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THE EFFECT OF SOME ADSORBENTS ON THE PROGRESS OF HYDROGENATION OF OILS

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The changes of the kinetics and the mechanism of the rapeseed and soybean oil hydrogenation in the presence of adsorbents have been determined. It has been proved, that bleaching earth distinctly accelerates the progress of hydrogenation and does not change the mechanism of the reaction.

INTRODUCTION

The problem of the effect of adsorbent presence on the change of hydrogenation progress has arisen during the studies on kinetic changes of hydrogenation of oils, due to the partial poisoning of a nickel catalyst. The bibliography does not supply detailed information on this subject except the publications on the interaction of a catalyst and a solid support [1—5].

The presented results are the introduction to the detailed studies on the mechanism of mutual interaction between a catalyst and bleaching earth present in the reaction system during hydrogenation of oils. The results illustrate the changes of reaction kinetics caused by the addition of different quantities of this adsorbent, without attempting to explain the physicochemical character of the interaction on the system. These problems are going to be the subject of our further studies.

EXPERIMENTAL PART

The determination of reaction rate changes of oil hydrogenation as the results of variable amounts of bleaching earth introduced to a reactor has been the subject of the first stage of our studies. Czechish

bleaching earth, used by our fats industry for decolourization of oils, has been employd through our studies.

The hydrogenation was carried out in a "dead-end" type laboratory reactor with the automatic recording of hydrogen absorption [6]. The quantity of added adsorbent was the variable of the process. Hydrogenation was performed as follows: in a reactor 50 g of oil was weighed, strictly defined amount of bleaching earth (0.3% to 3.0% with respect to oil) was added, and the whole was heated to 160°C with intense stirring in the system with the internal circulation of hydrogen. When the saturation of oil with hydrogen as well as the preselected conditions of the reaction were reached, 0.1 per cent (with regard to the metal) of the nickel catalyst were introduced to the oil. The reaction was continued till the defined level of hydrogen absorption was reached. Three different catalysts with the general characteristics shown in Table have been used in our studies.

Table

General characteristics of the used nickel contacts

Symbol	"Formate" type		NYSEL
	533	P 34	
% Ni	10.3	9.8	25.7
produced by	Zakłady Przemysłu Tłuszczowego w Gdańsku		Harshaw

The relations obtained for hydrogen absorption as a function of the reaction time for each catalyst and oil are called kinetic curves of hydrogenation. They are shown in Fig. 1—7. Bleached rapeseed oils as well as soybean oils have been taken from different batches of materials.

RESULTS AND DISCUSSION

The analysis of the changes of hydrogenation rate allows for a statement that the character of the interaction of bleaching earth is extremely complex and depends, among other things, on the type of the used catalyst and oil. It is also a function of the presence of hydrogenation inhibitors. In every case there is optimum quantity of adsorbent which added to the reaction system causes the maximum increase of hydrogen absorption rate.

During hydrogenation in the presence of "formate" type catalysts, the optimum quantity of bleaching earth for bleached rapeseed oil was

