TRANSFORMATIONS OF COD LIVER OIL FATTY ACIDS DURING HYDROGENATION *

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A number of cod liver oil hydrogenation runs has been carried out. The influence of process variables on the degree of transformations of fish oil fatty acids has been studied.

The studies of oil hydrogenation have not fally explained the nature of this complex process, though many research centres concentrate their efforts on the solution of this problem.

There is a number of papers on vegetable oil hydrogenation [1, 4, 6, 11], but the majority of them is concerned with kinetic studies and hydrogenation mechanism of model systems [2, 3, 9, 10].

Fish oil hydrogenation is much less extensively described in the literature.

Our studies had in aim the explanation of the mechanism of fish oil hydrogenation on a nickel catalyst and in consequence the choice of process conditions to obtain the product of defined characteristics.

EXPERIMENTAL

The baltic cod liver oil supplied by Zakłady Rybne in Gdyni (Fish Processing Works in Gdynia) was used for the studies. The fatty acid composition was determined by means of gas chromatography using SE-30 and PEGA-DEGS columns (Table). The characteristic values i.e. iodine value — JV and acid value — AV as determined by the standard methods were as follows: JV = 179.9 and AV = 0.7.

The hydrogenation process of was carried out in a specially desig-

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ned glass reactor with an internal circuit of hydrogen. A mechanical stirrer of high r.p.m. value ensured that the process was ran within the kinetic range. The hydrogenation was conducted at 170°C and 180°C, and at the pressures of 0.3, 0.5, 0.7, 1.0 and 1.2 atn. In the hydrogenation of cod liver oil the nickel catalyst type RCH, at levels 0.35 to 0.05 per cent have been used. The revolutions of the stirrer were maintained constant.

The samples of oil, 5 ml each, have been collected at predetermined time intervals and have been analyzed after the separation of the ca-

Table

Acid components of triglycerides in cod liver oil being studied

Acid	%	Acid	%
$C_{14}:_0$	3.5	$C_{18}:_4$	2.0
$C_{14}:_1$	0.4	$C_{19}:_0$	0.2
$C_{15}:_0$	0.5	?	0.3
$C_{15}:_1$	0.1	$C_{20}:_0$	—
$C_{16}:_0$	9.6	$C_{20}:_1$	6.1
$C_{16}:_1$	11.0	$C_{20}:_2$	0.7
?	0.3	$C_{20}:_3$	0.8
$C_{16}:_2$	0.9	$C_{20}:_5$	12.1
$C_{16}:_3$	0.5	$C_{22}:_0$	0.8
$C_{17}:_0$	0.8	$C_{22}:_1$	2.2
$C_{17}:_1$	0.7	?	traces
$C_{18}:_0$	2.2	?	traces
$C_{18}:_1$	26.8	?	traces
$C_{18}:_2$	3.2	$C_{22}:_5$	1.2
$C_{18}:_3$	1.8	$C_{22}:_6$	10.5

Saturated acids — 17.6%,
Monoenic acids — 47.3%,
Polyenic acids — 34.3%.

talyst. The process was stopped after two hours. The samples were then esterified with methanol in the presence of BF_3 [8] and the percentage content of geometric isomers [7] (Fig. 4 and 5) and the fatty acid composition were determined.

The compiled results refer to the composition changes of the groups of saturated, mono- and polyenic acids without distinguishing the individual components of the groups. The results obtained are interpreted graphically at Fig. 1, 2 and 3. For the sake of clarity the curves are not shown for each run but only for four sets of conditions deffering most markedly.

RESULTS AND DISCUSSION

EFFECT OF TEMPERATURE AND PRESSURE AND CONCENTRATION OF CATALYST ON THE SELECTIVITY OF HYDROGENATION

Fig. 1 and 2 represent the changes of each group of acids in the course of the hydrogenation runs at 170°C and 180°C, and the pressures of 0.3 and 1.2 atn.

