THERMAL CRYSTALLIZATION OF FATTY ACIDS AS A REASONABLE WAY OF FISH OILS — USE FOR TECHNICAL PURPOSES

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According to the actual and future situation of raw material shortage in chemical industry makes it necessary to increase the usage of fish oils. Because of their complicated fatty acids composition these oils are valuable raw material, however in some cases they need a preliminary fractionization in order to separate fatty acids in group according to their qualities. The eventual enrichment of the particular fraction with the given type of acids enables the independent utilization of the long-chain polyenoic acids, medium-long-chain acids, as well as saturated and monounsaturated acids.

The sulphation process of fish oil fatty acids [1], their reduction to fatty alcohols [2], which can be used for detergent production, for instance by means of esterification with saccharose or with monohydric alcohols, as well as, the use of polyene acids for insecticide and fungicide products' manufacture, require the preliminary fractioning of such a complicated mixture.

Owing to the presence of the susceptible to oxidation polyene acids in this mixture, the relatively drastic methods of distillation should be avoided and substituted by more mild processes, such as the thermal crystallization, provided that this process is sufficiently effective.

In this work the possibility of the effective fractionization of these mixture by thermal crystallization has been inevstigated.

The oils from mackerel, cod and partially hydrogenated mikture of fish oils, received from industry, were used in the tests. The mixtures of fatty acids were obtained by the saponification of the samples at the room temperature with 2nd solution of potassium hydroxide in methanol, and the subsequent acidification. The fatty acids fractionated by

crystallization according to pattern shown in Fig. 1, relating to the mackerel oil.

