Calculation of the molar heat of formation of fatty acid triglycerides from the heat of combustion of vegetable oils

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Abstract

The results of the research on estimation the molar heat of formation (enthalpy) of model triglycerides found in natural oils and fats are presented. In this work a calculation method and calorimetric one were used. It was found that combustion heat values determined by separate methods are comparable; their difference was a maximum of 155 kJ/kg, and thus was significantly lower than the tolerance for the calorimetric method according to PN 86/C-04062.

Keywords: vegetable oils, enthalpy, triacylglycerols

Introduction

Hydroconversion of vegetable oils and/or animal fats to bio-hydrocarbons is a process known to all engineers involved in the problem of producing liquid biofuels. The success of the Neste Oil company, which developed and implemented the MExBTL process on an industrial scale, as well as actions taken following its example by other leading companies in the industry, caused that many engine fuel producers are considering launching a similar process in their refinery. Taking into account the possibility of beginning the co-processing of vegetable oils / fats in Polish refineries in the near future, the subject of the thermal effect of the hydroconversion process is discussed [1].

The issue seems to be trivial only seemingly. Nevertheless, it is of key importance when it comes to the use of existing units for the implementation of co-processing. Hydroconversion of fatty oils is associated with a relatively high exothermic effect, which in practice leads to the formation of high temperature gradients and even to overheating the catalytic bed, for which existing units are not built [2]. The thermal effect can really cause a significant problem. It is evidenced by the fact that in 2007 in Parvoo (Finland) the first unit in the world according to NExBLT technology was launched. The thermal effect associated with the hydroconversion proved to be higher than anticipated, which caused the necessity to modify the reactor by introducing additional quench giving hydrogen as a cooling agent [2].

The relatively high thermal effect of the reaction is associated with strongly exothermic reactions of hydrooxidation, decarboxylation and decarbonylation of fatty acids, as well as hydrogenation of multiple bonds in fatty acid chains [3, 4]. The authors also pay attention to the occurrence of the strongly exothermic secondary methanation reaction during hydroconversion [3–5]. In the paper [6] the thermal effect of hydroconversion of 20% (V/V) mixtures of various vegetable oils with a liquid paraffin fraction was investigated. The thermal gradient accompanying the hydroconversion of these oils ranged from 5.5 to 9.2 ºC and was higher the more unsaturated fatty acids contained in the oil. The research was carried out on a laboratory scale using a 100 ml reactor. In work [7] an attempt was made to estimate the temperature gradient during co-processing of rapeseed oil with diesel oil fraction. It was found that this effect varies significantly depending on the assumptions made; whether the process in the liquid or steam phase is being considered. It was estimated at 26.6 ºC for a 20 (V/V) mixture of rapeseed oil in the liquid phase and 35.2ºC for a 30% (V/V). However, at 33.9 ºC for 20% (V/V) rapeseed oil in the steam phase and 46.3 ºC for 30% (V/V). In real conditions the process takes place in the liquid – steam phase [8]. According to Chen [8], the fraction with a boiling range of light vacuum oil (and thus slightly heavier than the diesel fraction) at 350 ºC, at a pressure of 5 MPa, is steamed in about 60%. On the other hand, the introduction of vegetable oil or animal fat into the crude oil derived naphtha fraction results in a reduction of the vaporization rate. According to [8], the pressure increase in the reactor leads to a decrease in the thermal effect, because the degree of vaporization is reduced.

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So far, research related to the development of the thermodynamic model of hydroconversion has been conducted in a limited way [9, 10]. It should be noted here that such a model requires the adoption of many variable assumptions depending on the conditions of the process as well as knowledge of thermodynamic data for the reagents present in the system, such as e.g. the heat of formation (enthalpy) of fatty acid triglycerides. An attempt to determine the molar heat of formation of model triglycerides of fatty acids occurring in vegetable oils obtained from plant seeds was made in the work [7]. In paper [9] an analysis of the thermodynamic aspect of the hydroconversion process was performed, taking into account all occurring reactions, primary and secondary, in connection with process conditions. In the paper [10] a thermodynamic model of stearic acid hydroconversion for standard conditions is presented, based on the results obtained in the paper [7].