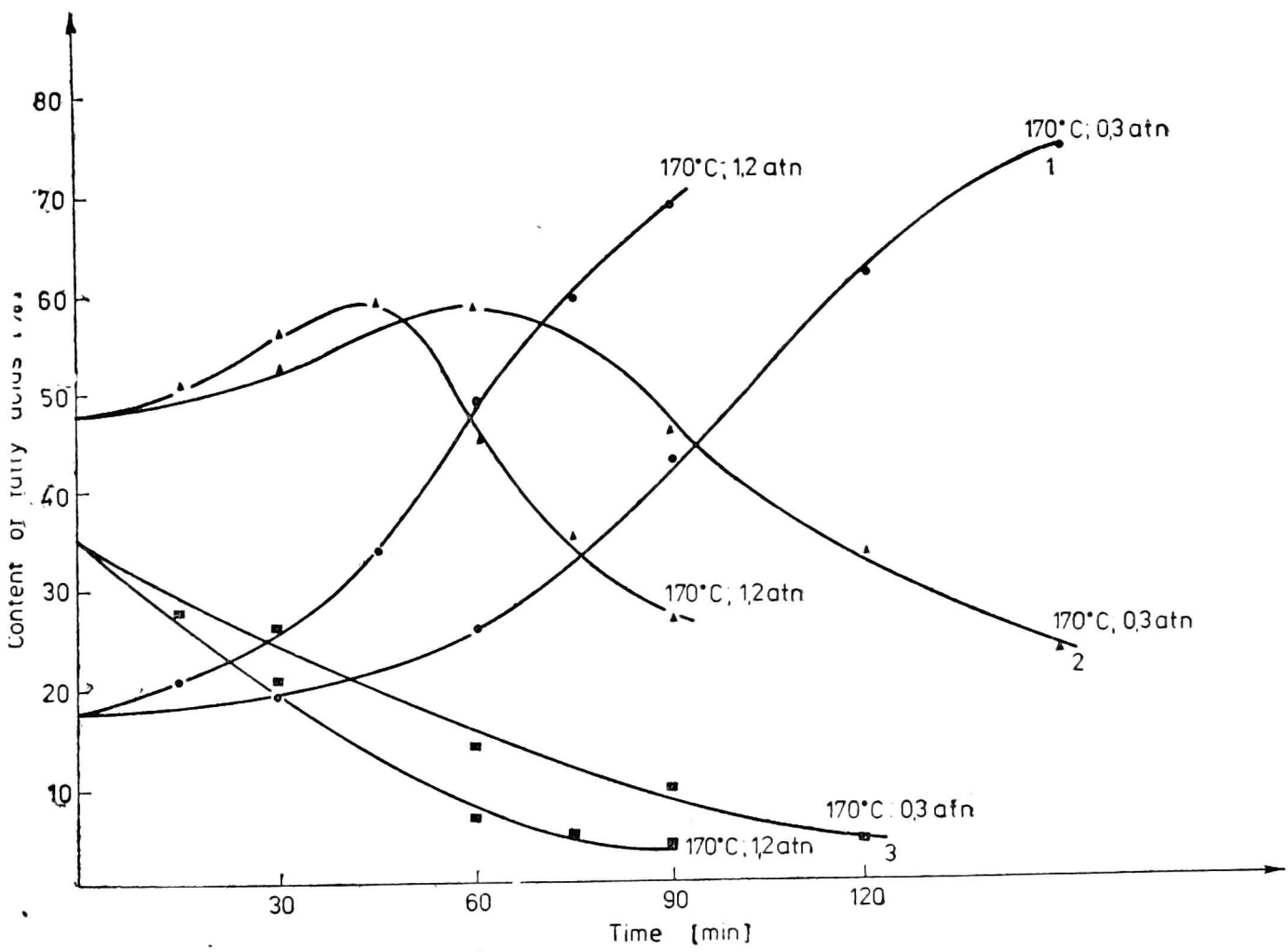

Fig. 1. Changes of saturated, monounsaturated and polyunsaturated fatty acids during hydrogenation of cod liver oil at 170°C and the pressures 0.3 and 1.2 atn.: *1* — saturated fatty acids, *2* — monounsaturated fatty acids, *3* — polyunsaturated fatty acids

In Fig. 3 there are shown the changes of fatty acids contents in the processes being carried out at 0.05 and 0.35% catalyst concentrations.

The very distinct differentiation of the curves for the lower temperature with the pressure change is the most characteristic feature of the process that can be observed from the very beginning. Instead, at higher temperature, the period of slight differentiation of the saturated acid increase is observed during the first 20-30 min of the process, irrespective of pressures being used.