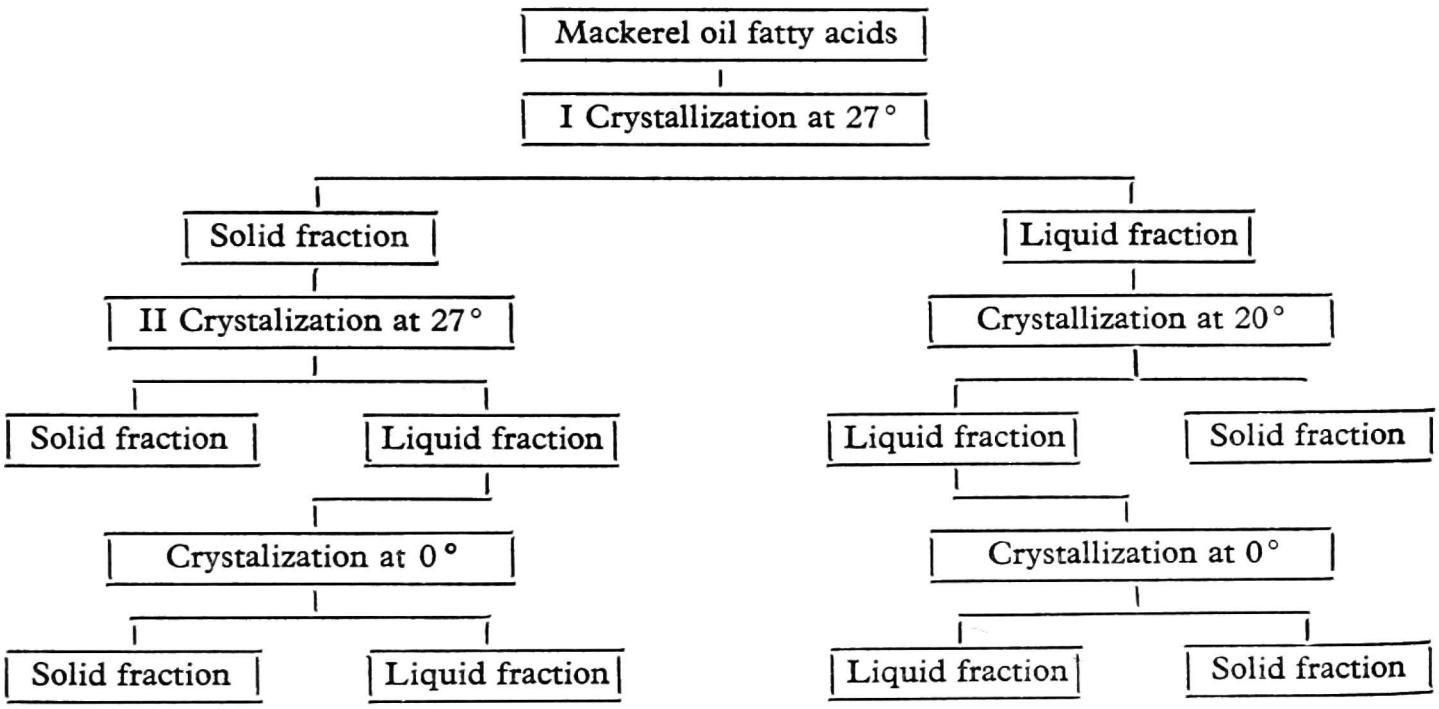

Fig. 1. Scheme of crystallization of fatty acids

The solid and liquid fractions were separated with the application of thermostatic centrifuge with 4500 to 5000 rpm (rotations per minute).

The joint yield obtained from this crystallization shows Table 1.

Table 1

Fractionated mackerel oil fatty acids

Cristallization temperature	Solid fraction (%)	Liquid fraction (%)
4°	49.0	51.0
20°	30.0	21.0
0°	17.0	4.1

The fractions obtained were characterized by iodine value and their fatty acids composition.

Differences in the iodine value of the particulary fatty acids fractions obtained from mackerel oil are presented in the Table 2.

The results show that there is a possibility to obtain by simple thermal treatment 4.1% of fatty acid fraction with iodine value increased by about 40 units (I.V. = 213.1), as compared with the original sample, and 21% fatty acid fraction with iodine value close to 200.

At the same time, this process makes it possible to obtain about 51% of fatty acids fraction with iodine value below 150 units.

Table 2

Iodine value FFA from mackerel oil

Start test	Solid fraction	Liquid fraction	Solid fraction	Liquid fraction	Solid fraction	Liquid fraction
	27°	27°	20°	20°	0°	0°
174.2	166.2	183.9	157.8	198.5	194.0	213.1

Table 3

The thermal crystallization effect of fatty acids mixture from mackerel oil (%)

Fatty acids	Start test FFA	Solid fraction at 27°	Liquid fraction at 27°	Solid fraction at 20°	Liquid fraction at 20°	Solid fraction at 0°	Liquid fraction at 0°
Saturated acids	25.8	35.1	20.4	32.8	17.6	24.6	13.5
$\Sigma C_{20:5}$ $C_{22:5}$ $C_{22:6}$	19.3	14.0	19.7	18.0	22.6	20.8	31.4
$\Sigma C_{20}—C_{22}$	40.7	32.3	43.7	36.1	45.4	40.5	59.3
ΣC_{16} C_{18}	20.2	28.7	14.8	27.0	12.4	19.2	6.7

The difference in fatty acids composition in obtained fractions are presented in the Table 3.

The subsequent crystallization carried out at lower temperatures permits to decrease the content of saturated fatty acids in the liquid fractions. At the temperatures 0° it is possible to lower the content of these acids from 25.8% to 13.5%.

At the same time the crystallization at 27° enables to obtain 49% of fatty acids fraction enriched by saturated acids up to 35.1% of the total acids.

The initial contens of polyene acids i.e. 19.3, increase in the liquid fraction at crystallization temperature 0° up to 31.4% and decrease in the solid fraction obtained at temperature of 27° down to 14%.

There are characteristic differences between the fractions in the content of the two saturated acids: palmitic and stearic, given as a sum with the decrease from 20.2% to 6.7% in the liquid fraction obtained at 0°, and increase up to 28,7% in the solid fraction obtained at 27°.

In the solid fraction obtained at 27° the content of long chain acids ($C_{20} + C_{22}$) decreases from 40.7% to 32.3% and in liquid fraction at 0° increases up to 59.3%.

There exist characteristic pheonomenon that the acid composition of solid fraction obtained at temperature of 0° is very close to that on of initial mixture of acids.

Table 4

The thermal crystallization effect of fatty acids mixture from cod oil (%)

Fatty acids	Start test (FFA)	Solid fraction at 22°	Solid fraction at 12°	Liquid fraction at 12°	Solid fraction at 0°	Liquid fraction at 0°
Σsaturated acids	19.0	21.7	19.3	11.8	13.1	8.9
$\Sigma C_{20:5}$ $C_{22:5}$ $C_{22:6}$	24.6	22.1	23.0	26.6	25.0	34.4
ΣC_{20}—C_{22}	33.1	29.5	31.5	35.5	32.6	42.3
ΣC_{16} C_{18}	15.3	18.1	15.7	8.4	10.0	6.1

The fatty acids of cod oil were crystallized at the temperatures of 22° and 12° only.