This article presents the results of research on the development of a thermodynamic model of hydroconversion, starting from the experimental determination of the heat of formation of model fatty acid triglycerides by a different method than in the work [7]. The practical significance and application of these data for conducting the hydroconversion process in real conditions was also indicated.

Experimental

Assumptions of the hydroconversion model – molar heat of triglyceride formation

A hydroconversion model involving the heat of combustion of model triglycerides has been discussed in papers [6, 7]. According to this article [7], the heat of combustion is a measure of the chemical energy contained in the fuel. According to the definition in PN-86/C-04062, the heat of combustion is the amount of heat released during the complete combustion of a mass of fuel containing only carbon, hydrogen, oxygen, nitrogen and sulfur, in an atmosphere of oxygen, the products of combustion being: dioxide carbon, sulfur dioxide, gaseous nitrogen and liquid water, and starting materials and combustion products are in standard conditions.

One of the basic features of heat of combustion is its additivity [9–11]. The consequence of the additive heat of combustion is the fact, that in the case of two organic compounds with different enthalpy of formation, the total heat of combustion will be the sum of the shares of heat of combustion brought by each of these compounds.

Similar reasoning can be made for a system containing *n* components. In the case where we have a mixture of n known compounds, but with unknown enthalpies of formation, theoretically, it is possible to determine these parameters based on the heat of combustion, at least n different mixtures of these compounds.

Of course, in practice, the described method may have significant limitations resulting e.g. from the specific properties of given substances. However, if we are dealing with a homogeneous mixture of substances of similar structure, not significantly differing in physico-chemical properties, e.g. triglycerides of fatty acids, this method may be considered [6, 7].

Let's assume that a given vegetable oil is composed solely of triglycerides of two fatty acids having saturated hydrocarbon chains of different length (different number of carbon atoms) -R1 and -R2, where the R1 chain is shorter than the R2 one. According to the heat of additivity principle, it can be said that the molar heat of combustion [*Q*(*s*)] of a triglyceride consisting of three identical R1 residues will be lower than for an analogous triglyceride but containing three identical R2 residues (dependence 1):

$$Q(s)\ C_6H_5O_6(R1)_3 < Q(s)\ C_6H_5O_6(R2)_3 \qquad (1)$$

It is easy to see that the dependence (2) will also be met:

$$Q(s)\ C_6H_5O_6(R1)_3 < Q(s)\ C_6H_5O_6(R1)_2R2 < Q(s)\ C_6H_5O_6(R2)_2R1 < \\ < Q(s)\ C_6H_5O_6(R2)_3 \qquad (2)$$

The average molar heat of combustion of such a mixture will depend on the share of individual fatty acids in triglycerides. Therefore, for the sake of simplicity, it can be assumed that the above-mentioned oil consists exclusively of two types of triglycerides: containing only R1 residues or only R2 residues, the proportion between them being identical to the practically indicated ratio between R1 and R2 fatty acids. In other words, in the proposed model, the shares of individual acids in triglycerides correspond to the shares of model triglycerides with three identical acid residues.

These conditions also apply to oils consisting of triglycerides of n fatty acids, of different length and with different amounts of double bonds in the chain.

Taking into account selected highly refined natural oils obtained from plant seeds, according to the proposed model, it can be assumed that they are mixtures of model triglycerides with identical $C_{14} \div C_{24}$ acid residues (thirteen different compounds) in different proportions (Table 1). It is assumed that acids present in trace amounts can be omitted. Similarly, compounds present in oils in relatively small amounts (dyes, sterols, alcohols, triglycerides, free acids, etc.). You can additionally take action to remove at least some of the compounds – the constituent natural oils, which are not triglycerides or triglycerides with an unusual structure, which will be discussed later.

