

## PROGRESS OF THE SOYBEAN OIL HYDROGENATION WITH PARTLY POISONED NICKEL CATALYST

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The changes of the reaction rate as the result of partial poisoning of the nickel catalyst by phosphorus and sulphur compounds have been studied. Besides, the effect of these inhibitors on the mechanism of hydrogenation has been examined.

### INTRODUCTION

Natural components of oils having sulphur and phosphorus in their chemical composition have serious poisoning effect on nickel catalyst. The understanding of the influence of these compounds on the rate and the course of hydrogenation, and directly on the nickel catalyst would not only allow for a rational control of the hydrogenation process but also of the refinement process. Phospholipids belong to the natural components of vegetable oils, and their content in oils varies. For example in soybean oil ranges from 0.06% P in raw oil to about 0.002% P in the oil subjected to full refinement [4]. The bibliography does not supply any detailed data concerning the effect of phospholipids on the kinetics of oil hydrogenation. Tiutiunnikow [9] mentions that the content of phospholipids in oils at the level of 0.0262% P inhibits to a large extent the progress of the reaction. More precise information connected with the matter can be found in the paper by Babuchowski and Rutkowski [1].

They have stated that the content of phospholipids at the level of 0.0062% P causes complete deactivation of examined Ni-catalyst, used in concentration of 0.08%.

Sulphur compounds belong to the natural components of cruciferae oils. These components can be found in the form of thioglucoside com-

plexes which can undergo decomposition, especially during enzymatic hydrolysis. The products of hydrolysis vary depending on the conditions of action of the parent enzymes [10 - 12]. For example, the content of sulphur in rapeseed oil subjected to complete refinement (including deodorization) reaches the level of 0.001% [2]. In our previous works [7, 8] dealing with the effect of various sulphur compounds on the rate of nickel contact poisoning we have observed an unusually strong toxic action of allyl isothiocyanate (ITC). Our present work is concerned with the studies on the effect of partial poisoning of nickel catalyst by phospholipids and allyl isothiocyanate on the rate and mechanism of the soybean oil hydrogenation.

## EXPERIMENTAL PART

### MATERIALS AND METHODS

**Soybean oil.** The studies have been made on soybean oil subjected to complete industrial refinement including the process of deodorization. General characteristics of soybean oil is shown in Table 1. The phosphorus content was determined by Becker-Krull's method [3].

Table 1

General characteristics of soybean oil

Determination	Values
Acid value	0.3
Peroxide value (Lea V.)	0.6
Refractive index $n_D^{60}$	1.4596
Phosphorus content (%)	0.0014

**Nickel catalyst.** The studies have been performed using two types of catalyst with the general characteristics shown in Table 2.

Table 2

General characteristics of examined nickel catalysts

Symbol	Nickel catalyst		Nickel content per cent
	type	produced by	
533	unsupported wet reduced, formate	Fat Factory in Gdańsk	10.3
RCH 55/5 FS	supported dry — reduced	Hoechst	21.0

**Phospholipids.** Phospholipids were prepared from soybean oil which was obtained on a laboratory scale by extraction of soybean

seeds with petroleum ether. The oil was then hydrated. Phospholipids were isolated from crude lecithin with the help of column chromatography. The neutral lipids were elued with chloroform, glycolipids with acetone and phospholipids with methanol [13]. After methanol evaporation phospholipids were dried over  $P_2O_5$  and transfered to the hardened soybean oil. So prepared sample was in a form of powder which has been introduced in the desired quantity to the oil subjected to hydrogenation. This sample contained 1.506% P.

**Allyl-isothiocyanate.** The sample produced by "Fluka AG, Chemische Fabrik Buchs SG." has been used in our studies. A standard oil solution was prepared from this sample which has been introduced in the desired quantity to the soybean oil subjected to hydrogenation.

**Conditions of hydrogenation.** The hydrogenation has been carried out in a reactor of "dead-end" type with automatic recording of hydrogen absorption [6], in the following conditions:

oil sample	— 50 g
temperature	— $160^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$
stirring	— 2700 r.p.m.
nickel concentration	— 0.1%

The soybean oil hydrogenation with partly poisoned nickel catalyst. Soybean oil after introducing phospholipids in the range of 0.025 to 0.25 per cent what corresponds 0.00113 to 0.01130 per cent of phosphorus has been subjected to hydrogenation. The changes of the catalyst activity with phosphorus concentration in the reaction system are shown in Fig. 1.

Allyl isothiocyanate was introduced to the reaction system in the quantities ranging from 0.00056 to 0.00336 per cent of sulphur in oil. The changes of the catalyst activity with sulphur concentration in the reaction system are shown in Fig. 2.

