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DEVELOPMENT OF A DSC METHOD FOR DETERMINATION OF CERTAIN TECHNOLOGICAL PARAMETERS OF MARGARINE AND MIXED-FAT SPREAD

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Nutritional-physiological research of near past decades had established the real nutritional value of fats and oils. In the former theory the nutritional value of fats and oils is influenced mainly by the rate of saturated/unsaturated fats. It was ruled out, and positive, inert or risk physiological effect of every single fatty acid had been established. The health-care effect of omega-3 fatty acid mainly by the favourable (<3:1) rate of omega-6/omega-3 was established, as inert was concerned the saturated C_{16} fatty acid and the maximal amount of trans-fatty acids carrying health risk in fats was legally regulated in some countries. These nutritional-physiological requirements were mainly fulfilled by margarine producers and the elementary fats were selected in such a way that they should meet these requirements.

Our method helps to the producers to quickly determine the amount of the liquid and solid fat at certain temperature and/or to adjust the technological temperature parameters. The main steps of our method are: a./ determination of cooling rate (K min^{-1}) of the crystallizer device; b./ determination of the rate of liquid/solid fat at 10°C temperature. This value is used for the determination of the rate of fats and oils as a function of technology and required consistency firmness (spread ability); c./ determination of the temperature from the cooling curve where the crystallization of most part of the fat has finished. This value is used for the determination of outlet temperature parameter of product coming out from the crystallizer device for margarines or mixed-fat spreads with water-in-oil system.

Keywords: *crystallisation, DSC, fat (saturated/unsaturated), margarine, nutrition*

Introduction

In the second half of 20th century the nutrition biological estimation of dietary fats was worldwide influenced by lipid-theory launched by Keys in 1954 [1]. According to this, first of all the saturated fatty acids, and secondly the cholesterol content were blamed for arteriosclerosis and consequently for high blood pressure, and finally for heart attack and stroke. Among natural lipids saturated fatty acids are mainly contained in that of animal origin, in order of succession tallow, butter and lard of bacon pigs, from vegetable origin lipids in palm and palm kernel fat and coconut fat. Both non-professional and professional (scientific) public opinion could be influenced by the lipid-theory uniquely in the history of mankind and science, respectively.

In three decades following 1960 the judgement of lipid-theory changed a little bit, but there were not significant scientific findings which could prevent the practical spreading of lipid-theory of Keys. Since the beginning of 90s the number of research has increased which dealt with many-sided and exact determination of physiological effects of different fats, fatty acids and fatty acid groups. Fortunately, only the smaller part of the concerning research is animal experiment, the main part is human clinical examination [2]. The research findings have been internationally accepted after more than a decade, and the most significant results can be summarized as follows.

First of all, it has been proved that the effect of different fatty acids on lipid profile of blood is not the same. The so-called short carbon chain (below 10) fatty acids are neutral, or have a cholesterol and triglyceride decreasing effect, do not create depot fat, in clinical practice they are good for slimming cure (e.g. coconut fat), from them butyric acid (C4:0) has definitely an anticarcinogenic effect. The long carbon chain stearic acid (C18:0) is at least neutral, but rather decreases cholesterol and triglyceride level. From the group between the above two groups the myristic acid (C14:0) remained undoubtedly bad, while palmitic acid (C16:0) is in some cases damaging, or neutral,

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and lauric acid (C12:0) is beyond the processes, a ‘silent observer’ [3].

In some fats, first of all in milk fat, five bioactive components (conjugated linoleic acid=CLA, sphyngomyelin, butyric acid, etherlipids, vitamin A and β-carotene) are found [4], that definitely hinder the process of carcinogenesis, metastasis, and are also efficient therapeutically. A good example for this is CLA, which became one of the components of human chemotherapeutical agents [5]. It is also proved that if the ratio of omega-6 to omega-3 fatty acid is 2:1, then it is optimal and provides an antiatherogenic effect [6].

