

## HYDROGENATION OF THE MIXTURE OF DIGLYCERIDES, TRIGLYCERIDES AND FREE FATTY ACIDS

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It is particularly advantageous to use randomized oils in basical researches concerned with the progress of hydrogenation of unsaturated fatty acids in triglycerides. The random rearrangement of acyls allows for direct observations of the course of the process in the internal and external positions on the basis of the fatty acid compositions, of the enzymatic hydrolysis products.

Simultaneously, in the course of our studies we have observed that the transesterification process was found to lead to the appearance of a certain quantity of the incomplete glycerides, mainly diglycerides. The presence of a polar group in diglycerides probably changes the mechanism of adsorption on the nickel catalyst during the process of hydrogenation. In this aspect the behaviour of free fatty acids appearing in the mixture with tri- and diglycerides has also been investigated.

### INTRODUCTION

The preliminary kinetic studies of hydrogenation of natural soybean oil and the same oil subjected to rearrangement prove the fact of slower hydrogenation of the former.

Analysing the randomized oil we have found that it always contains some amount of the incomplete glycerides, mainly diglycerides. We have assumed that their presence in the reaction system, oscillating at the level of a few per cent, might be the cause of slower hydrogenation rate of the interesterified oil due to their outstanding polar character.

Besides, the phenomenon of the selective adsorption of diglycerides and triglycerides on the catalyst might lead to varying rate of their

hydrogenation and thus to the false conclusions in the description of hydrogenation mechanism in glycerides.

The evaluation of this problem have been the main aim of the present paper. At the same time we tried to explain what is the effect of free fatty acids present in the fatty substrate.

In order to explain it the fixed amounts of free fatty acids have been added to mixture of tri- and diglycerides. Then the general kinetics of hydrogenation of the mixture and the behaviour of each of its components have been studied.

This problem is not only theoretically important but it has also practical significance. It is concerned mainly with the effect of free fatty acids present in the reaction system [2].

#### EXPERIMENTAL PART

Randomization of refined soybean oil was carried out by single-phase transesterification reaction at 130°C in the presence of 0.3% of sodium methylate, reaction time being 30 minutes. The product of the reaction was washed with water and after drying it was treated with bleaching earth. The content of the incomplete glycerides has been determined by the use of the preparative quantitative TLC. It has to be mentioned that diglycerides were the main component of the incomplete glycerides.

After separation of randomized oil by TLC method into DG and TG fractions, their fatty acid composition and then the glyceride structure have been determined.

In order to obtain free fatty acids, the component of the hydrogenated mixtures, the saponification of refined soybean oil has been carried out.

The analysis proved that the overall fatty acid composition of tri- and diglycerides and free fatty acids was the same.

The mixtures of tri- and diglycerides and FFA were hydrogenated in a reactor of "dead-end" type equipped with a mechanical stirrer. The employed system [1] allowed for the automatic recording of hydrogen absorption as a function of time and the obtained curve at once expressed the reaction kinetics. The following conditions of hydrogenation have been employed:

weight of oil sample	— 50 g
temperature	— 160°C
stirring	— 2600 r.p.m.
nickel concentration	— 0.1 per cent