It would be interesting to confirm whether the addition of inhibitors causes only a change of the reaction rate or if it has an effect on its progress from the point of view of selectivity and geometrical isomerization.

The selectivity has been determined on the basis of fatty acid composition changes, during the hydrogenation. The samples have been collected during the course of the reaction. The oil chosen for the studies of selectivity changes caused by the partial poisoning of the catalysts, contained 0.00226 per cent of the inhibitors with regard to phosphorus and sulphur. This content of poisons in the system corresponds to an approximately 50 per cent activity loss of the catalysts. The fatty

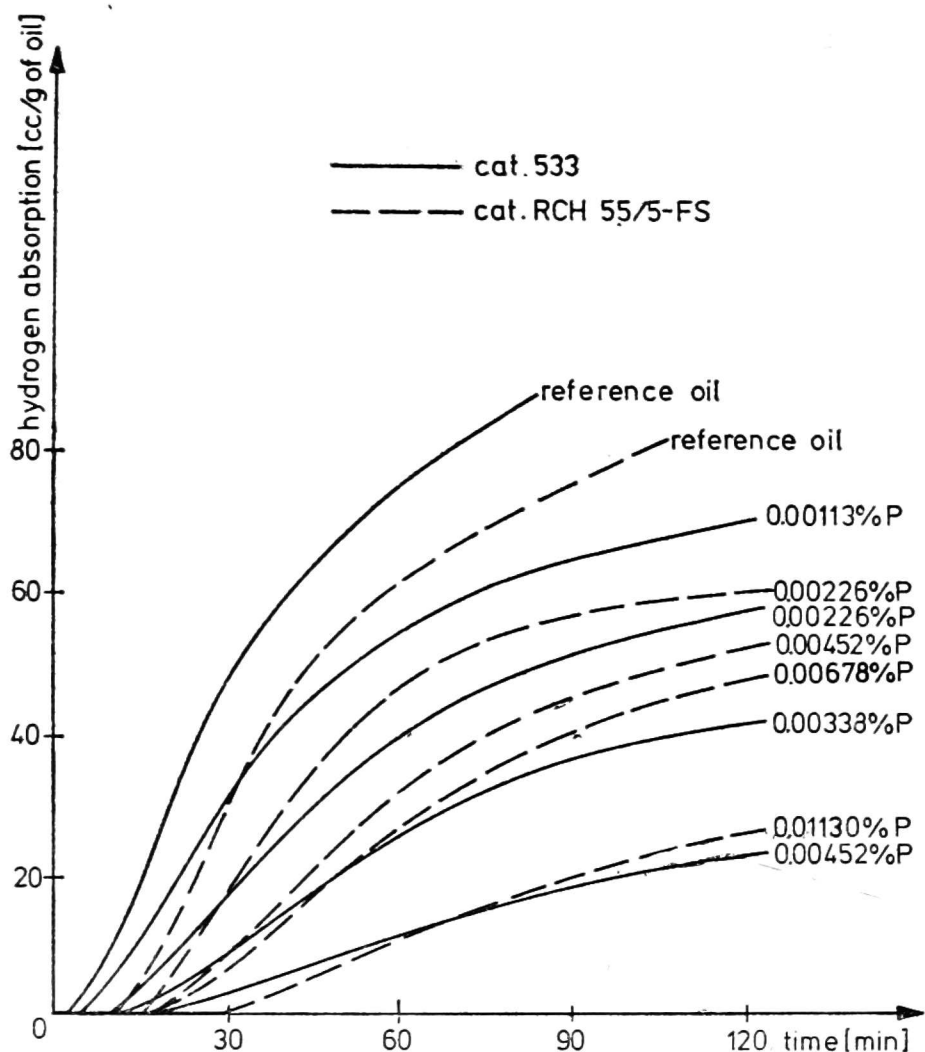


Fig. 1. Soybean oil hydrogenation kinetic curves in relation to the concentration of phosphorus. Catalyst concentration 0.1%