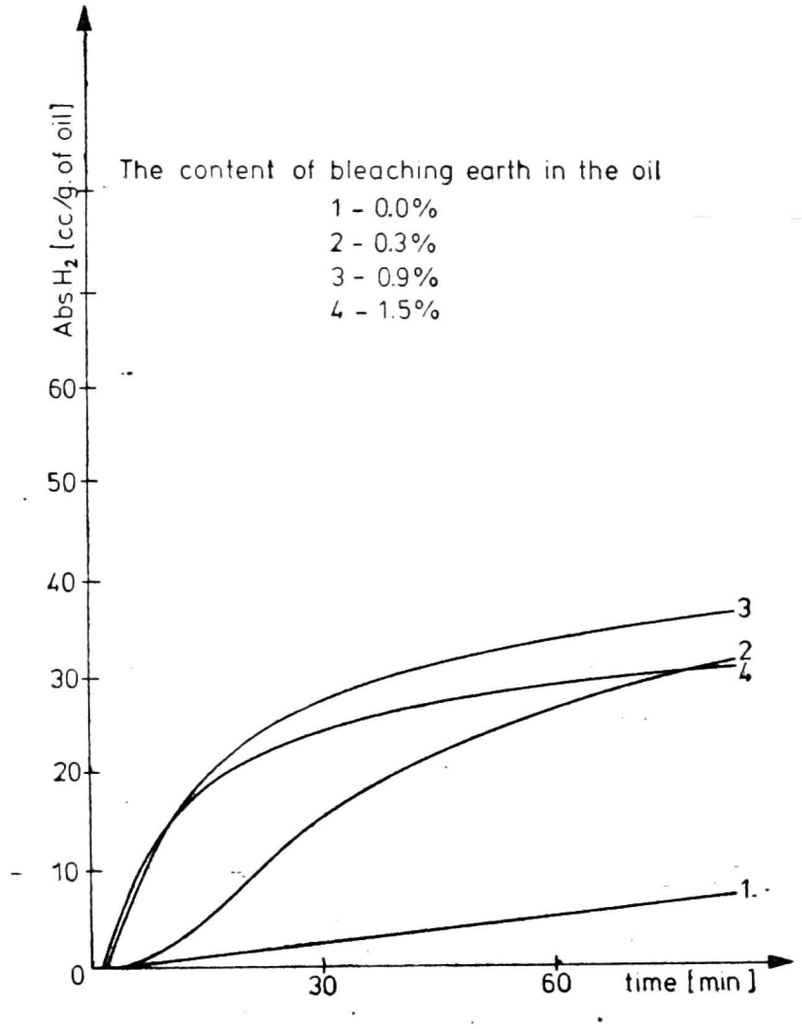


Fig. 1. Hydrogenation of bleached rapeseed oil in the presence of P-34 catalyst and bleaching earth

at the level of 0.9—1.5% (Fig. 1 and 2), while for bleached soybean oil it was 0.3—0.9% (Fig. 3 and 4).

The kinetics of rapeseed oil hydrogenation on the NYSEL catalyst was very similar (Fig. 5). The maximum increase of the reaction rate occurred at the level of 1.5% of bleaching earth in a reactor. No promoting effect of the adsorbent has been observed in the case of the hydrogenation of bleached soybean oil (Fig. 6). Its presence has caused the decrease of the reaction progress proportionally to the quantity of bleaching earth introduced to the oil.

From the analysis of kinetic curves it may be assumed that the efficiency of bleaching earth action depends to a considerable degree on the presence of the reaction inhibitors in oil. Therefore, deodorized soybean oil with the addition of 25×10^{-4} per cent of sulphur in the form of allyl-ITC [7] has been hydrogenated in the next stage of our studies. These investigations have been done in view of the compari-

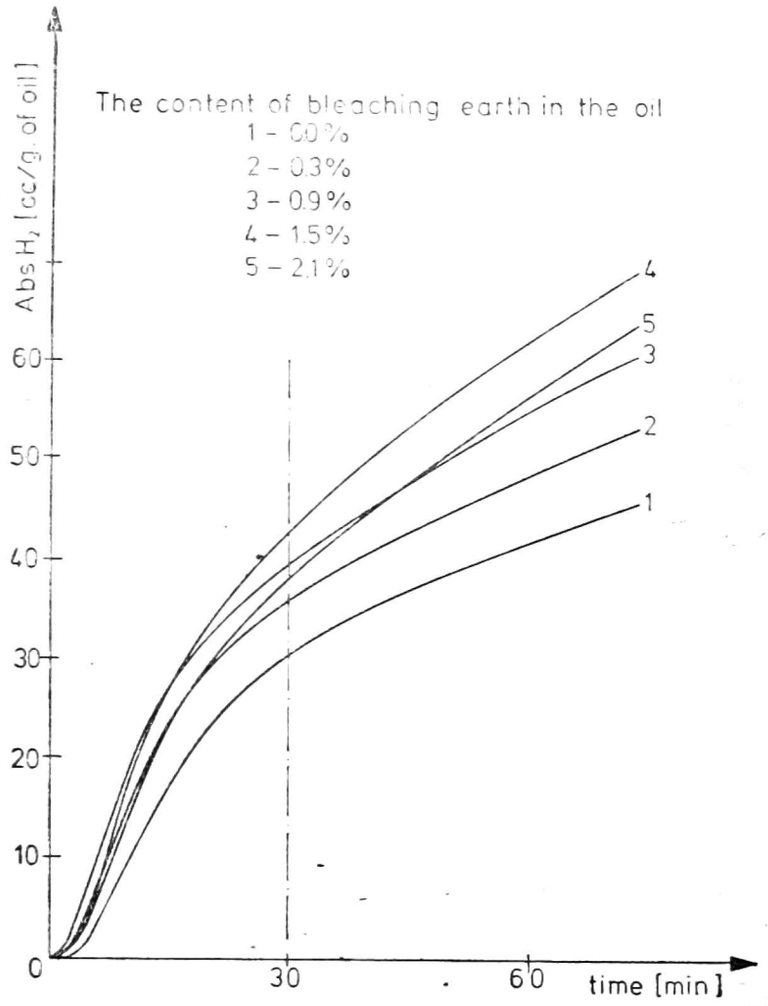


Fig. 2. Hydrogenation of bleached rapeseed oil in the presence of 533 catalyst and bleaching earth