The greatest breakthrough was the many-sided clearing up of the physiological role of trans fatty acids (TFA) [7]. A great number of human clinical examinations showed that trans fatty acids were incomparably more harmful for lipid profile of blood than the fats not containing trans fatty acids but rich in saturated fatty acids (SAFA) [8]. This is why, on a worldwide scale, the attention was drawn instead of fats rich in saturated fatty acids to the hydrogenated vegetable fats rich in TFA.

In Europe Denmark was the first country, where from 1 July 2003 only foods can be distributed in fat of which the TFA-content is below 2% that means a value below 1% in ratio of energy.

In our research we intend to help the production of margarines with TFA-content below 2% by elaboration of two quick methods. By using them the amount of liquid and solid fats can be determined at a given temperature, and the temperature can be selected at which the main part of fat blend used for production of margarine or mixed-fat spread will not be crystallized at cooling rate applied in margarine production.

At elaboration of the methods the calorimetric measurement was taken into consideration [9–16], by the help of which earlier we have found a relationship between the crystallization of butter fat and its texture [17], and between melting of butter fat and its spread ability [18, 19].

Experimental

Materials and methods

Fats

To elaborate the methods, two fats with a higher melting point (above 10°C) having TFA-content below 2% were taken into consideration as a model, which are first of all used by producers of margarines and mixed-fat blends. These are the hardened palm oil (Goldpack, the Netherlands) and milk fat. The milk fat was obtained from butter distributed in the market (Mizo butter, Hungary) in such a way that it was melted at 60°C, then centrifugated at the same temperature at 6000 rpm and the separated milk fat was dehydrated at 105°C for an h.

Crystallisation

In our experiments to determine the cooling rate an Armfield FT25 BP type experimental-scale crystallizer was used. On the one hand, the useful volume of its different units was measured, on the other hand, by margarine and mixed-fat spread productions the pump output, the inlet and outlet temperatures were determined at which the products could be made. From these parameters the cooling rate was calculated.

DSC measurements

For the calorimetric measurements in temperature range of –20 to 60°C a SETARAM Micro DSC-II, and in –60 to 60°C range a METTLER Toledo DSC 821^e calorimeters were used. The mass of samples was 200–500 mg, and ethyl-alcohol was used as a reference. The heating and cooling rate was 0.3 K min^{-1}, it was used also in further experiments, and to determine the crystallization temperature a cooling rate was used that was determined by the crystallizer.

Table 1 Data measured and obtained during the experiments to determine the necessary cooling rate

Crystallizer unit’s				
Denomination		Diameter/cm	Length/cm	Useful volume/cm^3
Rapid cooler	external	4.1	35	329
	inner	2.2		
Connecting tube		0.7	58	115
Crytallizer	external	4.3	26	1180
	inner	2.0		
Resting place		2.2	89	1353
Altogether				2977

Flow rate, v: 0.47 L min^{-1}; inlet temperature, T_1: 35°C; outlet temperature, T_2: 10°C

Results and discussion

The values measured to determine the cooling rate applied to calorimetric measurement of crystallization temperature adjustable in the production technology and the parameters obtained during the experimental plant examinations are contained in Table 1.

The cooling temperature to be applied at calorimetric measurements was calculated from the data of Table 1 as follows.

Definition of cooling constant:

$$t_{\mathrm{v}} = \frac{V}{v} \tag{1}$$

where: t_{v}=cooling constant for crystallizer, [min], V=total volume of crystallizer=2.98 L, v=flow rate=0.47 L min^{-1}.

Definition of cooling rate for crystallisation:

$$v_{\mathrm{t}} = \frac{t_1 - t_2}{t_{\mathrm{v}}} \tag{2}$$

where: v_{t}=cooling rate, K min^{-1}, t_1=inlet temperature=35°C, t_2=outlet temperature=10°C.

Substituting (1) in (2) equation the final result is obtained:

$$v_{\mathrm{t}} = \frac{(t_1 - t_2)v}{V} \tag{3}$$

Substituting the proper values into Eq. (3) the cooling rate will be 3.9 K min^{-1}, in round off value, and at calorimetric measurements 4 K min^{-1} cooling rate should be used.