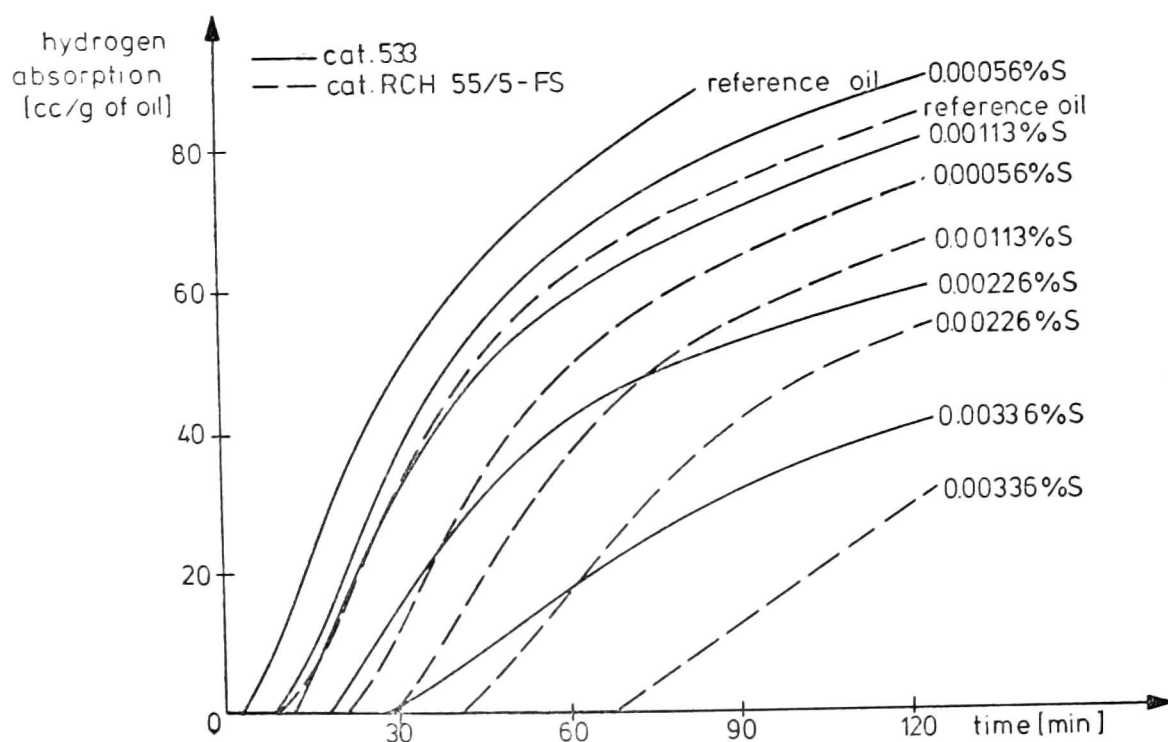


Fig. 2. Soybean oil hydrogenation curves in relation to the concentration of sulphur. Catalyst concentration 0.1%