The heat of combustion of the mixture of model triglycerides will be virtually identical to the heat of combustion of real vegetable oil having an analogous sequence of fatty acids, provided that all (or almost complete) removal of other chemical compounds except triglycerides that could significantly influence the measurement of the heat of combustion. With thirteen different mixtures of these model triglycerides (or real oils with an analogous sequence of fatty acids), one can determine the heat of combustion of each of these compounds by solving a system of thirteen (at least) equations with thirteen unknowns. In practice, there is a fourteenth unknown related to the so-called triglycerides "unmarked", hence fourteen mixtures and fourteen equations appear in the calculations [7].

Table 1. Fatty acids found in the tested vegetable oils and model triglycerides, their derivatives

Fatty acid / triglyceride	Number of carbon atoms in the acid molecule: number of double bonds in the hydrocarbon chain	Formula of a model fatty acid triglyceride
Mirystic	14 : 0	$C_{45}H_{86}O_6$
Palmitic	16 : 0	$C_{51}H_{98}O_6$
Palmitoleic	16 : 1	$C_{51}H_{92}O_6$
Stearic	18 : 0	$C_{57}H_{110}O_6$
Oleic	18 : 1	$C_{57}H_{104}O_6$
Linoleic	18 : 2	$C_{57}H98O_6$
Linolenic	18 : 3	$C_{57}H_{92}O_6$
Arachidic	20 : 0	$C_{63}H_{122}O_6$
Eikozeic	20 : 1	$C_{63}H_{116}O_6$
Behenic	22 : 0	$C_{69}H_{134}O_6$
Erucic	22 : 1	$C_{69}H_{128}O_6$
Lignoceric	24 : 0	$C_{75}H_{146}O_6$
Nervonic	24 : 1	$C_{75}H_{140}O_6$

Experimental procedure

Four natural vegetable oils with a clearly differentiated fatty acid sequence were selected to make triglyceride "mixtures": hazelnut oil (N), linseed oil (L), grapeseed oil (G), rapeseed oil (R). The selection criterion was the possibly diverse composition of fatty acids in these oils. Mixtures of these have also been prepared:

Two-component:

N + L; N + G; N + R; L + G; L + R; G + R

Ternary:

N + L + G; L + G + R; N + G + R

Quaternary:

N + L + G + R

Before determining the heat of combustion of oils and their mixtures by calorimetric method according to PN 86/C-04062, as well as before determining the composition of fatty acids present in triglycerides by the method according to PN-EN ISO 5508 and PN-EN ISO 5509, oil samples natural ones were refined according to the procedure described in work [7].

The purpose of refining was to remove solid oil components (solid residues after pressing), sterols, dyes (e.g. carotene), alcohols and possible mono- and triglycerides of fatty acids, free acids, i.e. substances that could potentially increase the mistake in determining the heat of combustion of oils. Because all of these compounds are characterized by relatively high polarity, bleaching earth was used to remove them. The effectiveness of this operation has been confirmed in IR studies.

The compositions of individual oils (N, L, G, R) were determined with an estimated tolerance of approximately (± 0.3%). For acids with a low content (less than 1%) this caused a significant mistake. In order to limit the influence of this factor, each determination was performed twelve times and after removing the extreme determinations, the average content was adopted.

Oil mixtures were prepared by weight, determining the mass of oils and the entire mixture on an analytical scale. Efforts were made to mix the oils in an equal weight ratio. Knowing the composition of fatty acids in individual oils and the exact masses of individual oils in mixtures, the content of individual fatty acids in these mixtures was calculated. These contents, for individual oils as well as their mixtures, are given in Table 2.

Ultimately, 14 samples consisting of fatty acid triglycerides (four individual vegetable oils, six two-component mixtures of these oils, three ternary and one four-component) were available.