An example has been given in Figure 1 of the course of hydroge-

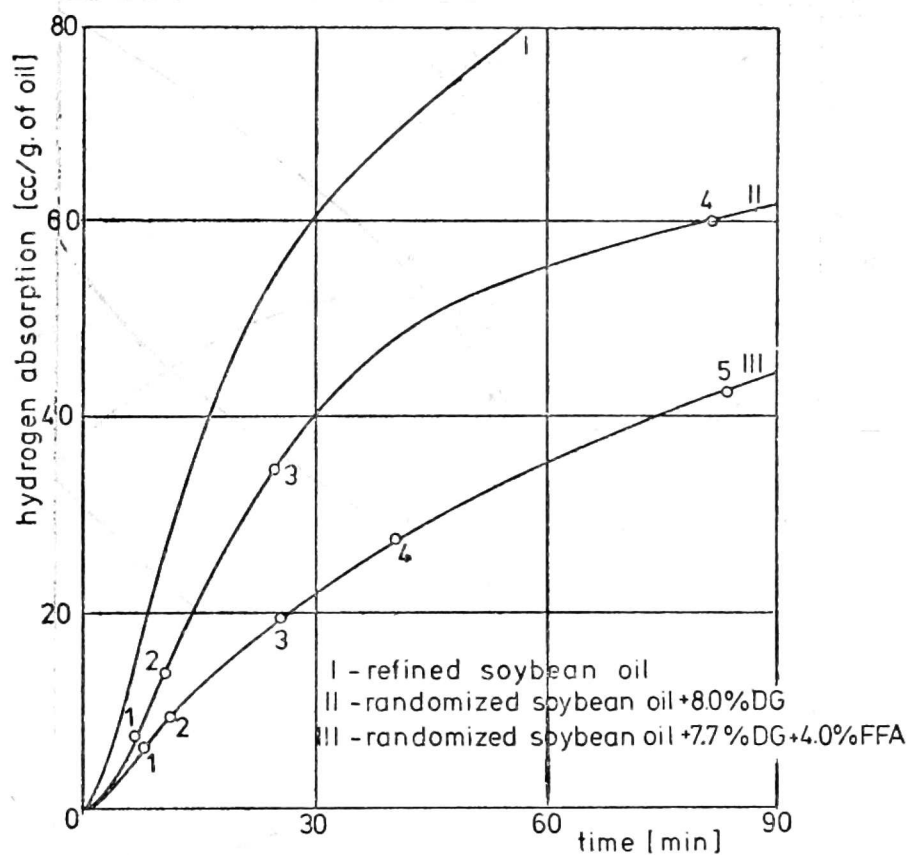


Fig. 1. Hydrogenation kinetic curves for refined soybean oil and randomized oil in a mixture with DG and FFA