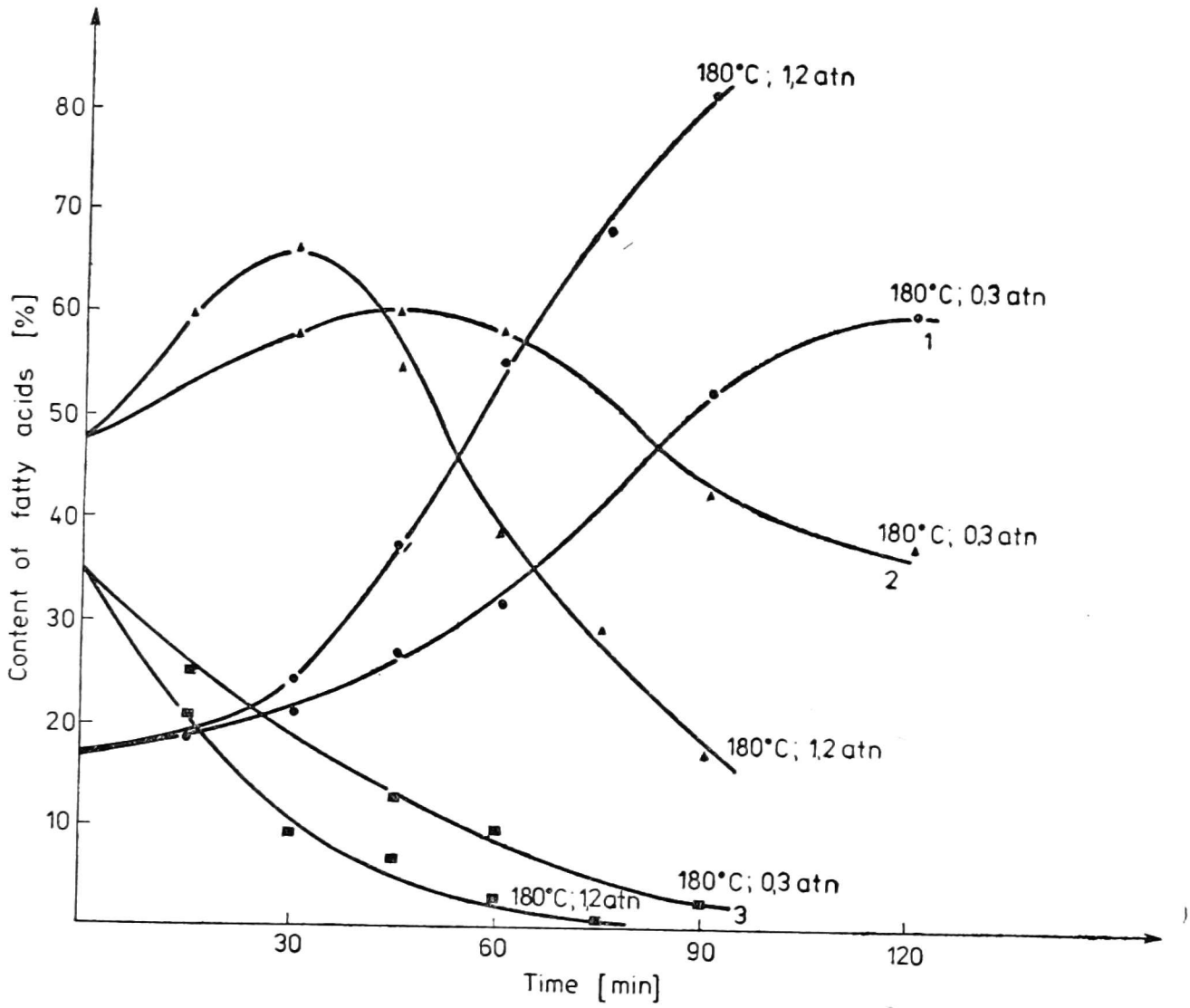

Fig. 2. Changes of saturated, monounsaturated and polyunsaturated fatty acids during hydrogenation of cod liver oil at 180°C and the pressures 0.3 and 1.2 atn.: *1* — saturated fatty acids, *2* — monounsaturated fatty acids, *3* — polyunsaturated fatty acids

In case catalyst concentrations change a short period of time may also be observed in which the changes in concentration of saturated and monoenic fatty acids are negligible, and only the contents of polyenic fatty acid changes distinctly.