According to the presented assumptions, refined natural oils and their mixtures were considered to be mixtures of model fatty

Table 2. The content of fatty acids in triglycerides of selected natural oils and their mixtures after refining. Average values for 12 determinations are given (after rejecting extreme values), % (m/m)

Model triglycerides	Hazelnut oil (N)	Lineseed oil (L)	Grapeseed oil (G)	Rapeseed oil (R)	N+L	N+G	N+R	L+G	L+R	G + R	N + L + G	L + G + R	N + G + R	N+ L + G + R
Mirystic	0.03	0.05	0.05	–	0.04	0.04	0.02	0.5	0.03	0.03	0.04	0.03	0.03	0.03
Palmitic	5.1	5.8	6.8	4.5	5.45	5.95	4.8	6.3	5.15	5.65	5.9	5.7	5.47	5.55
Palmitoleic	0.23	–	0.2	0.2	0.12	0.22	0.22	0.1	0.1	0.2	0.22	0.14	0.21	0.16
Stearic	1.9	0.1	3.9	1.8	1.0	2.9	1.85	2.0	0.95	2.85	1.97	1.94	2.54	1.92
Oleic	76.18	3.3	18.1	63.0	39.75	47.14	69.59	10.7	33.15	40.55	32.53	28.14	52.43	40.15
Linoleic	15.7	15.6	69.2	18.7	15.65	42.45	17.2	42.4	17.15	43.95	33.5	34.5	34.5	29.8
Linolenic	0.15	71.3	0.2	7.4	35.75	0.08	3.78	35.75	39.35	3.8	23.89	26.3	2.58	19.76
Arachidic	0.1	1.8	0.15	0.6	0.95	0.12	0.35	0.98	1.2	0.38	0.69	0.85	0.28	0.67
Eikozeic	0.16	0.3	0.27	1.7	0.09	0.22	0.93	0.29	1.0	0.98	0.25	0.76	0.71	0.61
Behenic	–	–	0.02	0.4	–	0.01	0.2	0.01	0.2	0.21	–	0.14	0.14	0.1
Erucic	–	–	–	1.3	–	–	0.65	–	0.65	0.65	–	0.44	0.44	0.33
Lignoceric	–	0.2	0.6	0.2	0.1	0.3	0.1	0.4	0.2	0.4	0.27	0.34	0.27	0.25
Nervonic	–	0.6	–	0.1	0.3	–	0.05	0.3	0.35	0.05	0.2	0.24	0.04	0.18
Unidentified	0.45	0.95	0.51	0.1	0.8	0.47	0.26	0.27	0.52	0.39	0.54	0.48	0.36	0.49

acid triglycerides (Table 2). Thus, the mass fractions of individual fatty acids in triglycerides of natural oils corresponded to the mass fractions of these model triglycerides in model natural oils.

A system of equations was created (their number was equal to the number of oils and mixtures used in the study – in this case = 14) with fourteen unknowns in which the coefficients for individual variables were weight percentages of individual fatty acids (Table 2). On this basis, in turn, a fourteenth-degree matrix was created from which the values of individual variables were determined. The calculation method has been comprehensively presented in the work [7], hence it is not discussed in detail here. Attention has been paid to several selected aspects. Appropriate confidence intervals [7] as well as limit values [7] were determined for variables, and then it was checked to what extent the calculated calorific values of individual oils were within the tolerance. The task required taking variable free words (within the appropriate confidence intervals), and then checking whether the obtained solution of the matrix is correct (whether all obtained values of the variables are within the accepted confidence intervals). Because the task was quite difficult, MathCad was used to solve it.

The last part of the experiment was checking the usefulness of the developed model for calculation of combustion heat of natural oils without an initial refining. This check consisted in a proportional addition of the heat of combustion brought in, according to the principle of additivity, by individual model triglycerides. Three natural vegetable oils were selected for this purpose: soybean oil, olive oil and sesame oil. Refined and unrefined samples of these oils were used in this study.