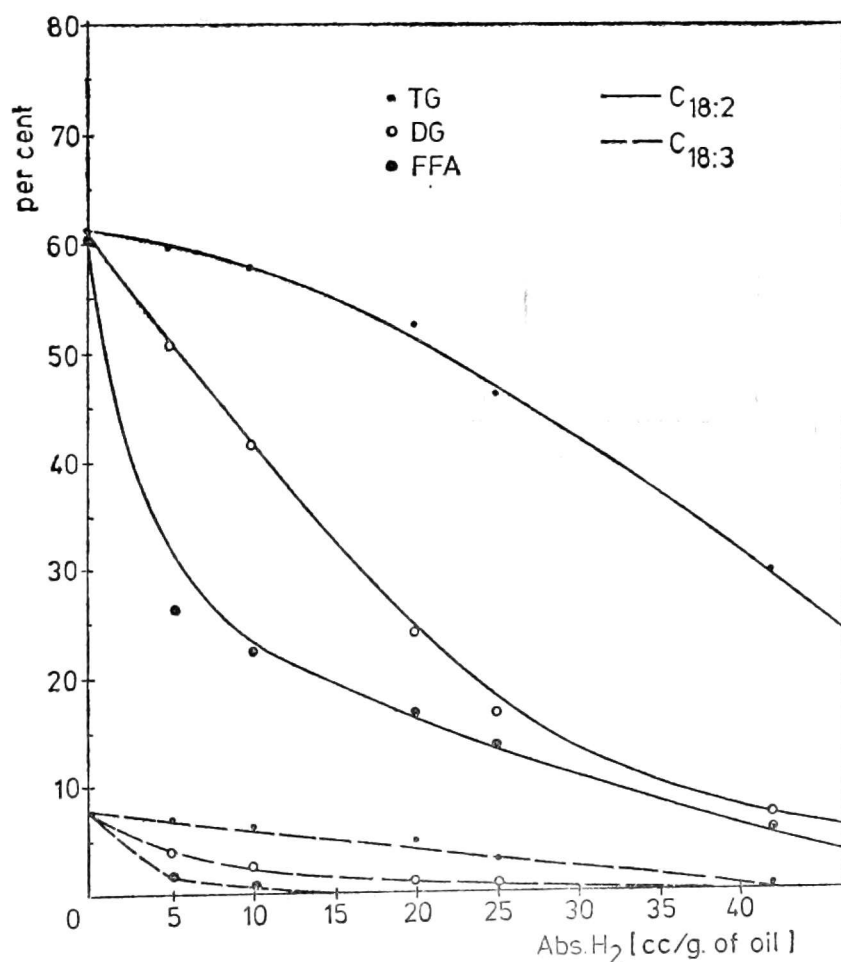


Fig. 2. The changes of linoleic and linolenic acid content as a function of hydrogen absorption for the DG, TG and FFA during hydrogenation of their mixture

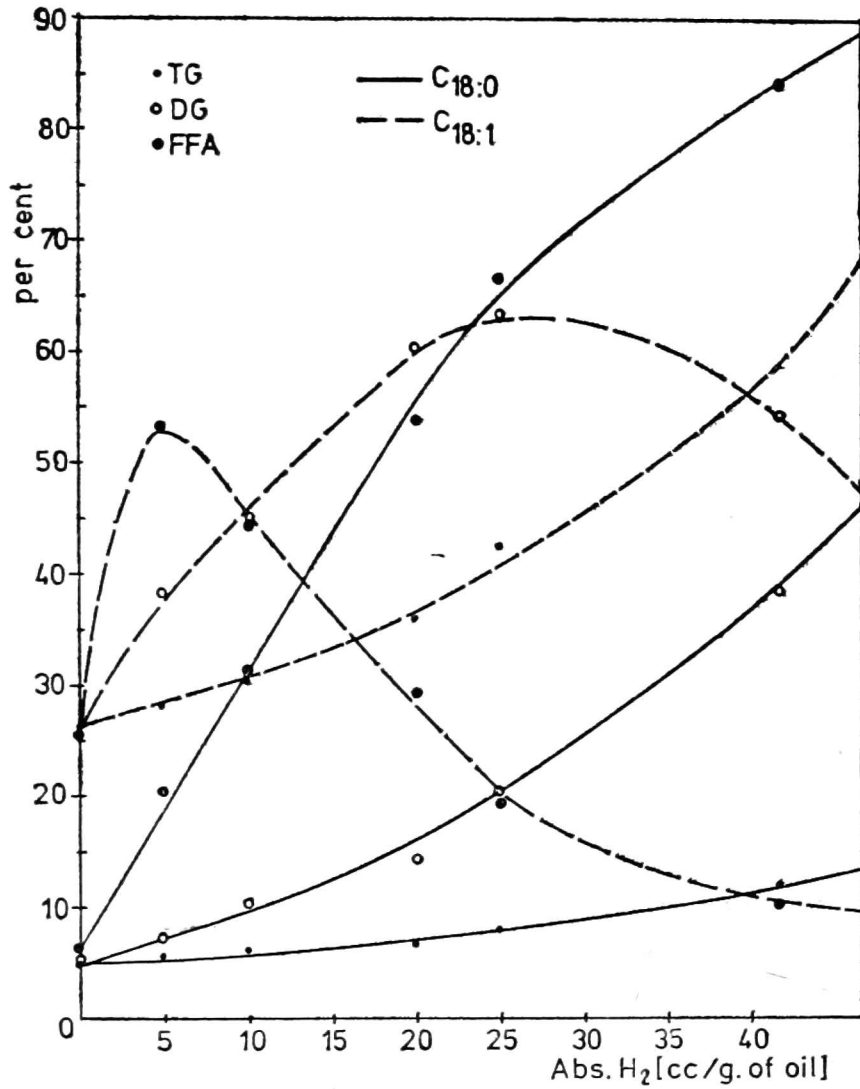


Fig. 3. The changes of oleic and stearic acid content as a function of hydrogen absorption for the DG, TG and FFA during hydrogenation of their mixture