Table 5 shows differences similar to the ones observed in mackerel oil fatty acids crystallization. The composition of fatty acids crystallized at temperature of 22° and 12° shows similar trends like the ones above mentioned, including the differences in fatty acids composition of original samples.

Table 5

Iodine value FFA from hydrogenated fish oil		
Start test	Solid fraction	Liquid fraction
65.4	60.4	70.3

For comparison purposes a partially hydrogenated fish oil was also crystallized at the temperature of 42°C.

The iodine value difference obtained in both fractions was up to 10 units.

The differences between the groups of fatty acids can by seen in the Table 5. The saturated acids contents decrease from 43.8% in the original sample down to 36.0% in liquid fraction. At the same time, in solid fraction the quantity of these acids increase up to 51.5%. However, the differences in the fatty acids composition, regarding the chain length, in the both fractions are small.

Total contents of acids with 22 carbons in chain in liquid fraction is 12.8% and in solid fraction 18.1%. The respective difference in con-

Table 6

The thermal crystallization effect of fatty acids mixture from partially hydrogenated fish oil (%)

Fatty acids	Start test (FFA)	Solid fraction at 42°	Liquid fraction at 42°
$\Sigma C_{14:0}$			
$C_{16:0}$			
$C_{18:0}$	43.8	51.5	36.0
$C_{20:0}$			
$C_{22:0}$			
$\Sigma C_{14} - C_{18}$	69.8	67.2	71.0
ΣC_{22} total	14.5	18.1	12.8

tent of fatty acid groups with 12 to 18 carbons in chain is even smaller. In solid fraction there are 67.2% and in liquid fraction 71.0%.

CONCLUSION

The results obtained during this work appear to be encouraging for further investigations; the elaboration of method for several step thermal crystallization of acids mixture obtained from fish oils, may be helpful in preparing this raw material for further chemurgy.

REFERENCES

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TERMICZNA KRYSTALIZACJA KWASÓW TŁUSZCZOWYCH OLEJÓW RYBNYCH JAKO JEDNA Z METOD PRZYGOTOWANIA ICH DO TECHNICZNEGO WYKORZYSTANIA

Streszczenie

W celu wstępnego rozfrakcjonowania skomplikowanej mieszaniny kwasów tłuszczowych otrzymanych z olejów rybnych, przeprowadzono próbę ich wielokrotnej krystalizacji termicznej. Po każdorazowej krystalizacji oddzielono frakcję stałą od ciekłej przy użyciu termostatowanej wirówki przy 4500-5000 obr./min. Uzyskane tą drogą frakcje stałe i płynne charakteryzowano przez oznaczenie w nich liczby jodowej i składu kwasów tłuszczowych.

Stwierdzono możliwość uzyskania w oleju makreli 24% frakcji o liczbie jodowej powyżej 200 jednostek. Zawartość kwasów polienowych wzrasta w tej frakcji ponad dwukrotnie w porównaniu z surowcem wyjściowym. Frakcja ta zostaje również wzbogacona w kwasy długołańcuchowe (20 i 22 węgle w łańcuchu). Przeprowadzono również krystalizację oleju dorszowego częściowo uwodornionego.

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ТЕРМИЧЕСКАЯ КРИСТАЛИЗАЦИЯ РЫБНЫХ ЖИРНЫХ КИСЛОТ КАК ОДИН ИЗ МЕТОДОВ ИХ ПОДГОТОВКИ ДЛЯ ТЕХНИЧЕСКОГО ИСПОЛЬЗОВАНИЯ

Резюме

С целью предварительного сфракционирования сложной смеси жирных кислот извлекамых из рыбных масел, предпринималась проба их многократной термической кристаллизации. После каждой кристаллизации отделяли твердую фракцию от жидкой с использованием термостатной центрифуги при 4500—5000 оборотов вминуту. Полученные таким образом твердые и жидкие фракции характеризовали путем определения в них иодного числа и состава жирных кислот.

Установлена возможность получения в макрелевом масле 24% фракции с иодным числом свыше 200 единиц. Содержание полиеновых кислот повышается в этой фракции больше чем двухкратно в сравнении с исходным материалом. Эта фракция обогащается также длинноценными кислотами (20 и 22 углей в цепи). Проводилась также кристаллизация частично гидрированного трескового масла.