In order to demonstrate this phenomenon more clearly, an arbitrary value A indicating the hydrogenation selectivity was determined. The value represents the ratios of absolute percentage changes of saturated acids to the sum of mono- and polyenic acids at the defined time intervals.

$$A = \frac{(\Delta_s)}{(\Delta_m)+(\Delta_p)}$$

where:

s — percentage changes of saturated acids,
m — percentage changes of monoenic acids,
p — percentage changes of polyenic acids.

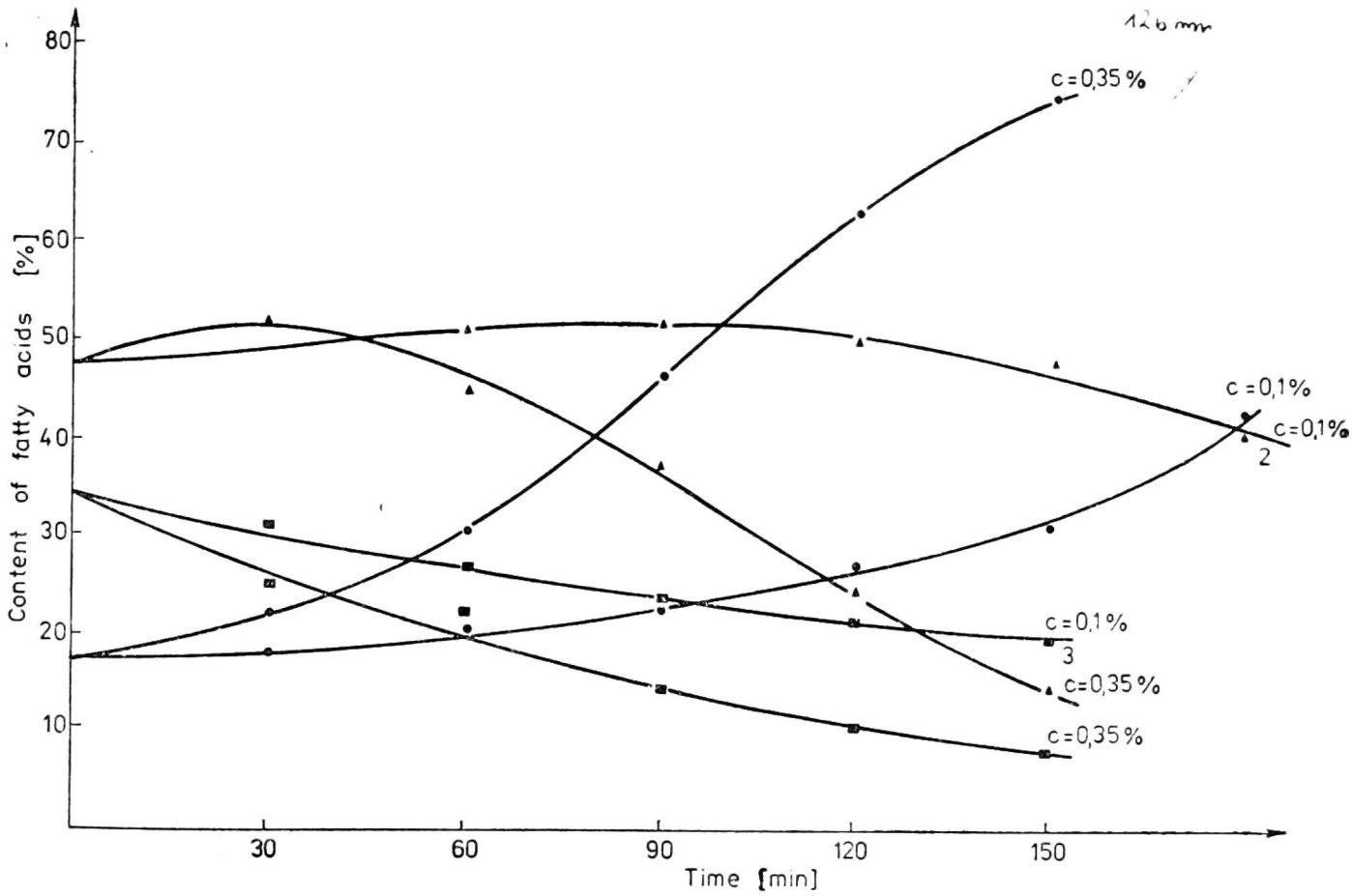

Fig. 3. Changes of fatty acids contents in the processes carried out at 0.05 and 0.35% catalyst concentrations: *1* — saturated fatty acids, *2* — monounsaturated fatty acids, *3* — polyunsaturated fatty acids

This value is enclosed within the limits 0 and 1. The relationship between the selectivity determined in this way and the conditions of hydrogenation is shown in Fig. 3 where the dashed curve illustrated the theoretically selective process. The marked differences of the pressure effect on the selectivity as the function of temperature have been observed. At higher temperatures the influence is much less distinct.

