

Contribution to the possibility of graphic-numerical expression of hydrogenated fats' selectivity by means of a "complex value" method

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Summary. New ways of determining selectivity parameter of the hydrogenation catalyst or hydrogenated triacylglycerols was studied. In contrast to the already known methods, in this new approach the secondary-isomerizing type of hydrogenation reaction with the possibility of being expressed as "cumulated complex selectivity" (CCS) is simultaneously taken into account besides the primary-additive type. The starting point for the determination of CCS are simple integer classifications of 5 equidistance values into which ranges are divided of specific reaction rates of individual unsaturated fatty acids. This also facilitates numerical and graphical expression of CCS. An adaptable polygonal system capable to express all kinds of plant oils or partial catalytic hydrogenation reaction models with minimum three and maximum sixteen rate constants, that can be applied in the case of mathematical expression of isomerizing and also non-subsequent-parallel hydrogenation transformations of individual fatty acids, is used for a very clear graphic interpretation of CCS. The CCS expressed graphically can be exactly quantified as percentual ratio of area (circumference) of the original polygon (theoretical CCS) to the area (circumference) of the obtained polygon.

In the industrial production of edible oils which represent an inseparable part of everyday human nourishment, the process of partial catalytic hydrogenation (PCH) is the decisive factor as far as both the aspect of capacity and the aspect of final product resulting properties (chemical, physical and biological) are concerned. The resulting representation of transformations of individual unsaturated fatty acids (UnFA) as well as of geometric *trans*-isomers (TI) is dependent first of all upon the kind of the catalyst and then upon the condition of its application. The application conditions can be identified with the technological-operating conditions of PCH in principle: operating temperature, pressure, mixing efficiency, catalyst concentration, purity and quan-

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tity of hydrogen, pre-refining efficiency, inhibitor quantity, reactor type, etc. The interdependences of these conditions, their effect on the whole process of PCH and also the catalyst response are given in works [1—5]. The dependence of PCH rate upon temperature, pressure, mixing efficiency and catalyst concentration was expressed by Eldib [6]. The mathematical model for making the most effective use of the whole complex of PCH industrial process operating conditions with respect to the selected melting point, or the iodine value of the final product is given in the works [7, 8].

From the aspect of the catalyst itself its basic parameters: activity, selectivity and TI formation are decisive. Reproducibility and exactness of catalyst activity determination proceeded from the expression by means of the melting temperature value [9], through the consumption of H_2 [10] to simpler methods by means of refractive index [11] or values classified by calculation [12], eventually functional dependence of activity and absolute temperature reciprocal value [13]. TI content can be investigated by means of absorption band size (975 cm^{-1}) and expressed by application of spectrometry in the IR zone of radiation [14]; more quickly and simply by calculation using derived empiric equations, or by simple reading from tables that can be prepared for each reactor by tabulating the obtained empiric equations [15, 16].

At present the selectivity parameter — one of the most important in relation to catalyst properties and hardened product properties — is considered in four possibilities of expression: primary-additive selectivity [17], eventually selectivity I or S_I [1]; secondary-isomerizing selectivity [17, 18], eventually specific isomerization, i.e. the fraction TI and eliminated double bonds [1]; isomerizing index expressed by the fraction TI formation rate and hydrogenation rate [19]; and finally the so-called triacylglycerol selectivity [1] concerning the formation of trisaturated triacylglycerol molecules.

The techniques of selectivity determination that are more sophisticated than, e.g. activity determination, proceeding from difference determination of melting and setting points (difference number) [20] through the triangular interpretation of FA ternary system, if the most unsaturated acid is the diene linoleic acid [21]. A broad utilization of the triangular method of selectivity determination is described by Pokorný [23]. More exact possibilities of PCH selectivity expression are obtained by calculations of specific reaction rates of pertinent FA. Simple relations for the determination of linolenic and linoleic acid selectivities, if their starting and final concentrations are known, are derived by Riesz [22]. A set of diagrams for reading the selectivity ratios on oils not containing linolenic acid was elaborated by Albright [24], and for oils with linolenic acid by Allen [25] and Schmidt [26]. Diagrams for reading the selectivity ratios for sunflower oils and rape oils with a high and low contents of erucic acid were elaborated by Koman [15, 27]. Only partial selectivity ratios S_{32} in plant