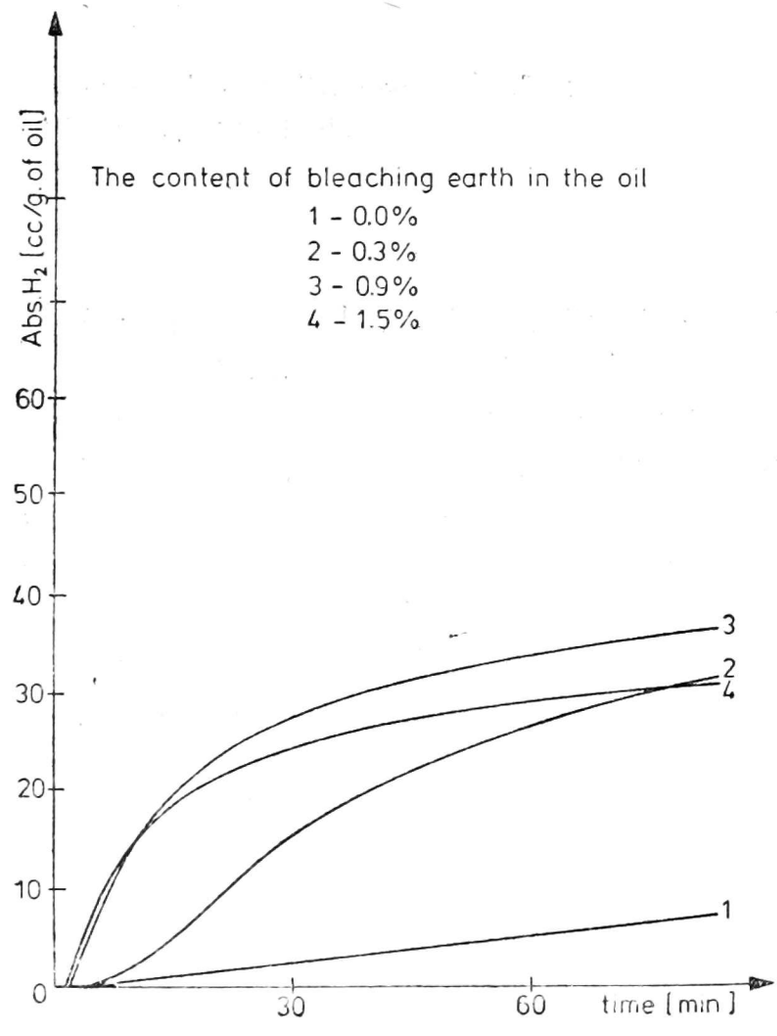
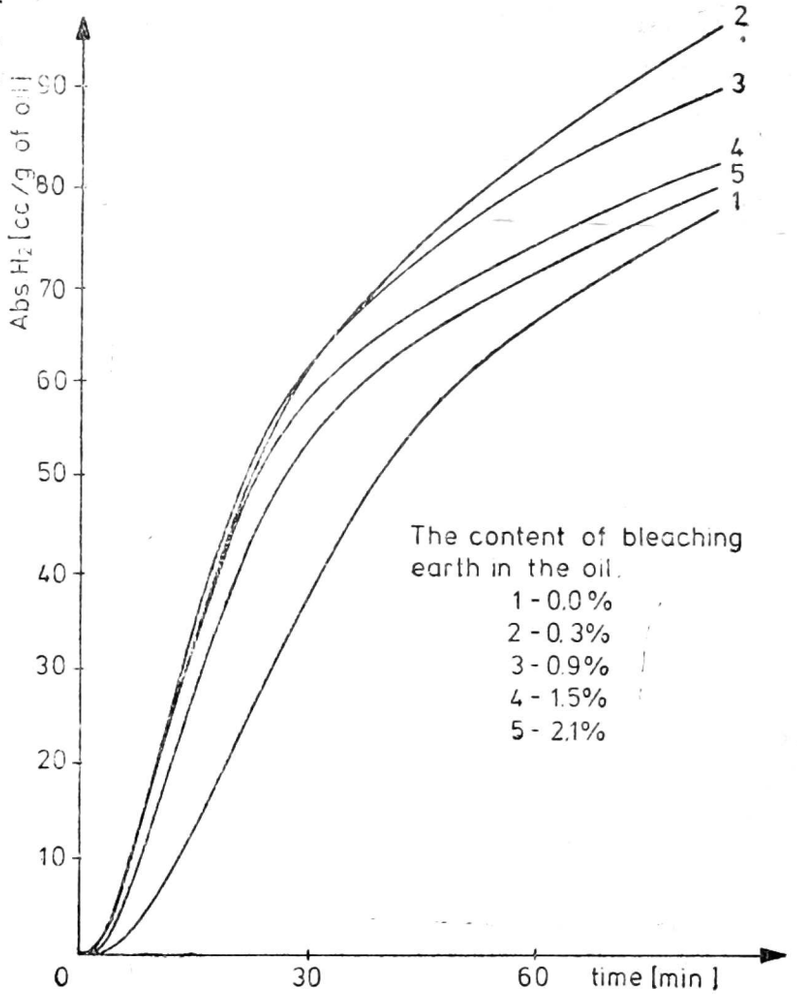


