

THE EFFECT OF TEMPERATURE DURING SOYBEAN OIL HYDROGENATION ON NICKEL CATALYST POISONING BY PHOSPHOLIPIDS

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The effect of temperature during hydrogenation of soybean oil on the degree of poisoning of nickel catalyst by phospholipids was investigated. Two wide porous catalysts with diverse particle sizes were used: catalyst No. 1, medium-grained and catalyst No. 2, fine-grained. Hydrogenation was conducted in a “dead end” type laboratory scale reactor in the temperature range of 160–190°C. The poisoning coefficient (the ratio of the hydrogenation rate constants in the presence and in the absence of inhibitors in the oil, $\alpha = k_{\text{with inhib.}}/k_{\text{without inhib.}}$) and changes in activation energy (E_a) of soybean oil hydrogenation in the presence of phospholipids were studied. It was affirmed that the effect of temperature on catalyst poisoning by phospholipids is significant; the lower the reaction temperature was, the greater the phospholipid inhibiting effect was. The fine-grained catalyst was more active and more resistant. Its resistance decreased at a slower rate than that for the medium-grained catalyst. For example, at 160°C, the coefficients (α) were 0.26 and 0.4 for catalyst No. 1 and 2, respectively. But at 190°C, the respective coefficients were 0.59 and 0.66. The studied catalysts were characterized by E_a similar to that of commercial catalysts: 35.21 and 28.66 kJ/mol for catalysts No. 1 and 2, respectively. The addition of phospholipids to soybean oil caused a decrease in the reaction rate and an increase in the activation energy. The absolute difference in activation energy (ΔE_a) for the medium-grained catalyst was 44.05 kJ/mol, and was almost two times higher than that for the fine-grained catalyst ($\Delta E_a = 26.02$ kJ/mol). The relative increase in activation energy was 125 and 94.3 %, respectively.

INTRODUCTION

Hydrogenation is one of the oldest methods of modifying the chemical and physical properties of vegetable oils [Patterson, 1983; Koetsier, 1997; Veldsink *et al.*, 1997]. The process was discovered and patented by Norman at the beginning of the last century. Because of its complexity, however, the process is still a subject of many studies. The aim of the hydrogenation process is the partial or total saturation of the double bonds of unsaturated fatty acids. As a result, the consistency of the hydrogenated oil changes from liquid to solid fat and its oxidative stability increases. Hydrogenated fats are components of margarine, shortenings and other products, in which they influence the rheological and chemical properties of the final product. The course of hydrogenation and composition of the final product depends on many factors, such as catalyst type and concentration, agitation intensity, hydrogen pressure and temperature. In addition, the type of oil and the presence of catalyst poisons have a significant influence on the process [Klimmek, 1984]. Nickel catalysts, commonly used in fat hydrogenation, are very sensitive to the influence of such poisons of which sulphur and phosphorus organic compounds have the strongest poisoning effects. Phosphorus compounds, mainly phospholipids (PL), although they exist in trace amounts in fat substrates, cause a decrease in catalyst activity [Drozdowski, & Zajac, 1980; Szukalska, 2000 a; b]. However, they do not influence the reaction chemistry including

linoleic and linolenic selectivity as well as the *cis-trans* isomerization rate [Szukalska, 2000 a; b]. It was also affirmed that the degree of catalyst poisoning varies and depends on the grain size of the catalyst and also on whether the phospholipids are native or products of their hydrolysis [Szukalska, 2000 a]. Because of the possibility of phospholipid transformation at high temperatures, it is important to consider this parameter during hydrogenation.

The aim of the present study was to determine the effect of temperature on the degree of nickel catalyst poisoning by phospholipids during the hydrogenation of soybean oil. Changes in the activation energy caused by the nickel catalyst poisoning were also determined.

MATERIALS AND METHODS

Oil. Industrially-degummed, neutralized and bleached soybean oil was used. It had the following acid composition: 16:0, 10.4%; 16:1, 0.2%; 17:0, 0.1%; 18:0, 4.2%; 18:1, 25.0%; 18:2, 51.6%; 18:3, 7.4%; 20:0, 0.4%; 20:1, 0.2%; and 22:0, 0.4%. Its iodine value calculated from composition of fatty acids was 130.2, acid value - 0.25±0.01 mg KOH/g, peroxide value - 8.5±0.2 meq. of oxygen/kg, and content of phosphorus - 5±1 mg/kg of oil. It was typical soybean oil used in industrial hydrogenation.

