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DSC INVESTIGATIONS OF THE THERMAL CHARACTERIZATION OF EDIBLE FATS AND OILS

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ABSTRACT

Heat flux DSC was used for the investigation of the melting, crystallisation and oxidation of edible oils and fats. The influence of composition, content of water, production methods, aging and heat treatment is shown by the changed melting characteristics and the solid-liquid ratio. The melting peak for free water in emulsified fats disappears with aging. A high content of unsaturated fatty acids leads to a reduced oxidation stability and a typical exothermal peak between 150 and 220°C.

INTRODUCTION

Fat is an important part of all living beings and can be found in every plant and animal cell. Higher developed organisms are able to store fat as an energy resource. Furthermore, fat is important in its function as a carrier of taste as well as vitamins (A, D, E, and K) and as a resource for the "essential" fatty acids (e.g. linoleic acid).

Natural fats and oils are predominantly mixed triglycerides (esters from glycerin and three fatty acids) with saturated and unsaturated fatty acids with even carbon numbers between C4 and C24. The most well-known C18 fatty acids are stearic acid (saturated), and the unsaturated fatty acids: oleic acid (mono), linoleic acid (di) and linolenic acid (tri). Mainly vegetable oils contain a considerably high amount of mono- or poly-unsaturated fatty acids.

When considering edible fats, the consistency plays an important role in the quality of the products and in the taste and texture when being consumed. The consistency is closely connected to the solid-liquid ratio and the size of crystallites and therefore also with the characteristics of melting and recrystallisation. The DSC offers a simple possibility of investigating the characteristics of melting and freezing of fats. The influence of composition, content of water, production methods, aging and heat treatment can be clearly shown on the basis of DSC-investigations.

Fats are changed during storing and heat treatment by oxidation and decomposition forming free, low-molecular fatty acids (rancid taste). Unsaturated triglycerides can polymerise in oxidising conditions to macromolecular solid products, which find application in paints and lacquers (e.g. linseed oil). The thermal stability of selected fats is shown by oxidation experiments in the DSC.

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EXPERIMENTAL

A heat flux DSC, NETZSCH model DSC 200, was used for the investigations on vegetable and animal fats and oils (Fig. 1). The samples were sealed in Al crucibles for melting and recrystallisation experiments (sample weight about 5 to 30 mg). The oxidation tests were carried out in open Al crucibles with a sample weight of 1 to 8 mg and a heating rate of 10 K/min up to 450°C in air.

All samples were commercial products of unknown condition of freshness.

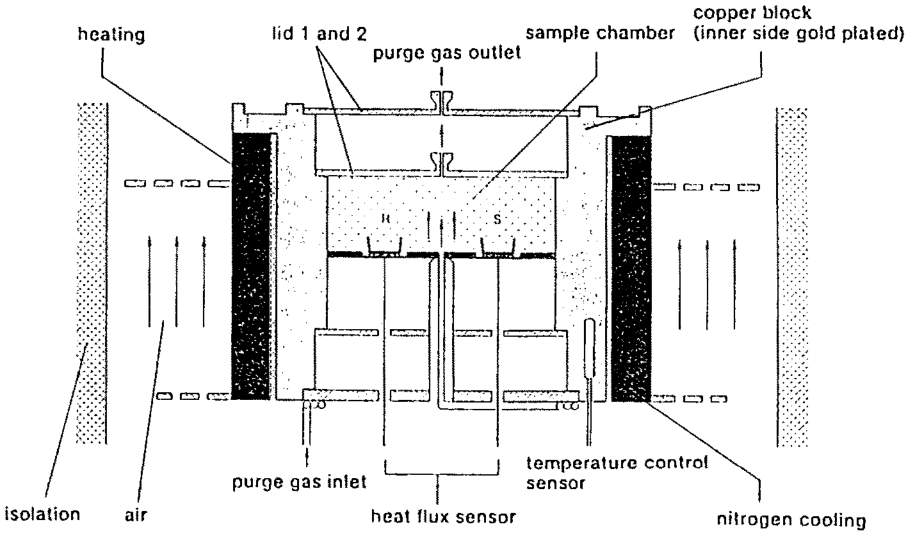

Fig. 1 Heat flux DSC, schematic

RESULTS AND DISCUSSION

By definition edible oils are liquids at ambient temperature. Figure 2 shows the typical melting curves for 4 vegetable oils obtained by heating with 5 K/min after initially cooling to -100°C. The melting range of these oils is -60 to +9°C. The melting enthalpy of the oils tested lies between 70 to 94 J/g.

Melting range and peak shape are the result of overlapping effects from composition (proportion of various fatty acids), polymorphism and thermal history.