oils with trienes and S_{21} in plant oils without trienes can be determined by means of the diagrams mentioned. In the sphere of solving catalyst and PCH triacylglycerol selectivities the necessary computer engineering was introduced by Butterfield, who first used an analog computer [28], and later a digital computer with elaborated programmes CATSEL and DRATE [29, 30]. The starting points for selectivity determination by calculation using the so-called selectivity ratios S_{32} , S_{21} , and S_{31} are in fact ratios of individual rate constants k_3/k_2 , k_2/k_1 , k_3/k_1 , ensuing from the mathematical description of irreversible reactions kinetics of following transformations: $T \xrightarrow{3} D \xrightarrow{2} M \xrightarrow{1} S$ proposed by Bailly [30] (T — trienes, D — dienes, M — monoenes, S — saturates, 1, 2, 3 — rate constants (RC) (specific reaction rate)).

The presented reaction model does not consider either the formation of positional or spatial isomers. A solution of these problems was outlined by Hashimoto applying Marquardt's method of least squares [32]. More general relations for the study of transformations of geometric isomers in dienes and monoenes in the process of PCH were derived by Albright [19]; an extended programme CATSEL enabling a simultaneous determination of rate constants of erucic acid and eikosenic acid of rape oils with a high and low contents of erucic acid as well as *cis*- and *trans*-isomers of monoene fatty acids was presented by Koman [33]. One of CATSEL programme versions was supplemented with selectivity testing possibility. Hitherto presented selectivity ranges: S_{32} to 25, S_{21} to 50 and S_{31} to 100 were divided into five equidistances that were added one of five numerical and alphabetic classifications: excellent (5), very good (4), good (3), satisfactory (2) and unsatisfactory (1) selectivities of catalyst, eventually of hardened fat [34].

All mentioned techniques of catalyst selectivity determination or of hydrogenated fat make it possible to express only the primary additive type of selectivity. A method to express simultaneously both the primary-additive and the secondary-isomerizing selectivity, which would make it possible to evaluate also the cumulate share of *cis*- and *trans*-isomers in properties of both the hardened product and the applied catalyst — by means of a complex value or in numerical or graphical interpretations — has been missing till now and hence became subject matter of this work.

Experimental part

Employed samples and materials. Samples of pre-refined plant oils of sunflower soya bean and rape with a high content of erucic acid and rape with low content of erucic acid were used.

Ni catalyst made by North-Bohemian Fat Industry Plants, Ústí nad Labem and with 13.9 wt % of Ni, specified in a complex metric way, and an imported catalyst Nysel DM-3 made by Harshaw and containing 24.9 wt % of Ni were used as hydrogenation catalysts. The weighed portions were made from them in such a way that after conversion they contained 0.02, 0.05 and 0.2 g of pure Ni.

Hydrogenation conditions. Laboratory hydrogenation of samples from the given plant oils was performed in a reactor and under conditions prescribed in the standard ON No. 58 0102. Withdrawing of samples followed after 60 min in selected time intervals. Samples hydrogenated industrially were withdrawn directly from the autoclave (made by n.e. Palma) and they were hydrogenated under prescribed conditions as follows: hydrogenated oil volume — 5000 l, electrolytic hydrogen flow quantity — 250 to 350 m³, revolving frequency — 146 s⁻¹, catalyst quantity — 15 kg of the fresh and variable quantity of the used catalyst, hydrogen supply start at the temperature of 120°C, hydrogenation temperature — 145 to 190°C, hydrogen pressure — 0.02 to 0.05 MPa, heating steam pressure — 6 to 6.5 MPa, steam temperature — 250 to 350°C.

Conditions of fatty acid chromatographic analysis. Research Gas Chromatograph Hewlett—Packard model 7620 A with flame ionization detector and fully automated Reporting Integrator model 3380 A was used. A stainless column of the length of 200 cm and inner diameter 0.2 cm with Celite AW DMCS packing wetted with 20% DEGJ was used for GLC analyses. Nitrogen flow as mobile phase was 47 ml/min, column space temperature 190°C, feed space temperature 250°C and flame ionization detector temperature 250°C. Quantities of 1 µl of 20% cyclohexane solution of FA methyl esters prepared according to Peisker [35] were charged.