Catalysts. Two wide porous catalysts with diverse particle sizes were used: catalyst No. 1, industrially-reduced

medium-grained, containing 21.1% Ni; and catalyst No. 2, laboratory-reduced fine-grained, containing 5.0 % Ni. Both catalysts were supplied by the Institute of Chemical Fertilizers, Puławy, Poland. The characteristics of the catalysts were given previously [Szukalska, 2000 a].

Phospholipids. Phospholipid preparation (phosphatidylcholine (PC) – 12.0%, phosphatidylinositol (PI) – 10.8%, phosphatidylethanolamine (PE) – 15.3%, phosphatidylglycerol (PG) – 19.3%, and phosphatidic acid (PA) – 42.6%), obtained from defatted soybean lecithin was used as the poison.

Hydrogenation. Hydrogenations were carried out in a „dead-end” type reactor with automatic recording of hydrogen absorption [Drozdowski, & Niewiadomski, 1972]. The conditions of hydrogenation were as follows: oil sample – 50 g; catalyst concentration – 0.02% Ni; temperature 160, 170, 180 and 190°C; stirring rate – 2700 rpm; atmospheric pressure; phospholipid dosage – 10 mg P/kg oil. The poisons were introduced into the reaction system in the initial phase of hydrogenation, before the addition of the catalyst. The process parameter used (intensive mixing, among others) was conducive for the reaction to occur in the kinetic range in which hydrogen concentration on the surface of the catalyst was high. In the kinetic range of the reaction, the increase in temperature caused an insignificant increase in hydrogen concentration on the surface of the catalyst, and the degree of unsaturation of oil has no effect on the hydrogen concentration [Drozdowski, & Szukalska, 2000].

The curves traced by the recorder illustrate the reaction kinetics and we shall refer to them as kinetic curves. Hydrogenation of oil was assumed to follow the first order reaction ($C_{18:3} \rightarrow C_{18:2} \rightarrow C_{18:1} \rightarrow C_{18:0}$). Its reaction rate was proportional to the degree of oil unsaturation. If the reaction occurs in the kinetic range, the relationship of logarithm of iodine value from hydrogenation time is linear. In this case, the reaction rate constant can be determined from the equation: $k = 1/t \cdot \ln IV_0 / IV_t$, where: t – reaction time (neglecting the induction period, *i.e.* the time during which hydrogen absorption is not observed); IV_0 and IV_t – iodine values of oil before and after hydrogenation. During hydrogenation, two stages differing from each other by reaction rate constants can clearly be observed. An analysis of the fatty acids composition showed that at stage-I mainly polyenoic acids are hydrogenated, while monoenoic acids are hydrogenated at stage-II. Between these stages exists a transition region.

The sensitivity of catalysts to poisons was determined by means of the poisoning coefficient (α), which is expressed as the ratio of the hydrogenation rate constant in the presence of inhibitors to the rate constant in the absence of inhibitors ($\alpha = k_{\text{with inhib.}} / k_{\text{without inhib.}}$).

The values of the rate constants at different temperatures were used to calculate the activation energy (E_a) according to the Arrhenius equation: $\log k = (-E_a/2.303R) \times (1/T) + \log A$, where k is the reaction constant; A , is constant; T [K] is absolute temperature; and R , is gas constant = 8.314 J/K·mol.

RESULTS AND DISCUSSION

A series of soybean oil hydrogenation was conducted in the presence of phospholipid preparation. Soybean oil hydrogenation in which poisons were not added was the control experiment. For example, Figure 1 shows the course of the kinetic curves of soybean oil hydrogenation with catalyst No. 2.