Polymorphism can easily be detected in grape oil: after melting of the low-temperature modification at -45°C an additional modification crystallises. At -14°C (peak temperature) this modification melts in combination with an originally existing crystallite of the same kind (ref. 1). Thistle oil shows similar melting behaviour like grape oil, but an additional low-temperature melting peak at -80°C and crystallisation of a polymorph at -72°C (Fig. 3).

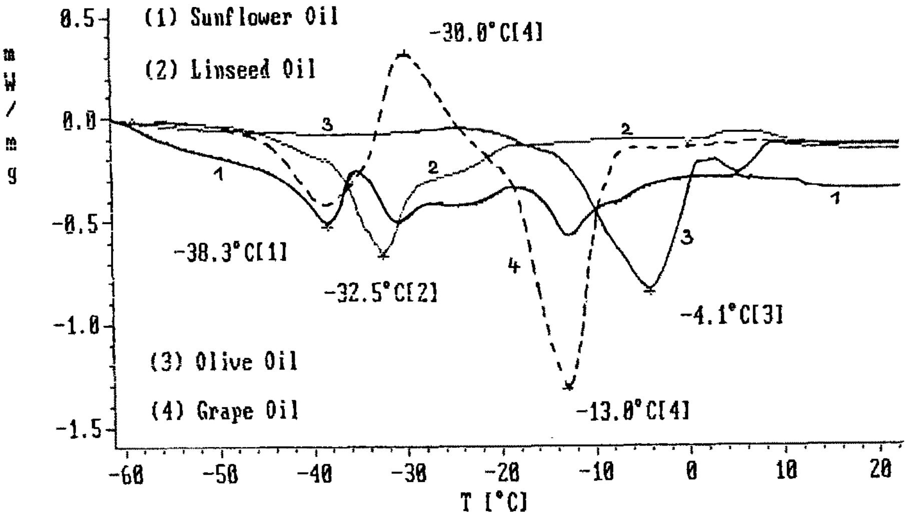

Fig. 2 Melting of sun-flower, linseed, olive and grape oil

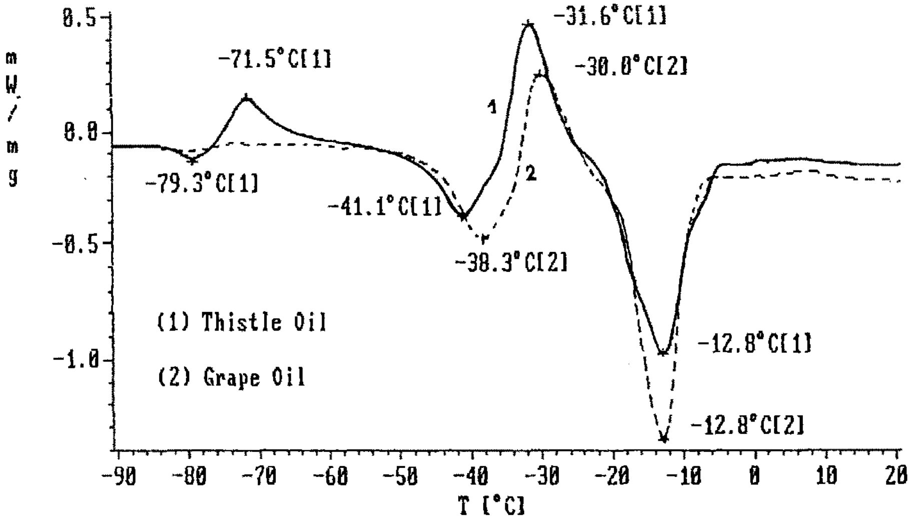

Fig. 3 Polymorphism of grape and thistle oil (melting curves)

Hardened oils and fats show melting at higher temperature. Butterfat, lard and hardened coconut oil (cocofat) start to melt around -30°C during heating and are liquid at +50°C (Fig. 4). Melting enthalpies for these fats were determined between 120 and 150 J/g.