Results and discussion

For the input data, variable values within the respective confidence intervals were obtained. Proposed on the basis of calculations of molar heat of combustion of individual model triglycerides and molar enthalpies of formation are given in Table 3. It should be said that in the literature generally no data on the molar heat of triglyceride formation of fatty acids. This limits the possibility of a wide discussion, as there is very little work on this subject.

For comparison, the values of molar heat of triglyceride formation obtained in the work were cited [7].

What are the calorimetric values of the heat of combustion of individual vegetable oils calculated and calculated from the system of equations? These data are presented in Table 4 and also illustrated in Figure 1. They were compared with the data obtained in the paper [7].

Considering calorimetrically determined heat of combustion of vegetable refined oils and comparing them with calculated values, very good agreement of these results was observed (Table 5). The obtained results testified to the good precision of calorimetric

Table 3. Calculated heat of combustion and molar enthalpies of model triglycerides of fatty acids in natural refined oil

Model triglyceryde	Chemical formula	Molar combustion heat [kJ/mol]	Molar heat of formation ΔH0 [kJ/mol] according to [7]	Molar heat of formation ΔH0 [kJ/mol]
Mirystic	$C_{45}H_{86}O_6$	27710.6	−2252.5	**−2296.6**
Palmitic	$C_{51}H_{98}O_6$	31638.1	−2385.1	**−2411.7**
Palmitoleic	$C_{51}H_{92}O_6$	31187.1	−2048.8	−2039.2
Stearic	$C_{57}H_{110}O_6$	35726.6	−2520.2	**−2434.8**
Oleic	$C_{57}H_{104}O_6$	35183.0	−2216.9	**−2180.6**
Linoleic	$C_{57}H_{98}O_6$	34507.1	−1979.6	**−1930.3**
Linolenic	$C_{57}H_{92}O_6$	34030.6	−1601.5	−1556.2
Arachidic	$C_{63}H_{122}O_6$	39511.5	−2801.5	**−2726.5**
Eikozeic	$C_{63}H_{116}O_6$	38722.3	−2551.0	**−2658.5**
Behenic	$C_{69}H_{134}O_6$	43311.5	−2924.3	**−3004.7**
Erucic	$C_{69}H_{128}O_6$	42896.5	−2620.4	**−2561.5**
Lignoceric	$C_{75}H_{146}O_6$	47264.3	−3010.3	**−3129.1**
Nervonic	$C_{75}H_{140}O_6$	46661.4	−2786.5	**−2873.9**

determinations, much higher than the uncertainty (± 318 kJ/kg) allowed by the PN 86/C-04062 standard. Calculated on the basis of the system of heat equations for the formation of model triglycerides of fatty acids, they were referred primarily to the results obtained in the work [7], in which a dozen or so natural vegetable oils (hazelnut, sesame, linseed, grape, pumpkin seed, poppy seed, avocado, apricot kernel, macadamia, olive oil, corn, soybean, sunflower, rice, rapeseed) were used as a standard. It was found that the results obtained in both works are similar. A comparison of these results is given in Tables 4 and 5.

Table 4. The heat of combustion of natural refined oils determined experimentally and obtained as a result of substitution of calculated values of heat into a system of equations

Vegetable natural oil	Combustion heat determined calorimetrically [kJ/kg] ± 318 kJ/kg	Combustion heat calculated [kJ/kg]	Combustion heat calculated according to [7] [kJ/kg]
Hazelnut oil (N)	39796	39700	39611
Lineseed oil (L)	39298	39344	39113
Grapeseed oil (G)	39474	39420	39338
Rapeseed oil (R)	39545	39660	39580
N+L	39402	39291	–
N+G	39643	39560	–
N+R	39599	39680	–
L+G	39335	39271	–
L+R	39566	39411	–
G+R	39487	39540	–
N+L+G	39520	39427	–
L+G+R	39477	39414	–
N+G+R	39642	39594	–
N+L+G+R	39515	39486	–