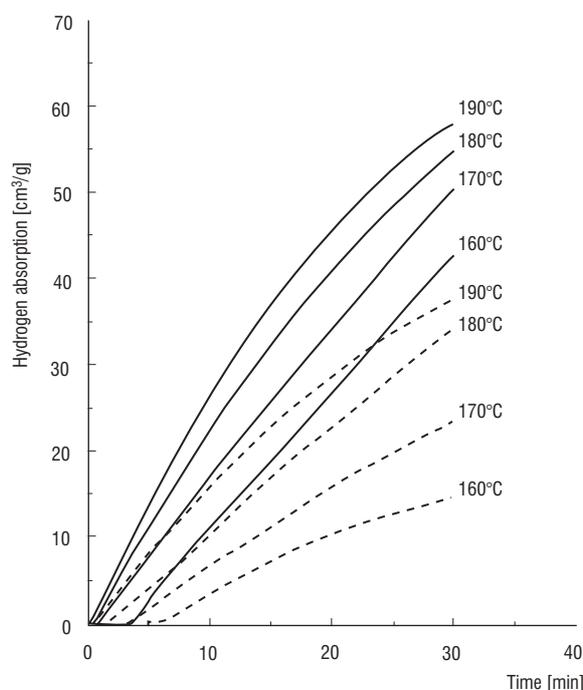


FIGURE 1. Kinetic curves for the hydrogenation of soybean oil without (—) and with (---) phospholipids (10 ppm P). Catalyst No. 2.

The reaction rate constants for the first stage of hydrogenation were calculated. The iodine value (IV) was determined after 10 min from the moment when the oil started to absorb hydrogen. Table 1 presents the reaction rate constants for both catalysts.

TABLE 1. Reaction rate constants.

Catalyst	Addition of phospholipids [mg P/kg of fats]	$k \times 10^3$ [min ⁻¹]			
		Temperature of reaction [°C]			
		160	170	180	190
No.1	0	10.3	14.1	17.3	19.3
	10	2.7	4.7	7.02	11.4
No.2	0	13.2	17.5	20.2	22.3
	10	5.3	7.8	10.3	14.7

Both catalysts used in this study can be classified as wide porous (diameters > 2 nm). It is important to mention that pores of a diameter < 2 nm are inactive in hydrogenation process because triacylglycerols (TG), which have molecular diameters > 1.5 nm [de Hault, A. & Demoulin, 1984], cannot diffuse through them. The difference between catalysts was their particle diameters.: catalyst No. 1 – was a medium-grained catalyst (40.9% particles of diameter 10 to 20 μm ; 32.6% particles of diameter 2 to 8 μm), whereas catalyst No. 2 – was a fined-grained catalyst (75.8% particles of diameter 2 to 8 μm). The catalyst No. 2, which

was characterized by higher rate constants, was more active than the catalyst No. 1. This activity is connected with the structure of the catalyst particles. It is directly proportional to the active catalyst area, which is composed of external and internal area. The internal area is the area of the catalyst pores. Studies have shown that activity increases along with an increase in pore diameters and decreases with an increase in the catalyst particles diameters [Coonen, 1986; Colen *et al.*, 1988]. Therefore, wide porous and fine-grained catalysts are characterized by high activity. Nevertheless, the use of such catalysts is limited by their filtrability, which for fine particles is a serious problem [Szukalska *et al.*, 1997].

The addition of phospholipids to oil causes a decrease in reaction rate constant (tab. 1). The poisoning coefficient (α) values are shown in Table 2 and Figure 2. The coefficient (α) expresses the influence of inhibitors upon the degree of catalyst poisoning. The lower the value is, the stronger is the poisoning effect upon the catalyst. When $\alpha = 1$, it implies that there is no inhibitory effect. However, when $\alpha = 0$, it implies complete poisoning of the catalyst. In the reaction temperature range (160–190°C), a significant temperature influence on the catalyst poisoning by phospholipids was affirmed, thus the inhibitory effect of PL was higher at a lower process temperature. The fine-grained catalyst (cat. No.2) was more resistant to poisoning. Along