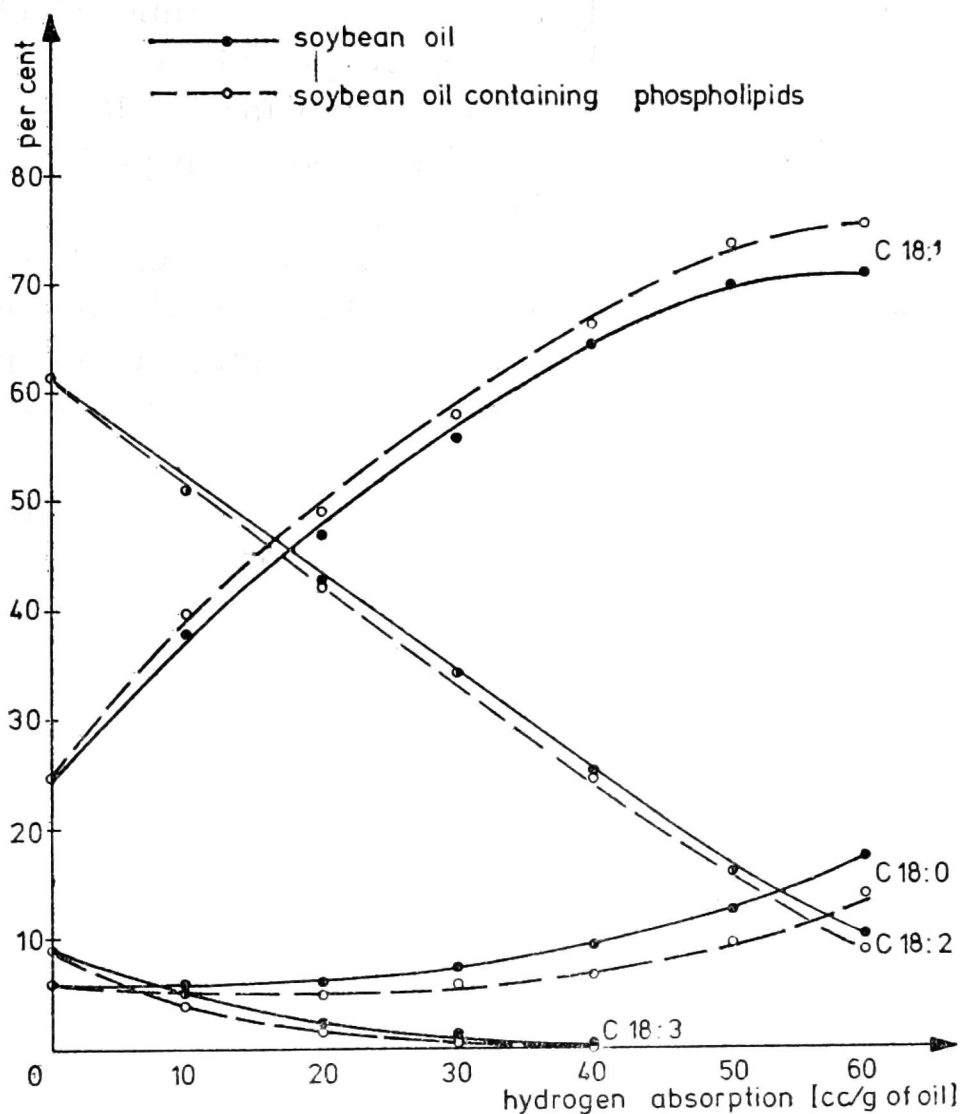


Fig. 3. Fatty acid composition changes during the hydrogenation of soybean oil and soybean oil containing phospholipids at concentration of phosphorus equal to 0.00226%. 533 catalyst concentration: 0.1%

acid composition has been determined by gas chromatography on the apparatus produced by "Jeol" equipped with a flame-ionization detector. The performed studies on the change of fatty acid composition have shown that the addition of phospholipids as well as the addition of allyl isothiocyanate improve the selectivity only to an insignificant degree for both catalysts. The changes of fatty acid content with the degree of soybean oil hydrogenation, for reference oil and with the addition of phospholipids in the presence of the 533 catalyst are given, by way of an example, in Fig. 3. The content of "trans" isomers the collected samples have also been determined by IR spectroscopy [5].

#### RESULT AND DISCUSSION

The analysis of kinetic curves (Fig. 1), allows for a statement that the hydrogen absorption does not occur immediately after the intro-

duction of the catalyst but only after a period of time which has been called an induction period. The induction period for the 533 catalyst in the case of the reference oil is shorter than for the RCH. In the presence of phospholipids the increase of the induction period for the 533 catalyst, is greater than for the RCH catalyst.

The slope of kinetic curves characterizes the catalyst activity. The curves for the RCH have a steeper slope than for the 533 catalyst (at the same level of phospholipid content in the oil), mainly in the first stage of hydrogenation that is till the distinct direction change of the curves.

The analysis of kinetic curves in the Fig. 2. maket it evident that the catalysts in the presence of sulphur compound in the reaction system have a much longer induction period than in the presence of phospholipids. When the induction period is over, the catalyst have relatively high activity. The curves have almost parallel displacement in comparison with the curves for the reference oil up to 0.00226 per cent of sulphur. This fact indicates that the activity of the contacts is maintained at a steady level, excluding the induction periods.

It can be inferred from the slope of the kinetic curves that in the first stage of the reaction, the degree of poisoning for both catalysts is almost equal. On the other hand, it is observed for the second stage that sulphur compounds have stronger toxic effect on the 533 catalyst as the curves for RCH are steeper than for the 533. In order to compare the effect of additions of phospholipids and allyl isothiocyanate on the change of kinetics of soybean oil hydrogenation in Fig. 4., we assembled the selected kinetic curves.

Comparing the effect of phospholipids and allyl isothiocyanate (at the same concentrations of both inhibitors) on the studied contacts, it can be concluded that the presence of sulphur in the oil causes considerably greater increase of the induction periods than in the case of the presence of phospholipids. Excluding the induction periods, it can be stated that in the first stage of hydrogenation phospholipids are less toxic for the RCH catalyst than a sulphur compound. On the other hand in the second stage of the process the situation is reversed; the sulphur compound has a weaker inhibitory effect than phospholipids. The 533 catalyst in the stage of hydrogenation of poliunsaturated fatty acids undergoes stronger dezactivation by the phosphorus compounds. In the second stage of hydrogenation the behaviour of this contact in the presence of each inhibitors is similar.