Fig. 3. Hydrogenation of bleached soybean oil in the presence of P-34 catalyst and bleaching earth

Fig. 4. Hydrogenation of bleached soybean oil in the presence of 533 catalyst and bleaching earth



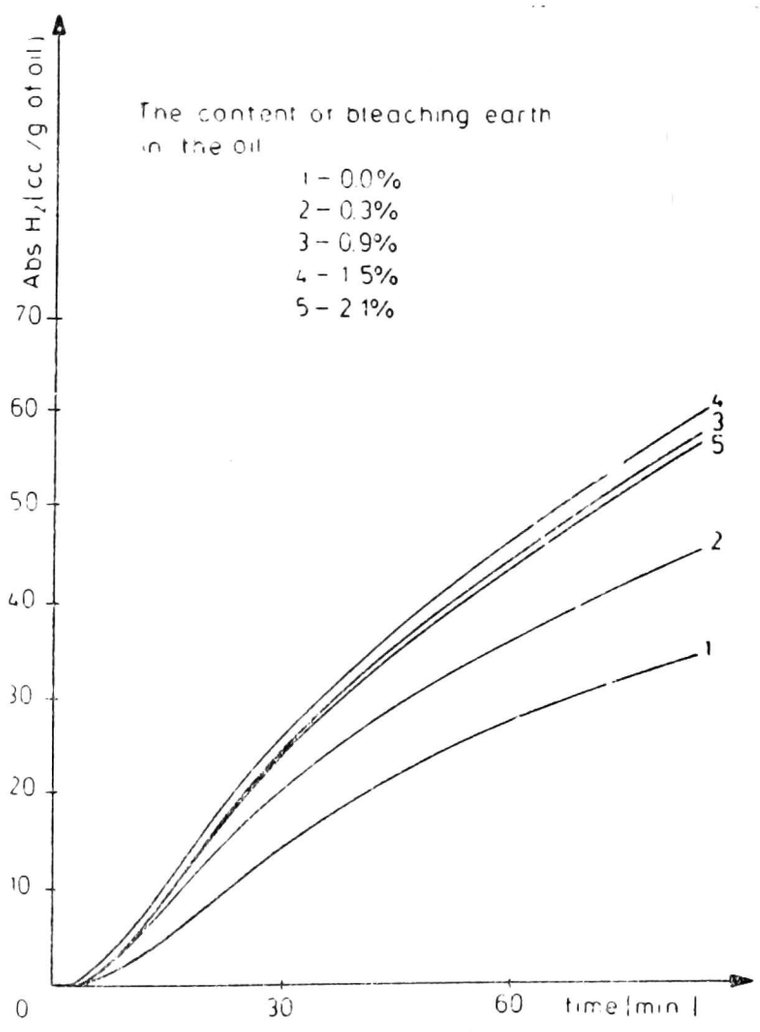


Fig. 5. Hydrogenation of bleached rapeseed oil in the presence of NYSEL catalyst and bleaching earth

son of the effect of the hydrogenation of this oil in the presence of variable amount of bleaching earth, with the oil having the same fatty acid composition but without majority of inhibitors. The kinetic curves of such hydrogenation on formate type catalyst are shown on Fig. 7. It has been noted that in order to the reach the maximum rate of the hydrogenation of oil containing sulphur, the addition of 0.9 per cent of the bleaching earth is needed, while for the oil free of sulphur, the optimum addition was equal 0.3 per cent. Higher quantities of the bleaching earth caused the reduction of the reaction rate.