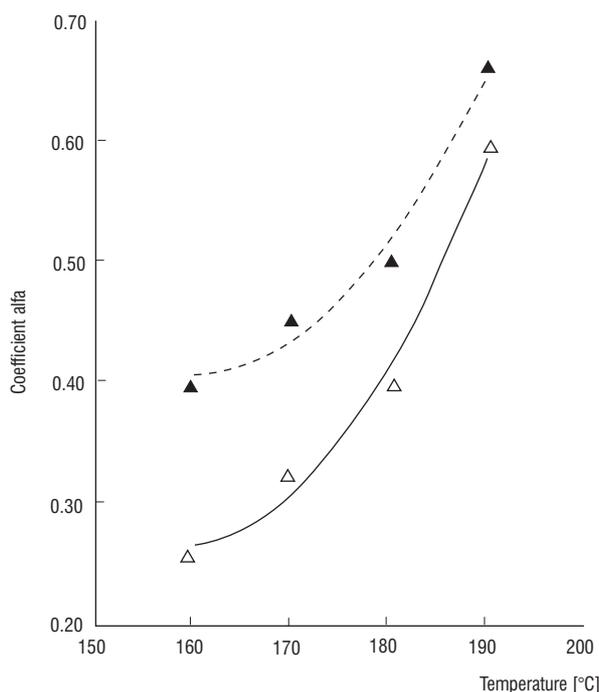


FIGURE 2. Dependence of coefficient α on hydrogenation temperature of soybean oil. Medium-grained catalyst-No. 1 (—), fine-grained catalyst-No. 2 (---).

TABLE 2. The poisoning coefficient (α) for different temperatures of hydrogenation.

Catalyst	α			
	Temperature of reaction [° C]			
	160	170	180	190
No. 1	0.26	0.32	0.40	0.59
No. 2	0.40	0.45	0.50	0.66

with a temperature decrease, the resistance of the fine-grained catalyst decreased, however, to a lesser extent than that for the medium-grained catalyst (cat. No. 1). This effect can be attributed to the larger active area of the catalyst. Hence, the catalyst possibly accumulated larger quantities of inhibitors without any negative effect. Further, by reducing the hydrogenation temperature, the curves diverged (Figure 2). The differences in the coefficient α for both catalysts are lower at higher temperature (190°C) than at lower temperature (160°C).

These are macroscopic observations and do not explain the processes taking place on the surface of the catalyst. The interaction of phospholipids with the catalyst is multi-directional. It is assumed that in the case of compounds containing free electron pairs (this includes phosphorus compounds), their interaction with nickel depends on giving away the electron to the vacant nickel atom *d* orbital and bond formation. Additionally, the interaction of phospholipids with the catalyst can be explained by the spherical effect of the phospholipid molecule, which because of its special configuration, can shield some active sites on the catalyst surface thereby making it difficult for the triacylglycerol molecules to reach them. The limited effect of phospholipids was observed at a high hydrogenation temperature. This is also probably connected with partial thermal degradation of these compounds at high hydro-genation temperatures, resulting in the formation of less poisonous products. The effect of all these interactions depends on the reaction temperature as well as on the characteristics of the catalyst.

The observed different effects of reaction temperature on the poisoning of catalysts No. 1 and 2 by phospholipids should be attributed to the energy activation value (E_a). By presenting $\log k$ vs. $1/T$ in Figure 3, four straight lines are obtained from whose slopes indicate the values of the activation energy (E_a). The obtained values are given in Table 3.