THE EFFECT OF TEMPERATURE AND PRESSURE AND CONCENTRATION OF CATALYST ON THE STEREOISOMETRIZATION

Two distinct periods of different pressure and temperature influence can be observed (Fig. 4).

For the first 50 min at the constant temperature, the "trans" isomer content increases at slightly higher rate at the higher pressures. After this period there is the decrease of isomer content having higher rate at higher pressures.

The same situation occurs in the case of constant pressure and varying temperature.

Lower temperature and pressures cause the slower increase of trans somer content, but on the other hand, the miximum value is higher

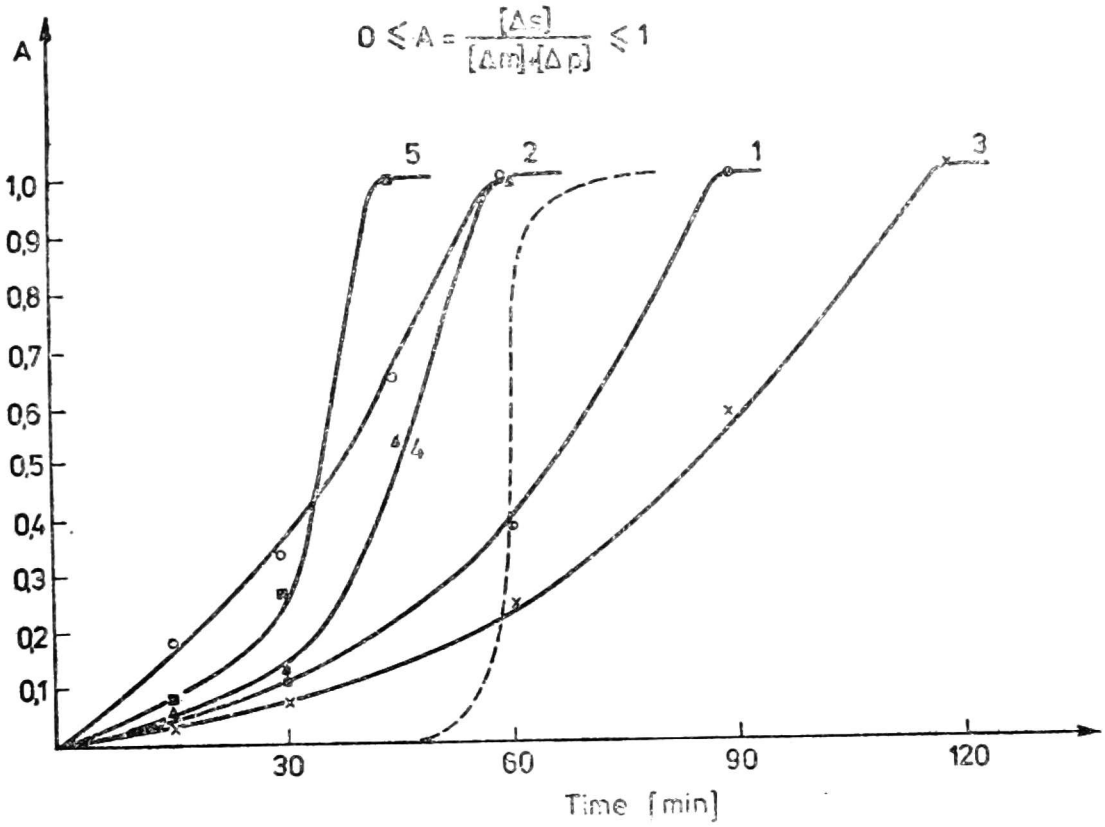

Fig. 4. Changees of selectivity during hydrogenation of cod liver oil at the variable parameters of processes: *1* — 170°C, 0.3 atn, c = 0.35%; *2* — 170°C, 1.2 atn, c = = 0.35%; *3* — 170°C, 1.0 atn., c = 0.10%; *4* — 180°C, 0.3 atn., c = 0.35%; *5* — 180°C, 1.2 atn., c = 0.35%