Conditions for the calculation of fatty acid specific reaction rates. A computing programme with the operating name CATSEL [33] enabling the computation of rate constants and selectivity ratios S_{32} to S_{31} was employed. Starting and final concentrations of FA hydrogenated samples after GLC analysis were used as input data. Approximately 200 samples were processed by computation under different conditions of hydrogenated samples using automatic digital computer Siemens 4004/150. The most probable rate constant ranges of individual FA were identified with their statistic mean values. The obtained rate constant ranges, after division into 5 equidistances, gave intervals expressed as integer classification values of points in the range from 1 to 5 thus expressing unsatisfactory to excellent selectivity.

Conditions of CCS graphic interpretation. In a circle with radius 5 cm a polygon with the number of apexes equal to the number of computed rate constants is constructed. The connecting lines of apexes with circles centre are

the "a" and "b" legs of triangles and at the same time the carriers of classified point values obtained according to the previous condition. The connecting lines of point values in the sides "a" and "b" form "c" legs of obtained triangles then, and "c" legs of all triangles of the selected polygon form its circumference expressed quantitatively as the percentage of the original polygon circumference that represents 100% or a theoretical value of CCS. The quantitative numerical expression of CCS is obtained from the graphical polygonal configurations:

1. from the ratio of the number of maximum attainable classifying values and actually obtained values;
2. from the ratio of original polygon circumferences (CCS theoretical value) and actually obtained polygon circumference (CCS studied value);
3. from the ratio of the original polygon areas (CCS theoretical value) and the actual area (CCS studied value).

Conditions for preparation of auxiliary tables. An auxiliary table is made for simplified computation of "c" legs of triangles to interpret selected polygon CCS. To this end the lengths of "a" and "b" legs are stimulated in the ranges of 1 to 5 cm. As two legs, radius and central angle are known, corresponding "c" legs are computed by means of programmable calculator TI-58, its software contained in the basic programme module Master Library, Module-1, namely programme ML-13; for the computation of the leg and area of the triangle if the central angle and radius of the circumcircle are known, or ML-2: for the computation of the area of the triangle if the angle and two legs are known, or ML-11: for the computation of the leg length if the angle and two legs are known [36].

Results and discussion

The ranges of mean values of rate constants of individual FA samples hydrogenated under different reaction conditions computed by means of the computing programme CATSEL were: 0.0 to 4.0/h for trienes, 0.0 to 2.0/h for dienes, 0.0 to 0.1/h for monoenes, 0.0 to 2.0/h for TI, and 0.0 to 1.0/h for *cis*-isomers. Their values after the division into 5 equidistant intervals as well as the corresponding point classifications are given in Table 1. A clear example for CCS graphic interpretation for the most simple model of reaction scheme is shown in Fig. 1a; in Fig. 1b they are given for the most intricate model of reaction scheme, showing the formation of *cis*- and *trans*-isomers as well as non-subsequent-parallel transformations of individual FA in the course of the PCH process (area in the thick frame represents CCS real value, area in the thin frame — theoretical — 100% CCS).

Table 1. Equidistance ranges of intervals of fatty acids rate constants with corresponding integer point classifications that are considered a basis for graphical and numerical interpretations of selectivity complex values (CCS)

Rate constants									
Trienes (k ₃)		Dienes (k ₂)		Monoenes (k ₁)		<i>cis</i> -Isomers (k _c)		<i>trans</i> -Isomers (k _t)	
Equidistances of the interval	CBK++	Equidistances of the interval	CBK++	Equidistances of the interval	CBK++	Equidistances of the interval	CBK++	Equidistances of the interval	CBK++
0.0—0.8	1	0.0—0.4	1	0.0—0.3	5	0.0—0.2	1	0.0—0.4	1
0.8—1.6	2	0.4—0.8	2	0.03—0.06	4	0.2—0.4	2	0.4—0.8	2
1.6—2.4	3	0.8—1.2	3	0.06—0.09	3	0.4—0.6	3	0.8—1.2	3
2.4—3.2	4	1.2—1.6	4	0.09—0.12	2	0.6—0.8	4	1.2—1.6	4
3.2—4.0	5	1.6—2.0	5	0.12—0.15	1	0.8—1.0	5	1.6—2.0	5