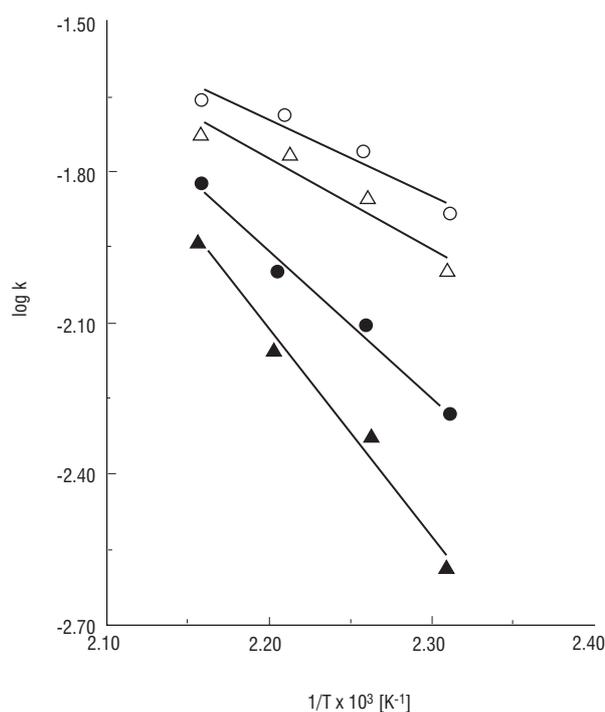


Figure 3. Arrhenius equation for catalyst No.1 without (Δ) and with 10 ppm P (\blacktriangle) and for catalyst No. 2 without (\circ) and with 10 ppm P (\bullet).

TABLE 3. Activation energies of tested catalysts.

Catalyst	Addition of phospholipids [mg·P/kg of fats]	Equation	r ^{1/}	E _a [kJ/mol]	ΔE _a [kJ/mol] ^{2/}	ΔE _a [%] ^{3/}
No. 1	0	y = -1817.7x + 2.2289	0.983	35.21	44.05	125.0
	10	y = -4139.6x + 6.9972	0.999	79.26		
No. 2	0	y = -1496.7x + 1.5959	0.976	28.66	26.02	94.3
	10	y = -2908.3x + 4.4427	0.998	55.68		

^{1/} curvefit coefficient; ^{2/} the absolute difference in activation energy; ΔE_a = E_a with inhibitor - E_a without inhibitor [kJ/mol]; ^{3/} the relative difference in activation energy; ΔE_a = (E_a with inhibitor / E_a without inhibitor - 1) x 100 [%].

The activation energies obtained with both catalysts (without PL) were of the same order of those found in the literature for conventional nickel catalysts. Chu and Lin [1991] found the values to range from 13.4 to 41.7 kJ/mol when refined soybean oil was hydrogenated with 7 different nickel catalysts. Further, Rodrigo and Mendioroz [1992] found the values to be 43.5 and 46.5 kJ/mol when refined commercial sunflower oil was hydrogenated with 2 nickel catalysts. The addition of phospholipids to oil and their multidirectional interaction with the catalyst causes the reduction of some of the catalyst active sites on which intermediate compounds form. In this case, the activation energy increases and this was observed in the presented studies. Table 3 shows that the absolute and relative increases in activation energy were higher for the medium-grained catalyst. Its absolute activation energy difference between the reaction in the presence and absence of PL is 44.05 kJ/mol, and this is almost 2 times higher than that for the fine-grained catalyst (cat. No.2, ΔE_a = 26.02 kJ/mol). The relative increase in activation energy is 125 and 94.3%, respectively. This means that at the same concentration of inhibitors in the reaction medium, the initiation of the reaction with medium-grained catalyst demands more energy than in the case of the fine-grained catalyst. Therefore, under industrial conditions, in the cases where the industry has only catalysts with approximate characteristics as those of catalyst No. 1, hydrogenation of oil-containing phospholipids should be carried out at the highest temperature possible.

CONCLUSIONS

This study is an extension of the a previous study into the activity and resistance of different catalysts to poisoning. An exact knowledge of the properties of several commercial nickel catalysts would make it possible for the industry to choose the correct type of catalyst for oil hydrogenation. In other cases, it is necessary to conduct pilot hydrogenation processes under laboratory scale conditions.

An exact explanation of the results observed demands very specific investigations about the phenomena occurring on the catalyst surface. Sorption processes, in addition to the degradation of phospholipid molecules and formation of transformation products require further study.