However, the effect of bleaching earth action on the reaction rate, is not only based on the adsorption of poisons present in oils. The performed experiments of preliminary treatment of oil containing sulphur with the adsorbent, have shown only insignificant increase of the hydrogenation rate. The reaction kinetics of such hydrogenation is presented on curve A, in the Fig. 7. Much higher reaction rate is observed when the same amount of bleaching earth is present in the oil during hydrogenation.

Therefore, there exist specific interaction of the bleaching earth and a catalyst. Probably one of them is the competitive adsorption of poisons present in oil. The decrease of hydrogenation rate after exceeding the optimum values of the adsorbent may signify, that the presence of the excessive amount of the bleaching earth results in the mechanical blocking of the active centers of a catalyst.

The overall effect of bleaching earth action in the process of hydrogenation may be taken as the resultant of the mutual interaction of a number of factors even with opposite effects. These relations, very important from the economical and technological as well as theoretical point of view going to be the subject of our further studies.

The practical considerations demonded the explanation whether the presence of the adsorbent in the system has the influence on the selectivity of the process and the trans isomer content in hydrogenated oil with the progress of the reaction has been determined previously [8].

It has been proved, that bleaching earth does not change the mechanism of the reaction, thought it distinstly accelerates the process of hydrogenation.

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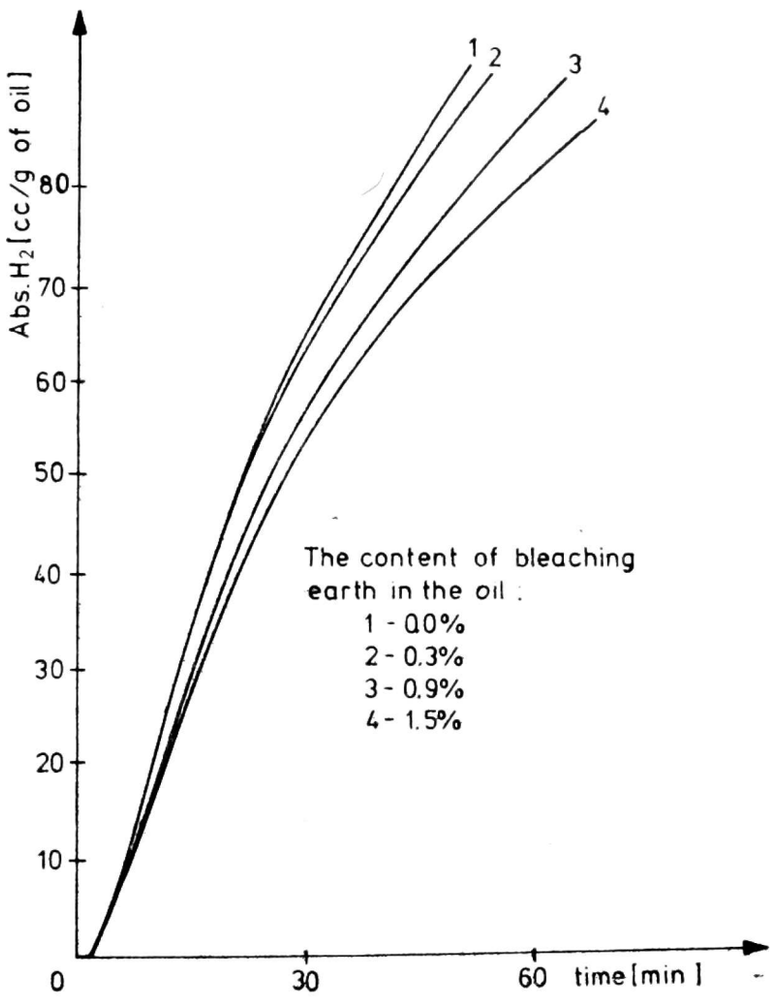

Fig. 6. Hydrogenation of bleached soybean oil in the presence of NYSEL catalyst and bleaching earth