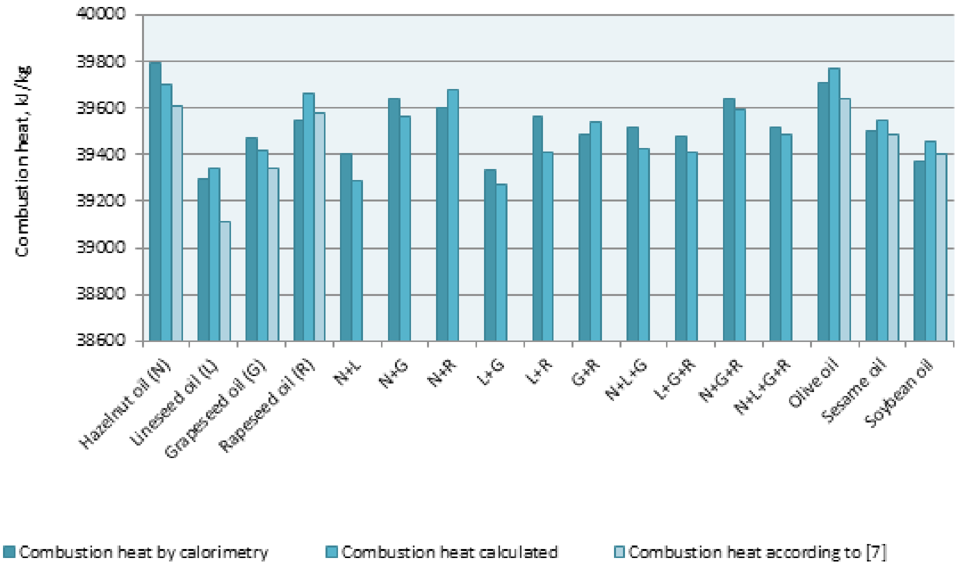

Figure 1. Comparison of the heat of combustion for selected natural refined oils and their mixtures; values determined calorimetrically and obtained as a result of substitution of calculated values of heat to the system of equations

The calculated heat of palmitin triglyceride formation was also compared with the result obtained for the reference compound. Palmitic triglyceride (Sigma-Aldrich CAS reagent: 555-44-2) was available. The heat of combustion of this compound was calorimetrically determined at 39329 kJ/kg, i.e. 31699.4 kJ/mol. The molar heat of formation of this compound was determined at −2425.3 kJ/mol (molar heat of formation calculated: −2411.7 kJ/mol). These values were therefore very similar. However, it should be remembered that this reagent had a degree of purity of about 95% (according to the Sigma-Aldrich specification) and contained admixtures of other triglycerides.

The obtained results were also compared with the works [6, 9, 10]. It was found that they are consistent with the previous data. In work [6], the heat of triglyceride formation was considered in the context of partial reactions of lipid hydroconversion. In works [9] and [10], the directions of glyceride transformations during catalytic hydroconversion and the thermal effects accompanying this process were investigated.

The calculations were verified for vegetable oils and their mixtures, comparing their heat of combustion obtained by two separate methods: based on the content of model triglycerides and calorimetrically. It was found that the heat of combustion values determined by these methods are comparable; their difference was a maximum of 155 kJ/kg, and therefore was definitely lower (twice) than the allowable uncertainty value for the calorimetric method according to PN 86/C-04062 (± 318 kJ/kg), but also significantly lower than the maximum difference obtained at work [7], i.e. 254 kJ/kg. Greater differences were obtained between the values of heat of combustion of triglycerides – calculated and calorimetrically determined than for the method described in this paper, in which only four oils were used. The key parameter determining the precision of the calculations was the accuracy of the determination of fatty acid composition in individual oils. On the other hand, calorimetrically determined heat of combustion was of secondary importance in this case, because the algorithm used to calculate the value of heat of combustion for individual triglycerides in the course of calculations estimated calorimetrically determined values according to imposed assumptions (discussed in the testing methodology). It should be noted that the determined heat values of the combustion of vegetable oils, theoretically, could be at almost the same level for most samples, taking into account the uncertainty of the methodology according to PN 86/C-04062. In fact, the maximum difference between the obtained heat of combustion values of all vegetable oils and their mixtures was 498 kJ/kg. On the other hand, the difference was greater than 318 kJ/kg for only three samples, while the number of all samples was fourteen.