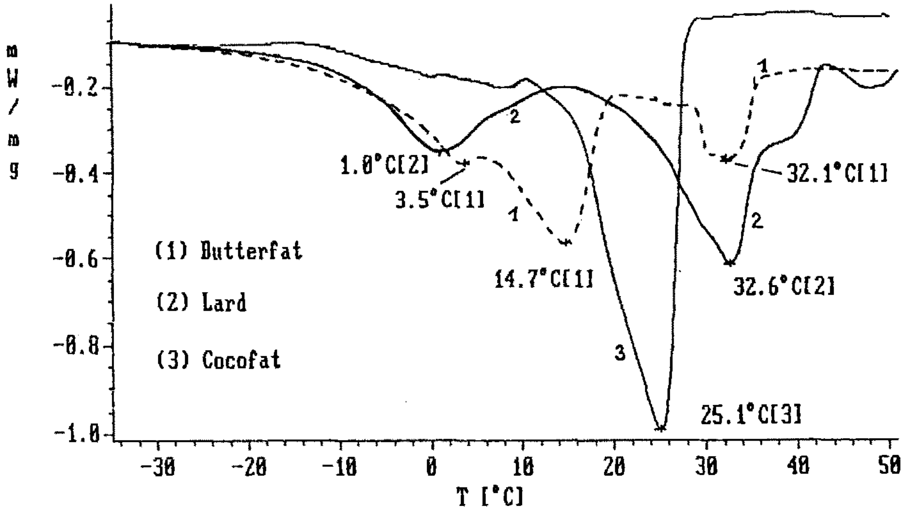

Fig. 4 Melting of butterfat, lard and hardened coconut oil (cocofat)

Fats obtain a good workability by emulsifying and therefore many application possibilities exist in a wide range of food types (spreadable fats, fat glazes ...). The most important emulsified fats are butter and margarine. The melting behaviour of fresh, emulsified fats is characterised by the melting of the water-content as well as by smaller melting peaks for the fat mixture (Fig. 5).

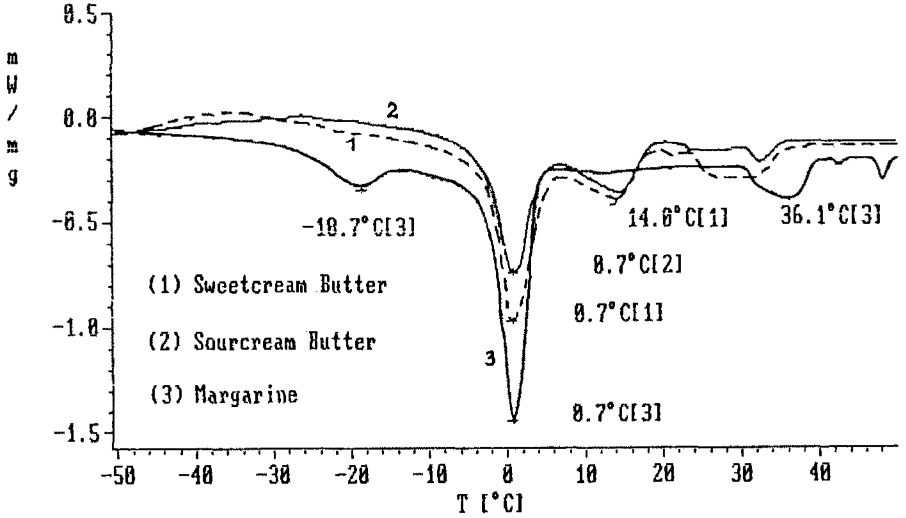

Fig. 5 Melting curves of the emulsified fats sweet cream butter, sour cream butter, margarine

The melting behaviour of the butters tested is qualitatively equal as the same origin determines the mixture of fatty acids (composition). Different proportions of water (determined from the DSC peak around 0°C) indicate different storing times of the butter.

Margarine, which is manufactured by the fast-cooling of fat-oil mixtures, shows a more complex behaviour of melting in comparison with butter. This is based on a higher proportion of unsaturated fatty acids and on the addition of hardened vegetable fats. By adding emulsifiers polymorphic changes can be hindered (2, 3).

On the basis of DSC investigations on aged, emulsified fats it could be shown that there is a relationship between the size of the water melting peak at 0°C and time of storing. Storing at ambient temperature leads after only 4 days to a complete disappearance of the peak for water (Fig. 6).

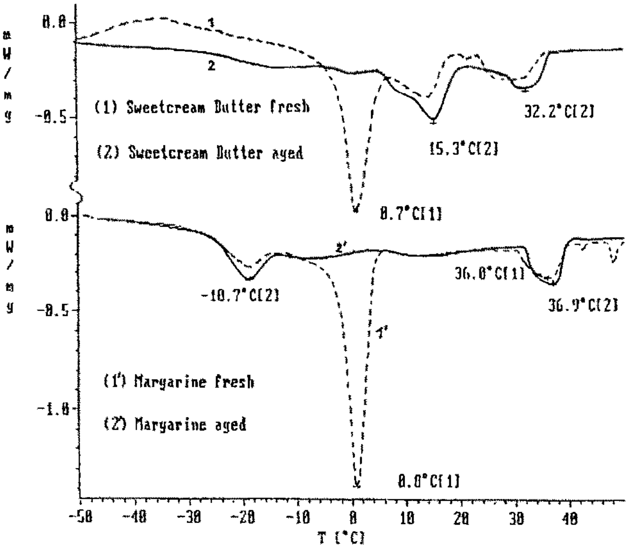

Fig. 6 Influence of aging on the melting behaviour of butter and margarine

Systematic DSC investigations are necessary to show whether this appearance can be used to determine the condition of freshness of emulsified fats.