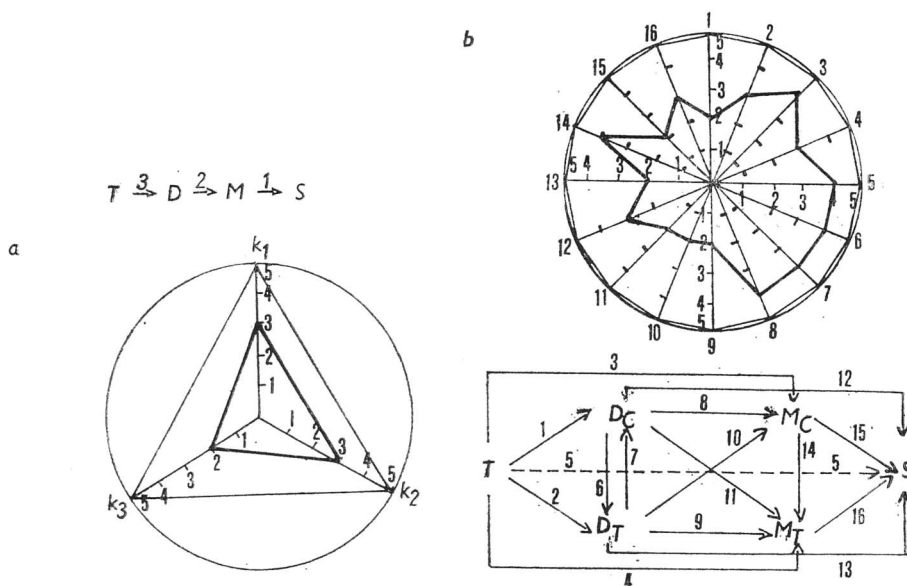


Fig. 1. Polygonal diagrams for the possibility of a graphical depiction of selectivity complex values (CCS) of hydrogenated triacylglycerols. a — Depiction of the simplest reaction sequence expressible in a triangular diagram. b — Depiction of the most intricate reaction scheme of hydrogenation, showing both isomerizing and non-subsequent (parallel) transformations of fatty acids expressible in a 16-angular diagram. D — dienes, D_c — dienes *cis*-, M_c — monoenes *cis*-, M — monoenes, D_t — dienes *trans*-, M_t — monoenes *trans*-configuration, S — saturates. Numbers given in reaction sequences are rate constants of the pertinent fatty acids. Numbers inside the polygons are integer point classifications of equidistances according to Table 1. Numbers in the apexes of polygonal diagrams again express the pertinent rate constant of the chosen reaction scheme.

An example of a real graphic depiction of sample CCS in time dependence of sunflower oil hydrogenated industrially, expressed according to the extended scheme of the reaction model [33], when the selected polygon was a quadrangle, is shown in Fig. 2. A graphic representation of CCS of rape oil hydrogenated both industrially with a commercial catalyst and in laboratory with an imported Nysel DM-3 catalyst, expressed according to the extended reaction scheme [33] and interpreted by means of a pentagonal diagram, is given in Fig. 3.