On the basis of the obtained results we can conclude that in the conditions for the conducted hydrogenation, phospholipids and allyl isothiocyanate have a distinct effect on the change of the reaction rate. On the

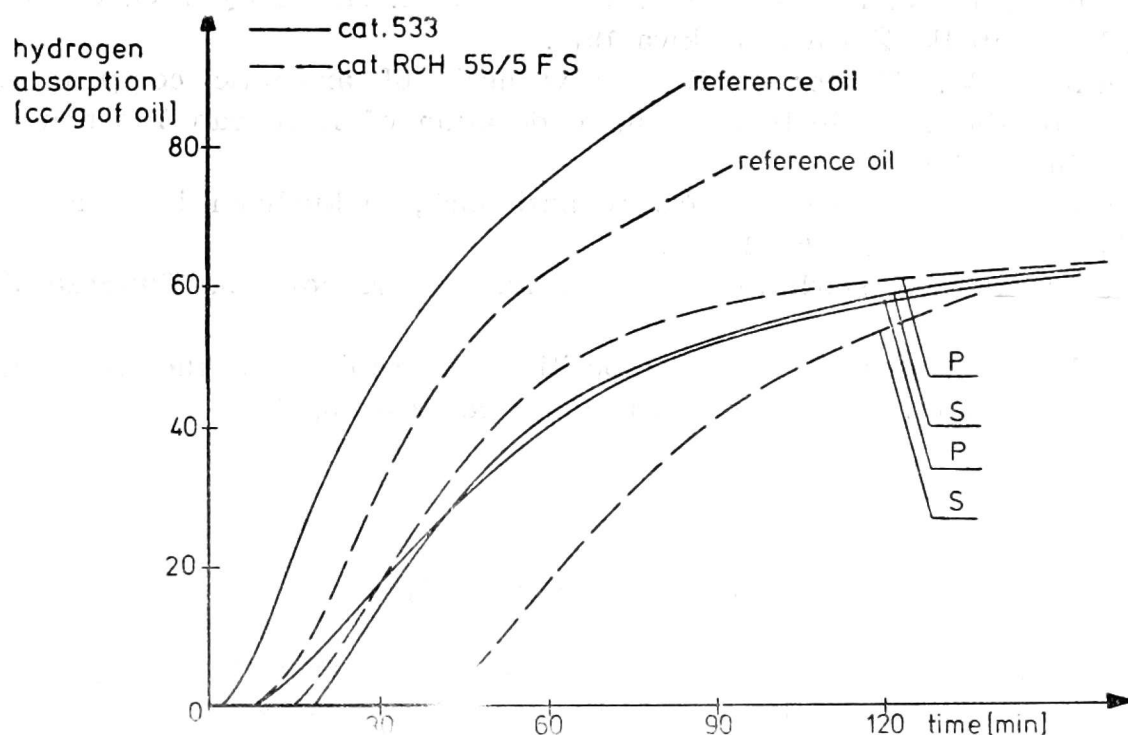


Fig. 4. Hydrogenation of soybean oil containing 0.0026% of phosphorus and sulphur introduced as phospholipids and allyl isothiocyanate

other hand we have proved that their presence in the reaction system does not considerably effect the selectivity of the process and the isomerization.

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## PRZEBIEG UWODORNIENIA OLEJU SOJOWEGO W OBECNOŚCI CZĘŚCIOWO ZATRUTEGO KATALIZATORA NIKLOWEGO

### Streszczenie

Katalizator niklowy na nośniku i beznośnikowy zatrutowano częściowo związkami siarki i fosforu. Stwierdzono, że pierwszy z nich jest bardziej odporny na ich toksyczne działanie. Przy tej samej zawartości w układzie reakcyjnym badanych związków, w przeliczeniu na siarkę i fosfor, substancje siarkowe powodują wystąpienie dłuższych okresów indukcji.

Zmiany kinetyki uwodornienia oleju sojowego w wyniku częściowego zatrucia obu katalizatorów zilustrowano odpowiednimi krzywymi kinetycznymi. Nie zaobserwowano istotnych różnic w odniesieniu do mechanizmu reakcji uwodornienia.

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## ХОД ГИДРИРОВАНИЯ СОЕВОГО МАСЛА В ПРИСУТСТВИИ ЧАСТИЧНО ОТРАВЛЕННОГО НИКЕЛЕВОГО КАТАЛИЗАТОРА

### Резюме

Никелевый катализатор на носителе и без носителя частично отравляли соединениями серы и фосфора. Установлено, что первый из них более устойчивый к их токсическому действию. При одинаковом содержании в реакционной системе исследуемых соединений в пернсчете на серу и фосфор, серные вещества вызывают появление длительных периодов индукции.

Изменения кинетики гидрирования соевого масла в результате частичного отравления обоими катализаторами иллюстрируются соответствующими кинетическими кривыми. Не наблюдались существенные различия по отношению к механизму реакции гидрирования.