Eight DSC-curves are shown in order to elaborate the two calorimetric methods (determination of liquid/solid fat ratio at 10°C, determination of cooling temperature of margarine and mixed-fat spread). Melting (a) and crystallization (b) DSC-curves of

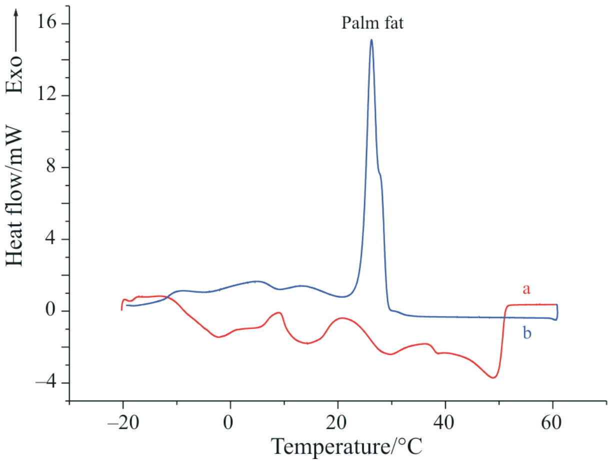

Fig. 1 a – Melting and b – crystallization DSC-curve of palm fat in –20 to 60°C temperature range at 0.3 K min^{-1} scanning rate

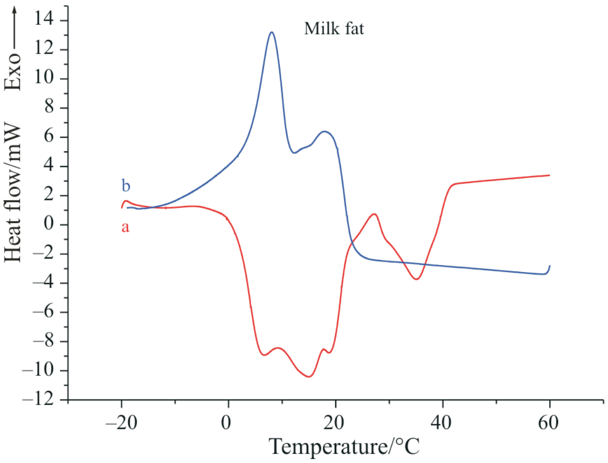

Fig. 2 a – Melting and b – crystallization DSC-curve of milk fat in –20 to 60°C temperature range at 0.3 K min^{-1} scanning rate

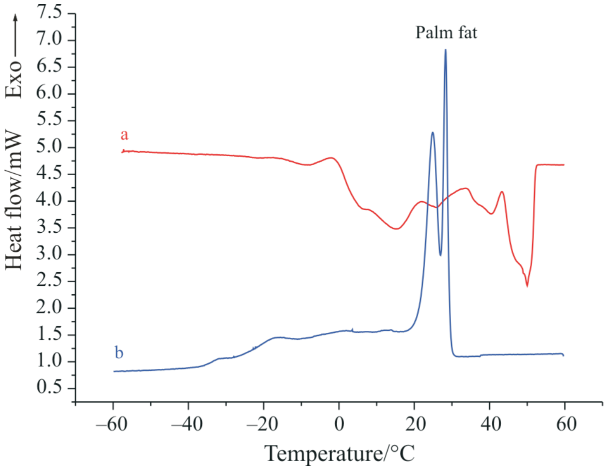

Fig. 3 a – Melting and b – crystallization DSC-curve of palm fat in –60 to 60°C temperature range at 4 K min^{-1} scanning rate