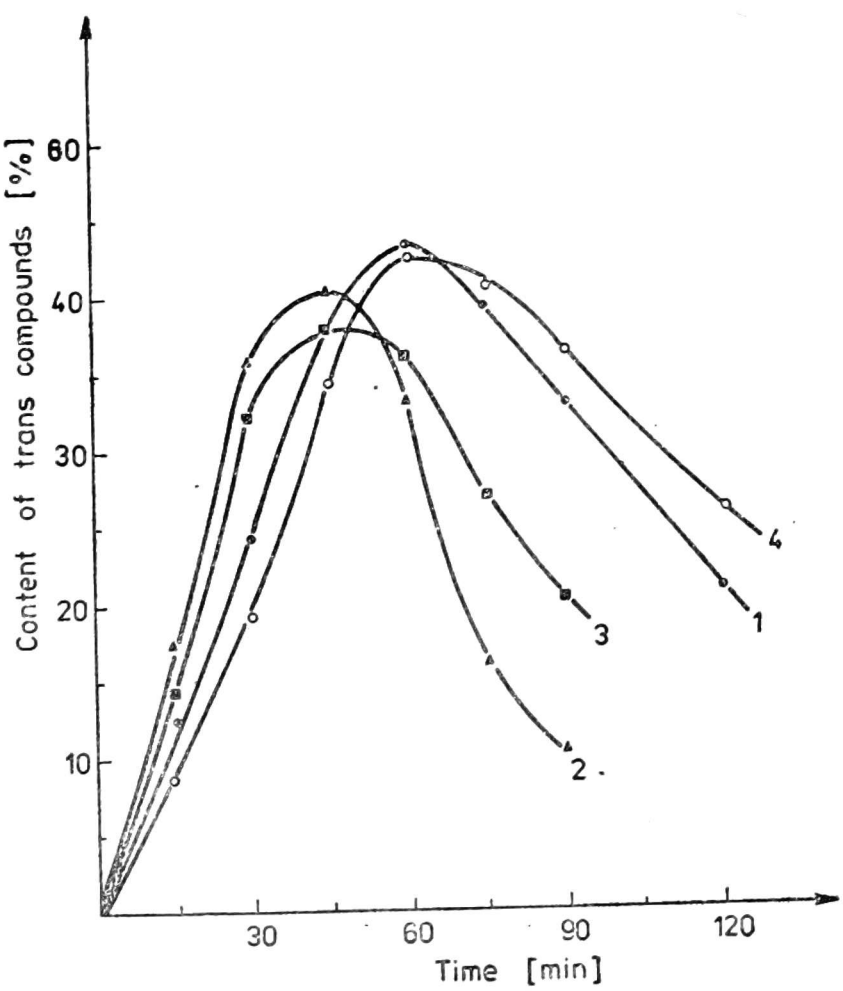

Fig. 5. Percentage content of geometric isomers during hydrogenation of cod liver oil at the variable parameters of processes: *1* — 180°C, 0.3 atn., *2* — 180°C, 1.2 atn., *3* — 170°C, 1.2 atn., *4* — 170°C, 0.3 atn.