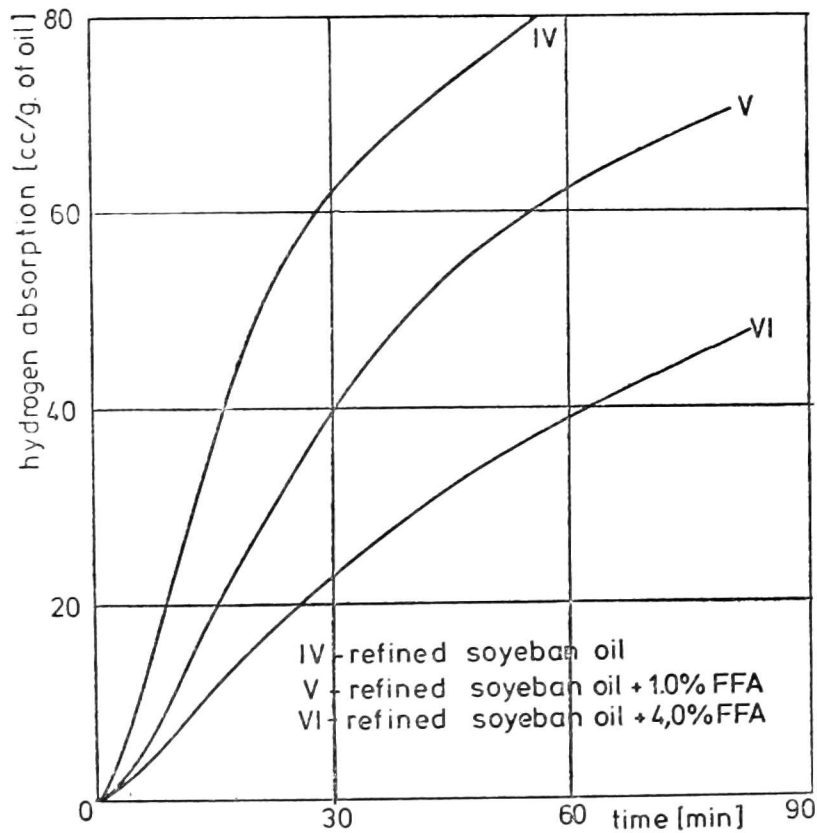


Fig. 4. Hydrogenation kinetic curves for refined soybean oil and for a mixture of that oil with FFA

nation kinetic curves for refined (curve I) and randomized (curve II) soybean oil, in which 8% diglycerides was found to be present. Monoglycerides and free fatty acids were present only in traces. In the same figure a kinetic curve (curve III) has been given for the hydrogenation of randomized oil, into which 4% FFA were introduced additionally. During the reaction course samples have been collected (the points of sampling are marked with arabic letters on the figure) and after their separation by preparative thin-layer chromatography the fatty acid composition of tri-, diglycerides and free fatty acids has been determined. The obtained results are compiled in Table and their graphical representation is shown in Fig. 2 and 3.

For better illustration of FFA effect on triglycerides hydrogenation rate, the additional hydrogenation of refined soybean oil to which 1% and next 4% of free fatty acids was added, has been carried out. The obtained kinetic curves are shown in Fig. 4.

#### RESULTS AND DISCUSSION

It is evident from the Figure 1 that the randomized oil (curve II) is hydrogenated more slowly than the refined oil (curve I). We may suppose than, that slower hydrogenation is due to the presence of diglycerides and more exactly to the presence of free hydroxyl groups in their molecules which should restrict their desorption from the surface of the catalyst. Similar, but more distinct action is exhibited by free fatty acids (curve III). As it is seen on Figure 4, the presence of free fatty acids has a strong inhibitory effect on the reaction rate. The presence of 1 per cent of FFA lowers the reaction rate approximately by 30 per cent, taking as a reference the progress of the reaction after 30 minutes.