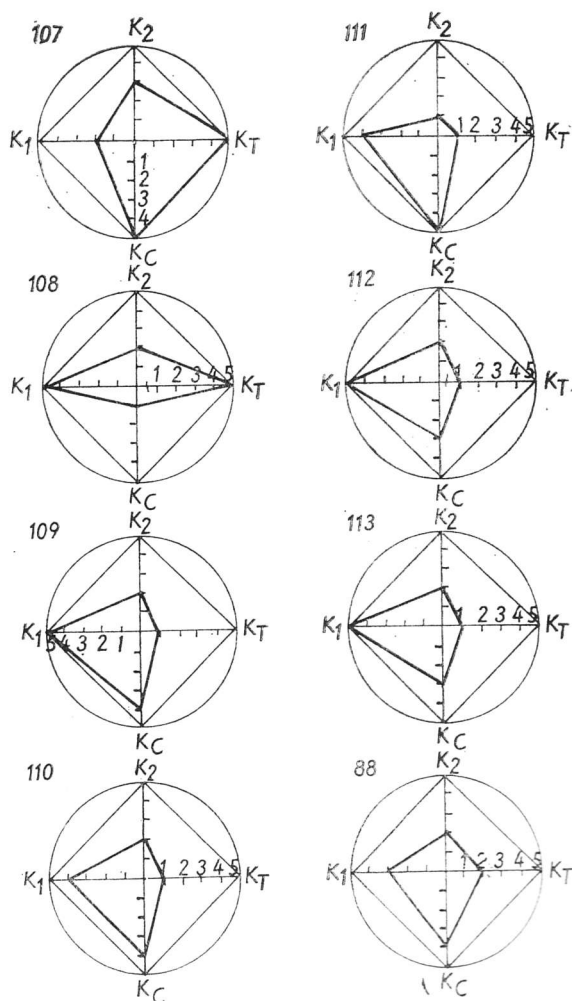


Fig. 2. Selectivity complex values and their changes due to time dependence of hydrogenated sunflower oil, expressed by a quadrangular diagram. Time characteristics of hydrogenated samples and quantitative relations corresponding to the generated configurations are given in Tables 2 and 4.

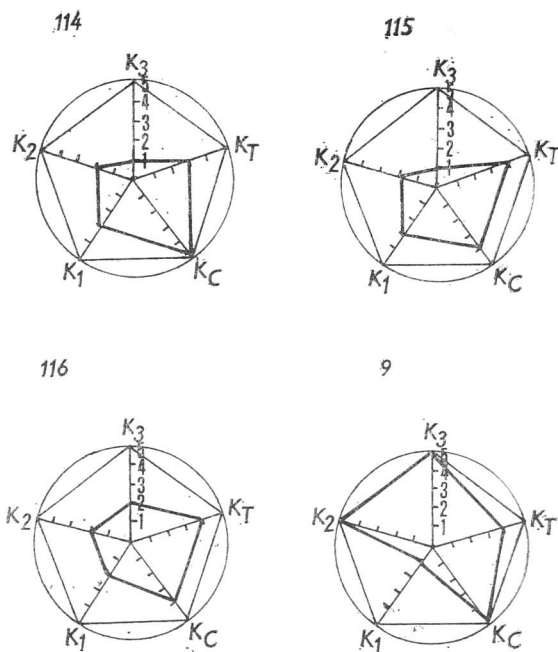


Fig. 3. Selectivity complex values and their changes due to time dependence of hydrogenated rape oil, expressed by a pentagonal diagram. Time characteristics of hydrogenated samples and quantitative relations corresponding to the generated configurations are given in Tables 2 and 4.

In the figures we can see that the connecting lines of qualified point values of actually measured rate constants form a polygonal configuration, which already from the qualitative aspect makes it evident that the smaller and more irregular it is in comparison with the original one the smaller and more differentiated will be the CCS value. Additional auxiliary tables for a simplified determination of "c" legs in quadrangular, pentagonal and hexagonal diagrams are given in Table 2. CATSEL-programme computed values of specific reaction rates of individual FA of selected samples of hydrogenated sunflower and rape oils, and their corresponding point classification according to specified conditions of interval equidistances from Table 2, are summarized in Table 3. Quantitative expression of CCS is possible using the given graphic configurations in the three ways as follows:

1. the sum of maximum theoretical point values of individual FA is considered a 100% CCS: its ratio to the sum of actual point values is the searched for percentual CCS value;

2. by means of the relation: $\% \text{ CCS} = c \cdot 10^2 / O$ (O — the circumference of the originally chosen polygon);

Table 2. Specific reaction rates of FA in hydrogenated sunflower and rape oils, integer classification values and corresponding selectivity complex values according to Table 1

Sample No.	Time PCH [min]	Specific reaction rates of UnFA (l/h)					Rate constants class. val.					Real point values %CCS (1)	Real point values % CCS (2)	
		k ₃	k ₂	k ₁	k _c	k _t	k ₃	k ₂	k ₁	k _c	k _t			
Sunflower oil	107	30	—	0.913	0.094	1.988	1.687	—	3	3	2	5	70.40	91.91
	108	60	—	0.494	0.015	0.169	1.900	—	2	5	1	5	74.08	71.41
	109	90	—	0.430	0.001	0.636	0.325	—	2	5	4	1	64.18	63.64
	110	120	—	0.454	0.042	0.649	0.188	—	2	4	4	1	58.29	53.03
	111	150	—	0.394	0.014	0.638	0.099	—	1	5	4	1	60.24	53.03
	112	180	—	0.432	0.009	0.532	0.082	—	2	5	3	1	58.74	53.03
	113	210	—	0.411	0.027	0.500	0.075	—	2	5	3	1	58.74	53.03
	88a	30	—	0.793	0.062	0.744	0.730	—	2	3	4	2	56.24	53.03
Rape oil	9b	45	5.188	1.887	0.288	0.893	1.476	5	5	1	5	4	88.88	92.62
	114	180	0.615	0.480	0.084	0.835	0.118	1	2	3	5	3	60.45	50.61
	115	170	0.787	0.540	0.069	0.655	0.128	1	2	3	4	4	60.28	49.36
	116	160	0.882	0.464	0.920	0.718	0.148	2	2	2	4	4	50.36	49.38