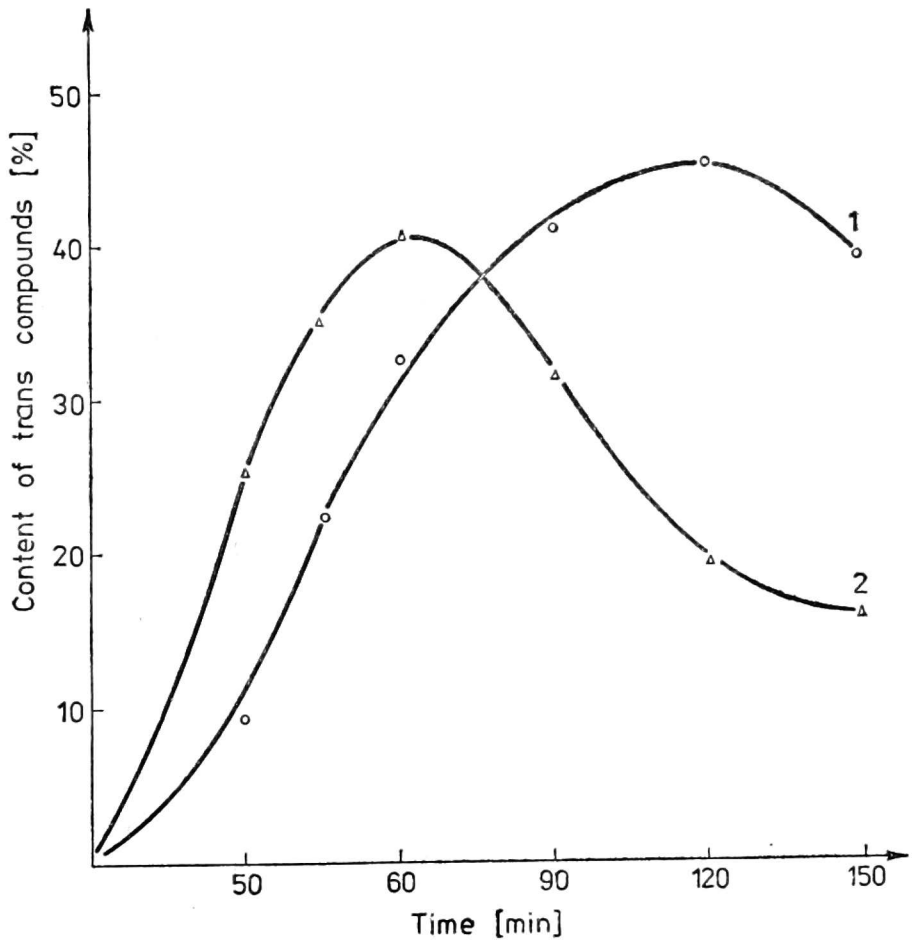

Fig. 6. Percentage content of geometric isomers during hydrogenation of cod liver oil at the variable concentrations of catalyst: *1* — 170°C, 1.0 atn, c = 0.10%; *2* — 170°C, 1.0 atn., c = 0.35%

than in the case of the higher pressure (t = const.) or the higher temperature (p = const).

At lower catalyst concentrations (Fig. 6) such as 0.1 and 0.05% during the first 30 min of hydrogenation, there appears a moderation of izomerisation reaction.

The phenomena observed can be considered as the evidence of the defferentiation in the hydrogenation rate of "cis" and "trans" forms of fatty acids as the function of the conditions of the process.

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PRZEMIANY SKŁADU KWASÓW TŁUSZCZOWYCH OLEJU Z WĄTRÓB DORSZA PODCZAS UWODORNIENIA

Streszczenie

Uwodornienie oleju z wątrób dorsza prowadzono przy zmiennych parametrach procesu. Proces w skali laboratoryjnej wykonano w autoklawie zamkniętym przy 170 i 180°C i ciśnieniu wodoru od 0,3 do 1,2 ath. Katalizator używano w stężeniu od 0,05 do 0,35% wag. niklu. W każdej próbie, pobieranej podczas uwodornienia, oznaczano liczbę jodową, zawartość izomerów trans i zawartość kwasów tłuszczowych nasyconych, monoenowych i polienowych.

Na podstawie otrzymanych wyników określono wpływ ciśnienia, temperatury i stężenia katalizatora na proces uwodornienia oleju z wątrób dorsza.

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ИЗМЕНЕНИЯ СОСТАВА ЖИРНЫХ КИСЛОТ МАСЛА ИЗ ПЕЧЕНИ ТРЕСКИ ВО ВРЕМЯ ГИДРОГЕНИЗАЦИИ

Резюме

Гидрогенизация масла из печени трески проводилось при изменчивых параметрах процесса. Процесс в лабораторном масштабе проводился в закрытом автоклаве в температуре 170° и 180°С и при давлении водорода 0,3—1,2 атп. Катализатор использовывали в концентрации 0,05—0,35% веса никеля. В каждом образце отобранном во время гидрогенизации определяли иодное число, содержание транс-изомеров и содержание насыщенных моноеновых и полиеновых жирных кислот.

На основании полученных результатов определяли влияние давления, температуры и концентрации катализатора на процесс гидрогенизации масла из печени трески.