As it is seen from Table hydrogenation is highly selective with regard to the tri- and diglycerides. The progress of the reaction is a se-

Table

The fatty acid composition changes of tri — and diglycerides during hydrogenation of mixture "M" containing 92 per cent of TG and 8 per cent of DG

Acid	Subsequent samples collected during the process									
	0		1		2		3		4	
	DG	TG	DG	TG	DG	TG	DG	TG	DG	TG
18 : 0	5.0	4.8	7.5	5.8	12.2	5.8	23.9	8.2	62.2	20.5
18 : 1	26.1	26.2	48.2	31.3	64.4	36.5	65.5	55.5	35.9	75.2
18 : 2	61.2	61.4	41.8	56.5	21.4	53.2	10.6	35.1	1.9	4.3
18 : 3	7.7	7.7	2.5	6.4	1.0	4.5	—	1.1	—	—

veral times higher for diglycerides than for triglycerides. The sample "2" can be taken as an example. The content of linolenic acid is four times less in DG than in TG, correspondingly twice less of linoleic acid, twice more of oleic and stearic acid.

Also the fatty acid compositions in sample "3" indicate that the progress of the reaction in DG is much faster; the content of stearic acid is there three times higher than in TG. It has to be stated that before hydrogenation (in the Table it is the sample "zero"), the overall fatty acid composition of all components was identical and the fatty acid distribution in tri- and diglycerides was random.

It can be inferred from Fig. 2 that the content of linoleic acid decreases at the highest rate in free fatty acids and then in diglycerides. In triglycerides this decrease is much slower. The same dependence is observed for linolenic acid. On the other hand, on Fig. 3 it is shown that in free fatty acids, already in the initial stage of hydrogenation, the amount of oleic quickly decreased in contradistinction to diglycerides, where it took place at hydrogen absorption equal to 25 cc/g of oil and triglycerides where the amount of this acid has slowly but constantly increased. Consequently the content of stearic acid has increased at highest rate in FFA and next in diglycerides. In triglycerides the increase of stearic acid content was insignificant.

It is clear from the above graphs that the free fatty acids and incomplete glycerides, though they are hydrogenated at a higher rate than triglycerides have inhibitory effect on the process of their hydrogenation due to the restricted desorption from the surface of the catalyst caused by the presence of strongly polar carboxyl and hydroxyl groups.

The preliminary anticipations on the selective adsorption of free fatty acids, diglycerides, and triglycerides have been thus confirmed.

#### REFERENCES

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## UWODORNIANIE MIESZANINY DWU- I TRÓJGLICERYDÓW ORAZ WOLNYCH KWASÓW TŁUSZCZOWYCH

### Streszczenie

W reaktorze z wewnętrznym obiegiem wodoru uwodorniano mieszaniny dwu-, trójglicerydów oraz wolnych kwasów tłuszczowych. Na podstawie uzyskanych krzywych kinetycznych uwodornienia oraz zmian w składzie kwasów tłuszczowych stwierdzono, że proces przebiega w sposób selektywny w odniesieniu do odpowiednich składników mieszaniny, oraz że obecność wolnych kwasów tłuszczowych działa hamująco na szybkość uwodornienia.

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## ГИДРИРОВАННЫЕ СМЕСИ ДВУ- И ТРИГЛИЦЕРИДОВ И СВОБОДНЫХ ЖИРНЫХ КИСЛОТ

### Резюме

В реакторе с внутренним оборотом водорода гидрировали смеси дву- и триглицеридов и свободных жирных кислот. На основании полученных кинетических кривых гидрирования и изменений в составе жирных кислот установлено, что процесс происходит селективно по отношению к соответствующим составным смеси и что наличие свободных жирных кислот оказывает тормозящее действие на скорость гидрирования.