a — Laboratory hydrogenation with commercial Ni catalyst.

b — Laboratory hydrogenation with Nysel DM-3 catalyst.

Table 3. Auxiliary table values for reading the "c" legs or areas of triangles enabling the calculations of selectivity complex values in polygonal diagrams

Leg		In a square		In a pentagon		In a hexagon	
"a"	"b"	"c" leg	Area	"c" leg	Area	"c" leg	Area
		[cm]	[cm ²]	[cm]	[cm ²]	[cm]	[cm ²]
5	5	7.0711	12.500	5.9131	11.9215	5.0000	10.8253
5	4	6.4031	10.000	5.3826	9.5372	4.5826	8.6603
5	3	5.8309	7.500	4.9979	7.1529	4.3588	6.4952
5	2	5.3852	5.000	4.7944	4.7686	4.3589	4.3301
5	1	5.0990	2.500	4.7951	2.3893	4.5826	2.1651
4	4	5.6568	8.000	4.7305	7.6297	4.0000	6.9282
4	3	5.0000	6.000	4.2169	5.7223	3.6055	5.1962
4	2	4.4721	4.000	3.8973	3.8148	3.4641	3.4641
4	1	4.1231	2.000	3.8203	1.9074	3.6055	1.7321
3	3	4.2426	4.500	3.5479	4.2917	3.0000	3.8971
3	2	3.6056	3.000	3.0646	2.8612	2.6457	2.5981
3	1	3.1622	1.500	2.8628	1.43057	2.6457	1.2990
2	2	2.8284	2.000	2.3652	1.90243	2.0000	1.7321
2	1	2.2360	1.000	1.9486	0.9372	1.72205	0.8661
1	1	1.4142	0.500	1.1826	0.47685	1.0000	0.4330

3. by means of the relation: $\% \text{ CCS} = P \cdot 10^2 / P_0 \cdot n$ (P — the area of the actually obtained polygon, P_0 — the area of the original polygon, n — three- to sixteen-sided polygon).

In the case of sunflower and rape oils, hydrogenated under different conditions and with different catalysts, the CCS values, graphically expressed in

Table 4. Comparison of quantitative data of selectivity complex values calculated by means of sum values of qualifications or circumferential and area relations of selected polygons

Sample No.		% CCS calculated by			Mean values	Differences [%]	
		sum values (1)	circum. values (2)	area values (3)		2—1	2—3
Sunflower oil	107	75.0	77.40	91.91	81.44	2.4	6.51
	108	65.0	74.08	71.41	70.16	9.08	2.67
	109	60.0	64.18	63.64	62.61	4.18	0.54
	110	55.0	58.29	53.03	55.44	3.29	5.26
	111	55.0	60.24	53.03	56.10	5.24	7.31
	112	55.0	58.74	53.03	55.60	3.74	5.71
	113	55.0	58.74	53.03	55.60	3.74	5.71
	88a	55.0	56.24	53.03	54.76	1.24	3.21
Rape oil	9b	80.0	88.88	92.62	87.17	8.88	3.74
	114	56.0	60.45	50.61	55.69	4.45	9.84
	115	56.0	60.28	49.36	55.21	4.28	10.92
	116	56.0	50.36	49.38	51.91	5.64	10.98
					$\varnothing = 4.68$	6.25	
					$\delta = 4.95$	9.99	
					$v_c = 105.8\%$	166.0%	

a — Hydrogenated 30 min with commercial Ni catalyst in laboratory. b — Hydrogenated 45 min with Nysel DM-3 catalyst in laboratory. \varnothing — mean values of difference, δ — relevant deviations, v_c — variation coefficients.