Estimating the uncertainty of the determined heat values for the formation of model triglycerides is very important because of the usefulness of these parameters to develop a thermodynamic model of hydroconversion [9, 10]. Such estimation was carried out in work [7] for the value of heat of creation determined for the methodology using fourteen vegetable oils. Referring to the methodology described in [7], as well as to the methodology of this paper, it was found that the uncertainty of the determined values is primarily affected by the accuracy of the determination of fatty acid composition in triglycerides, and to a lesser extent the accuracy of the determination of the heat of combustion. Initial refining of samples and the use of average values for calculations, from several measurements, improves precision [7]. It should be noted that the poor precision of the trace fatty acids in vegetable oils, below 1% (e.g., lignoceric, behenic, nervonic acid) carries a high risk of mistake. Taking into account the obtained results, the measurement uncertainty in determining the heat of formation of model triglycerides was estimated to be less than ± 5%, which for the molar heat of formation of 2000 ÷ 3000 kJ/mol is ± (100 ÷ 150) kJ/mol. This result was similar to the one in [7].

The last part of the discussion was the assessment of the usefulness of the presented method for estimating the heat of combustion of vegetable oils other than those used to determine the heat of combustion of triglycerides, in connection with the assessment of the effect of refining these oils with JELTAR 300 bleaching earth on their heat of combustion. For selected vegetable oils: soybean oil, sesame oil and olive oil, good compliance of the calculated heat of combustion with calorimetrically determined heat was found (Table 5). For the tested oils, the differences found did not exceed 93 kJ/kg. The obtained results could therefore indicate a small impact of the initial refining of vegetable oils on the estimation of the heat of combustion using the accounting method.

Table 5. Heat of combustion of selected natural oils, pre-refined and not refined, determined calorimetrically in comparison to calculated value

Vegetable natural oil	Combustion heat (oils unrefined) [kJ/kg] ± 318 kJ/kg	Combustion heat (oils refined) [kJ/kg] ± 318 kJ/kg	Combustion heat calculated [kJ/kg]
Olive oil	39706	39799	39768
Sesame oil	39504	39525	39550
Soybean oil	39372	39391	39458

Summary and Conclusions

The molar heat of formation of model fatty acid triglycerides contained in natural vegetable oils was calculated with good accuracy. It was found that combustion heat values determined by separate methods are comparable; their difference was a maximum of 155 kJ/kg, and thus was significantly lower than the tolerance for the calorimetric method according to PN 86/C-04062. These data, so far, have generally not been available in the literature to this extent. The molar heat values of the model formation of fatty acid triglycerides determined in the course of this work constitute an important contribution to the development of the thermodynamic model of hydroconversion. Based on the molar heat values determined for model triglyceride formation, the heat of hydroconversion of these compounds can be estimated.

The presented method also allows to estimate, with high probability, the heat of combustion of other vegetable oils, which was carried out for three selected oils: olive oil, soybean oil and sesame oil, obtaining very good compliance with calorimetrically determined values. The effect of the initial refining was assessed as negligible.

Based on the determined heat of combustion, the molar heat of model triglyceride formation was calculated. The differences related to the uncertainty of their determination was estimated at about 100–150 kJ/mol.

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