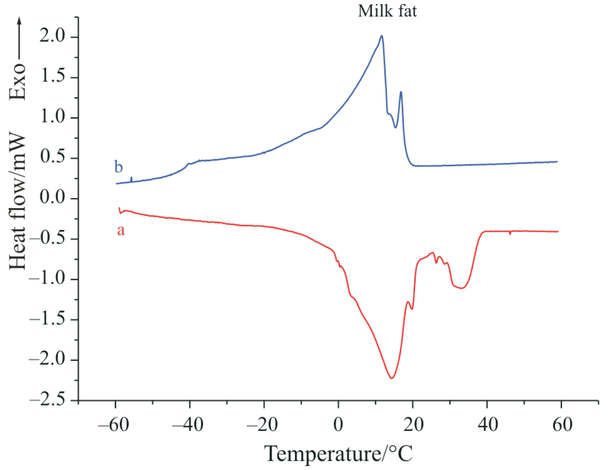

Fig. 4 a – Melting and b – crystallization DSC-curve of milk fat in –60 to 60°C temperature range at 4 K min^{-1} heating/cooling rate

palm fat (Fig. 1) and of milk fat (Fig. 2) from –20 to 60°C temperature range with 0.3 K min^{-1} heating and cooling rate, as well as of palm fat (Fig. 3) and of milk fat (Fig. 4) from –60 to 60°C temperature range with 4 K min^{-1} heating and cooling rate are shown.

Analysing the DSC-curves the following statements can be made.

- Based on melting curves (3a, 4a) recorded in temperature range from –60 to 60°C it can be stated that below –20°C the melting is negligible.
- The melting curves recorded at different scanning rates (1a and 2a, 3a and 4a) are of different shape and it is obvious that the higher cooling rate has lower resolution.
- When the crystallization curves recorded at different scanning rates (1b and 2b, 3b and 4b) are compared, it can be stated that crystallization of fats (palm fat and milk fat) depends on cooling rate, and as a consequence in the case of quicker cooling the crystallization takes place at a lower temperature.

Conclusions

Based on calorimetric measurements two quick methods can be elaborated for determination of two production parameters of margarines and mixed-fat spreads, respectively, that are followings.

Determination of liquid/solid fat ratio of raw materials of margarines and mixed-fat spreads at 10°C

The aim of the examination is to determine the ratio of fats and oils serving as raw materials of margarines and mixed-fat spreads in order to guarantee the consistency firmness and spreadability of the finished product targeted. Raw materials were involved into examinations which obviously also contain solid fat components above 0°C. Those raw materials which contain aqueous emulsion phase too are melted at 60°C, separated by centrifugation at 6000 r.p.m. and the fat part is dehydrated at 105°C (1 h).

200–500 mg of raw materials are filled into the batch sample holders, and etanol is used as reference during the recording of melting DSC-curves in –20 to 60°C temperature range with 0.3 K min^{-1} heating rate. The recorded DSC-curve is divided into two parts; below 10 and above 10°C, then the areas under curves are measured, which are compared with the area under the whole curve and in such a way the percental fat ratio of liquid part below 10°C and solid part above 10°C could be determined. This ratio is 22.5% liquid below 10°C and 77.5% solid above 10°C in case of the examined palm fat. (The component being liquid below 10°C makes the consistency of the final product softer and the component which is solid above 10°C makes it firmer.)

Knowing the ratio of liquid and solid fat components, the ratio of raw materials can be determined in order to attain the consistency firmness and spreadability targeted.

Determination of cooling and outlet temperature of margarine and mixed-fat spread raw materials

The aim of the examination in the case of use of new fat blend (e.g. made according to the above description) is the quick determination of the optimal cooling temperature of the raw material. If the temperature is higher than the optimal one the product will be too soft leaving the producing equipment, in case of a lower compared to the optimal temperature there will be a risk of ‘freezing in’ and the producing line will be stopped.

200–500 mg of raw material fat blend is filled into the batch sample holders, and ethanol is used as reference during the recording of crystallisation DSC-curves in 60 and –60°C temperature range with the cooling rate characteristic for the producing equipment, that is calculated as follows.

Based on technical data of the producing equipment the inner product volume (V) is calculated, taking the generally used inlet (t_1) and outlet (t_2) temperatures and the average applied product flow speed (v), then by the help of Eq. (3) the cooling rate can be calculated that is used as cooling rate at recording the crystallization DSC-curve. In our case this value was 4 K min^{-1}, and the values of plant-scale producing lines do not differ significantly from it.

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