Figs. 2 and 3, are numerically expressed and compared in Table 4. From the table it is clearly seen that CCS values reflect most sensitively computations made according to Method 2, namely those obtained from proportionate, circumferential theoretical and actual selectivity values. These acquire the character of mean, most probable CCS values as far as sum and area possibilities of CCS quantification are concerned. Besides this, from the data in Table 4 it follows that the CCS values decrease in the course of PCH, further, that CCS of sunflower oil hydrogenated 30 min under laboratory conditions reaches the same value as when hydrogenated for 3.5 h under industrial conditions (i.e. when hydrogenation had finished), that the industrial hydrogenation of sunflower shows higher CCS values (by 10% approximately) than that of rape oil, and that the highest CCS has been obtained with the catalyst Nysel DM-3 in the case of laboratory hydrogenation after 45 min though it was rape oil. Advantages of the described CCS expression compared with those referred to in literature till now are as follows:

1. permanent and common recording of both the primary-additive and secondary-isomerizing hydrogenation reactions;

2. flexible and almost universal adaptability to any reaction model of the PCH process;

3. besides graphical interpretation, it also provides an easy and intelligible percentual quantitative value of CCS.

To this time, it is the determination of all rate constants indicated for the 16-angular diagram in the reaction model scheme (Fig. 1b) that remains an unsolved problem in our conditions. Approaches to the solution of this problem outlined in the work [33] seem to be promising.

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О возможности численно-графического способа выражения селективности гидрогенизированных жиров путем „комплексной оценки“

Резюме

Решалась возможность определения параметра селективности катализатора гидрогенизации, или же гидрогенизированных триацилглицеринов по новому способу. В противоположность существующим, в этом способе, наряду с первично-аддитивным типом учитывается одновременно и вторично-изомеризационный тип реакции гидрогенизации с возможностью выражения как „кумулятивно-комплексная селективность“ (ККС). Исходными для определения ККС являются простые, целочисленные классификации пяти значений эквидистантностей, на которые разделены диапазоны удельных скоростей реакций отдельных ненасыщенных жирных кислот. Это позволяет выразить ККС численно и графически. Для весьма наглядной графической интерпретации ККС использована адаптабельная полигональная система, способная охватить все виды растительных масел, или же модели реакций парциальной каталитической гидрогенизации с минимально тремя, а максимально шестнадцатью константами скорости, которые могут быть использованы в случае математического описания изомеризационных, а также непоследовательнопараллельных гидрогенизационных изменений отдельных жирных кислот. Графически выраженная ККС является точно квантифицируемой как процентное отношение площади (контура) исходного (теоретическая ККС) к площади (контуру) полученного полигона.

**Príspevok k možnosti graficko-numerického spôsobu vyjadrovania
selektivity hydrogenovaných tukov metódou „komplexnej hodnoty“**

Súhrn

Riešila sa možnosť určovania parametra selektivity hydrogenačného katalyzátora, resp. hydrogenovaných triacylglycerolov novým spôsobom. Oproti doterajším spôsobom sa v tomto popri primárno-adičnom type berie do úvahy súčasne aj sekundárno-izomerizačný typ hydrogenačnej reakcie s možnosťou vyjadrenia ako „kumulovaná komplexná selektivita (KKS)“. Výhodiskovými na určovanie KKS sú jednoduché, celočíselné klasifikácie 5 hodnôt ekvidistancií, na ktoré sú rozdelené rozsahy špecifických reakčných rýchlostí jednotlivých nenasýtených mastných kyselín. Tým sa umožňuje numericky i graficky vyjadriť KKS. Na veľmi názornú grafickú interpretáciu KKS sa používa adaptabilný polygonálny systém, schopný vystihnúť všetky druhy rastlinných olejov, resp. reakčné modely parciálnej katalytickej hydrogenácie s minimálne troma a maximálne šesťnástimi rýchlostnými konštantami, ktoré sa môžu uplatniť v prípade matematického opisu izomerizačných, ako aj nenásledných-súbežných hydrogenačných zmien jednotlivých mastných kyselín. Graficky vyjadrená KKS je exaktne kvantifikovateľná ako percentuálny pomer plochy (obvodu) pôvodného (teoretická KKS) k ploche (obvodu) získaného polygónu.