REFERENCES

1. Chu Y.-H., Lin L.-H., An evaluation of commercial nickel catalysts during hydrogenation of soybean oil. *J. Am. Oil Chem. Soc.*, 1991, 68, 680–683.
2. Colen G., Van Duijn G., Van Oosten H., Effect of pore diffusion on the triacylglycerol distribution of partially hydrogenated trioleoylglycerol. *Appl. Catalysis*, 1988, 43, 339–350.
3. Coonen J., Catalytic hydrogenation of fatty oils., *Ind. Eng. Chem. Fundam.*, 1986, 25, 43–52.
4. De Hault E., Demoulin A., Partial hydrogenation of polyunsaturated fatty materials. *J. Am. Oil Chem. Soc.*, 1984, 61, 195–200.
5. Drozdowski B., Niewiadomski H., Polish Patent No. 88608, 1972.
6. Drozdowski B., Szukalska E., Effect of rapeseed oil hydrogenation conditions on *trans* isomers formation. *Eur. J. Lipid Sci. Technol.*, 2000, 102, 642–645.
7. Drozdowski B., Zajac M., Kinetics of nickel poisoning. *J. Am. Oil Chem. Soc.*, 1980, 57, 149–153.
8. Klimmek H., Influence of various catalyst poisons and other impurities on fatty acid hydrogenation. *J. Am. Oil Chem. Soc.*, 1984, 61, 200–205 .
9. Koetsier W., Hydrogenation of edible oils, 1997, *In: Lipid Technology and Applications* (eds. F.D Gunstone, F.D. Padley), Marcel Dekker Inc., New York, Basel, Hong Kong, pp. 265–303.
10. Patterson H., 1983, *Hydrogenation of fats and oils*, 1983. Applied Science Publishers, London, New York.
11. Rodrigo M., Mendioroz S., A new catalyst for the selective hydrogenation of sunflower seed oil. *J. Am. Oil Chem. Soc.*, 1992, 69, 802–805.
12. Szukalska E., Pawłowicz R., Hazuka Z., Tynek M., Polański A., The effect of nickel catalyst granulation on its activity in the process of the rapeseed oil hydrogenation and on the filtration rate. *Przem. Chem.*, 1997, 76, 133–134 (in Polish).
13. Szukalska E., Effect of phospholipid structure on kinetics and chemistry of soybean oil hydrogenation with nickel catalysts. *Eur. J. Lipid Sci. Technol.*, 2000 a, 102, 739–745.
14. Szukalska E., Effect of presence of phospholipids in oil on kinetics and chemism of hydrogenation reaction. *Przem. Chem.*, 2000 b, 79, 341–343 (in Polish).
15. Veldsink J., Bouma M., Schoon N., Beenackers A., Heterogeneous hydrogenation of vegetable oils: A literature review. *Catal. Rev.-Sci. Eng.*, 1997, 39, 253–318.

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WPLYW TEMPERATURY REAKCJI UWODORNIENIA OLEJU SOJOWEGO NA ZATRUCIE KATALIZATORA NIKLOWEGO PRZEZ FOSFOLIPIDY

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Badano wpływ temperatury reakcji uwodornienia oleju sojowego na stopień zatrucia katalizatora przez fosfolipidy. Stosowano 2 szerokoporowate katalizatory nikłowe, średnio- (nr. 1) i drobnoziarnisty (nr. 2). Uwodornienie prowadzono w reaktorze laboratoryjnym typu „dead end”, w zakresie temperatur 160–190°C. Wyznaczono współczynniki zatrucia, wyrażone stosunkiem stałych szybkości uwodornienia w procesie prowadzonym w obecności inhibitora w oleju i bez inhibitora ($\alpha = k_{z \text{ inhib}}/k_{\text{bez inhib}}$) oraz zmiany w energii aktywacji (E_a) wywołane obecnością fosfolipidów w oleju.

Stwierdzono znaczący wpływ temperatury na zatrucie katalizatora fosfolipidami – im niższa była temperatura procesu, tym inhibitujący wpływ fosfolipidów był większy. Katalizator drobnoziarnisty był bardziej aktywny (tab. 1) i bardziej odporny na zatrucia. Ponadto ze spadkiem temperatury jego odporność malała wolniej niż katalizatora średnioziarnistego (tab. 2, rys. 2).

Badane katalizatory charakteryzowały się E_a podobną do typowych kontaktów handlowych: 35,21 kJ/mol dla katalizatora nr. 1 i 28,66 kJ/mol dla nr. 2 (tab. 3). Dodatek fosfolipidów powodował spadek szybkości reakcji i wzrost energii aktywacji (rys. 1, tab. 3). Bezwzględna różnica E_a dla katalizatora średnioziarnistego wynosiła 44,05 kJ/mol i była prawie dwukrotnie wyższa niż dla drobnoziarnistego (tab. 3).