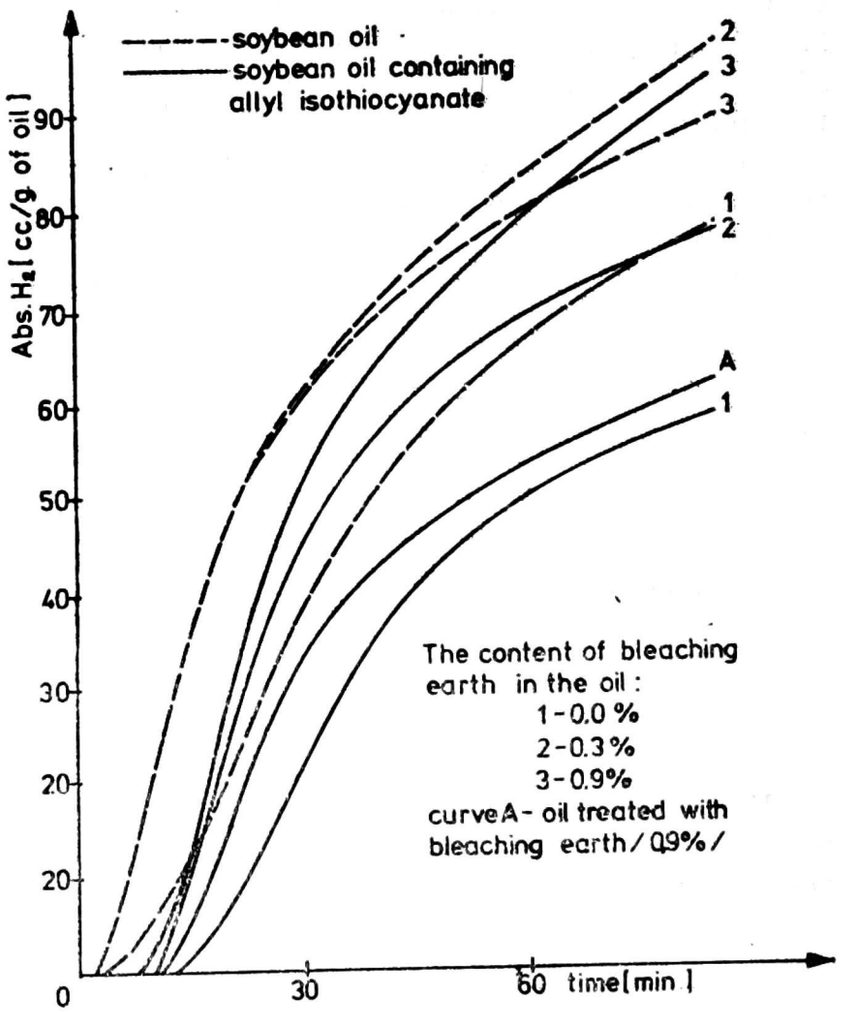

Fig. 7. Hydrogenation of soybean oil containing $25 \cdot 10^{-4}$% S, in the presence of 533 catalyst and bleaching earth

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WPŁYW NIEKTÓRYCH ADSORBENTÓW NA POSTĘP REAKCJI UWODORNIENIA OLEJÓW

Streszczenie

Badano zmianę kinetyki i mechanizmu reakcji uwodornienia oleju rzepakowego i sojowego w obecności adsorbentów (ziem bielących), wprowadzonych do układu reakcyjnego. Oznaczenia prowadzono w reaktorze laboratoryjnym typu „dead end" z automatyczną rejestracją absorpcji wodoru, stosując różne katalizatory niklowe.

Stwierdzono, że wzrost szybkości uwodornienia wywołany obecnością adsorbenta zależy od typu katalizatora i rodzaju użytego oleju. Szczególnie korzystny wpływ zaobserwowano podczas uwodornienia oleju rzepakowego. Wprowadzenie adsorbenta nie zmienia selektywności procesu ani stopnia cis-trans izomeryzacji w stosunku do uwodornienia bez jego udziału, znacznie zwiększając szybkość reakcji uwodornienia.

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ВЛИЯНИЕ НЕКОТОРЫХ АДСОРБЕНТОВ НА ХОД РЕАКЦИИ ГИДРИРОВАНИЯ МАСЕЛ

Резюме

Исследовали изменение кинетики и механизма реакции гидрирования рапсового и соевого масла в присутствии адсорбентов (отбеливающих земель) введенных в реакционную систему. Определения проводились в лабораторном

реакторе типа „дэд энд", с автоматической регистрацией абсорбции водорода, при применении разных никелевых катализаторов.

Установлено, что повышение скорости гидрирования вызванное присутствием адсорбента зависит от типа катализатора и вида используемого масла. Особенно благоприятное влияние наблюдалось во время гидрирования рапсового масла. Введение адсорбента не изменяет селективного процесса и степени цис-трансовой изомеризации по отношению к гидрированию без его участия, значительно ускоряя ход реакции гидрирования.