Being important for the food industry, the information on the solid-liquid ratio at the application temperature can easily be determined from the DSC melting curves by partial integration. The ratio between partial area and total area reflects the amount of melting at a given temperature (Fig. 7).

The steepness of the slope of the curve decreases with increasing variety of the fatty acid distribution and also indicates the range of working temperatures for the substance. The changes of oils and fats in the technically and commercially important process of fat hardening (fat hydration) can be quickly visualised from DSC melting curves and evaluating from them the solid-liquid ratio.

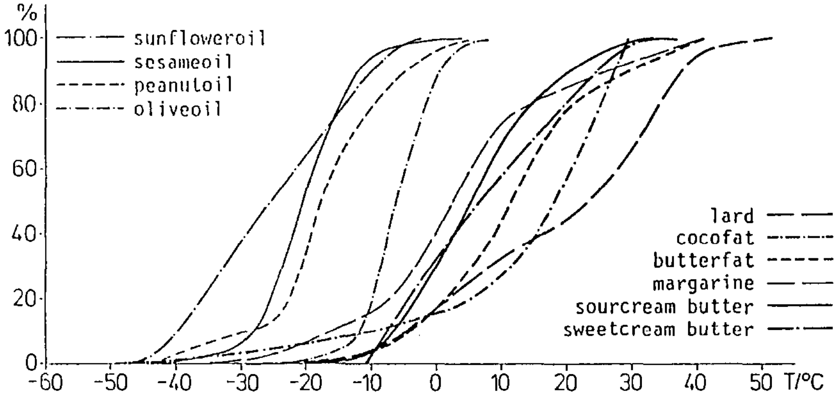

Fig. 7 Liquid fraction of fats and oils in the temperature range -60 to +50°C

Unsaturated fatty acids age by the attack of atmospheric oxygen, hydrolysis and microbiological decomposition (bacteria). The oxidation sensitivity is considerably high compared to the saturated fatty acids as can be seen from the comparison of the DSC-oxidation curves of oils (Fig. 8) and of fats (Fig. 9).

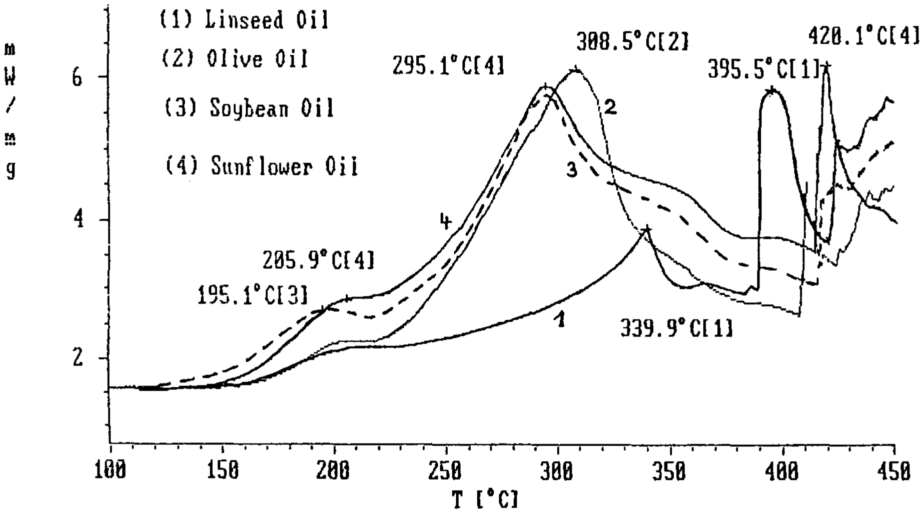

Fig. 8 DSC-oxidation curves of sun-flower, soybean, linseed and olive oil in static air atmosphere

The onset of oxidation at sun-flower and soybean oil can already be seen below 150°C. Comparing the behaviour of oxidation of all tested fats and oils the exothermic peak in the range of 150 to 220°C has to be related to the oxidation of unsaturated fatty acids (see fig. 10).

