reactors with low-speed turbine mixers, which include autoclaves used in the republic for hydrogenation with external circulation of hydrogen, dispersion of hydrogen in fat is achieved primarily by hydrogen bubbling. An approximately linear dependence is

observed between the gas-liquid interface area (total surface of hydrogen bubbles in fat) and the hydrogen flow rate through the bubbler holes:

$$S_g = n \cdot V_H \quad (10)$$

where, S_g is the total surface area of hydrogen bubbles;

V_H is the volumetric rate of hydrogen bubbling;

n is the coefficient of proportionality.

Respectively

$$-\frac{d.I.n.}{d.\tau} = k_1 \cdot n \cdot V_H \cdot P_H \quad (11)$$

Thereby, in the deep hydrogen diffusion area, the observed hydrogenation rate does not depend on the amount of catalyst and the degree of unsaturation of the fat, but increases with increasing pressure and intensity of hydrogen bubbling.

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