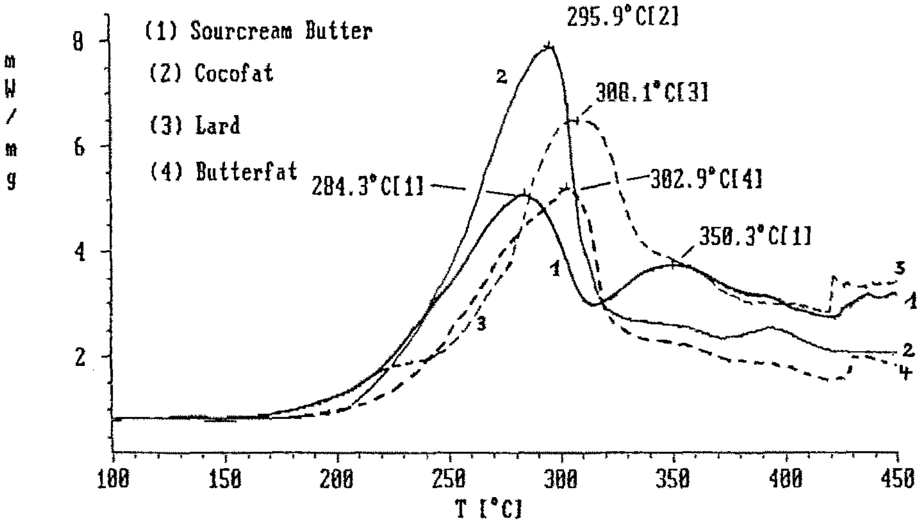

Fig. 9 DSC-oxidation curves for cocofat, lard, butter and butterfat in static air atmosphere

The main oxidation peak is detected between 280 and 310°C for the tested fats and oils. Further minor exothermal peaks in the range 340 to 380°C are followed by sharp exotherms at 390 to 440°C. Figure 10 clearly indicates the changed oxidation behaviour for the highly unsaturated sun-flower oil (up to 55% linolenic acid) and the hardened coconut oil (cocofat, 1% linolenic acid).

The onset of oxidation of unsaturated fats and oils lies below the temperature for roasting and frying which explains the short usage time and the quick change of colour, smell and taste.

Regarding polymerising oils which are used as binders for paints for many antique paintings, attempts have been made to identify them by comparing the peak heights of characteristic oxidation peaks (4).

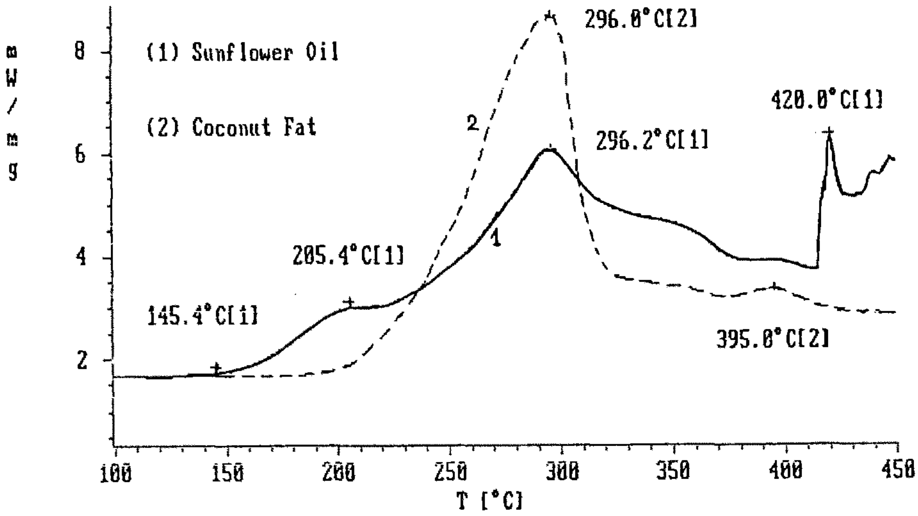

Fig. 10 Comparison of the oxidation curves of the unsaturated sun-flower oil and hardened cocofat

SUMMARY

With a simple and quick performance of the tests, the DSC investigations on fats and oils show the different melting and crystallisation behaviour caused by different composition, application temperature and aging. Polymorphism and stereoisomeric effects clearly appear in non-emulsified fats and oils. The aging of emulsified fats (rancidity) can be shown on the basis of the disappearance of the water peak. A high proportion of unsaturated fatty acids leads to a low oxidation stability with a typical peak at 150 ... 220°C.

Reasonable reproducibility for DSC melting curves on fats and oils can be achieved only if the thermal history, i.e. the pretreatiment of the samples, is identical. Because of the overlapping melting ranges of the different fatty acid components in natural fats and the polymorphism a determination of single components of a fat mixture is not possible from DSC melting curves.

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