APPLICATION **NOTE**

Characterization of Cooking Oils by Means of Differential Scanning Calorimetry (DSC)

Dr. Ekkehard Füglein

Introduction

Most cooking oils are extracted from plants or plant seeds. The first targeted cultivation of olive trees is believed to have taken place on the island of Crete around the year 3500 B.C. Besides human consumption and the production of soap, olive oil was also used in Catholic liturgy. Presented in figure 1 is an oil mill (olive crusher) in Pompeii from the cear 80 B.C.

The fruits and seeds from which oils are to be extracted are first cleaned and then crushed between rollers. Since freshly pressed oils usually also contain associated materials such as odorous-, flavoring- or bitter-substances – or plants parts, clouding agents or mucilage – they are often refined to help preserve them. To do so, the raw oil is heated; however, this leads not only to the loss of a portion of the raw oil, but also to the reduction of nutritionally and physiologically

beneficial substances such as tocopherols. The polyunsaturated fatty acid content, however, is unaffected by this treatment step. Refined oils are characterized by a neutral smell and taste, a longer shelf life, and a lack of any solid sedimentaion during storage.

Cold-pressed oils are not refined but are extracted only by pressing and subsequent filtration. The heat generated during pressing is dissipated by cooling the press. The oil thus obtained is called "cold-pressed", "cold-drawn", "untreated", or "unadulterated"; it is classified as very high quality [2, 3].

Fats and oils are triglycerides or triple esters of the trivalent alcohol glycerin (1, 2, 3- propanetriol). The fatty acids with which glycerin is esterified are classified as saturated, unsaturated or polyunsaturated. The reason that fats are solid at room temperature while oils are liquid is due to the unsaturated fatty acid content. Because of the increased unsaturated fatty acid content (mainly cis-positioned), crystallization is hindered and the melting point of the oils is lowered. Therefore, a correlation is to be expected between the melting and crystallization temperatures of oils and their unsaturated fatty acid content levels.

Experimental

The melting and crystallization behavior of commercially available cooking oils was investigated by means of the NETZSCH DSC 204 **F1** *Phoenix*® with μ-sensor. Nitrogen was used as a purge gas (5.0); the purge gas rate amounted to 40 ml/min. The oils were introduced into standard aluminum crucibles with pierced lids in such a way as to entirely wet the bottom area of the crucibles. The measurement parameters and sample masses are summarized in tables 1 and 2.

1 Olive crusher in Pompeii from the year 80 B.C. [1]

NETZSCH

Tab. 1 Measurement conditions

Measuring instrument	DSC 204 **F1** *Phoenix®*
Sensor	μ-Sensor
Cooling	GN$_2$, auto
Crucible	Al, pierced
Atmosphere	Nitrogen
Gas flow rate	40 ml/min
Heating/cooling rate	5 K/min

Tab. 2 Sample Masses [mg]

	Olive Oil	Peanut Oil	Sesame Oil	Rapeseed Oil	Sunflower Oil	Walnut Oil
Producer	**A**	**B**	**C**	**C**	**D**	**B**
Measurement 1	2.527	2.565	2.546	2.529	2.528	2.507
Measurement 2	2.526	2.541	2.529	2.554	2.528	2.505
Measurement 3	2.522	2.568	2.545	2.529	2.514	2.545
Maen Value (MW)	2.525	2.558	2.540	2.537	2.530	2.519
Deviation (ABW)	0.005	0.027	0.017	0.025	0.034	0.040

Results and Discussion

The cooking oils were investigated under the above-listed measurement conditions in the temperature range from -100°C to room temperature. Crystallization of the samples can be seen in the respective cooling segments and melting can be observed in the heating segments. Since the oils each have different content levels of saturated, monounsaturated and polyunsaturated fatty acids, and the triglycerides additionally consist of mixtures of different fatty acids, all of the samples have a relatively broad area within the melting and crystallization range in common. Figure 2 shows a comparison of the melting behavior of the various oils.
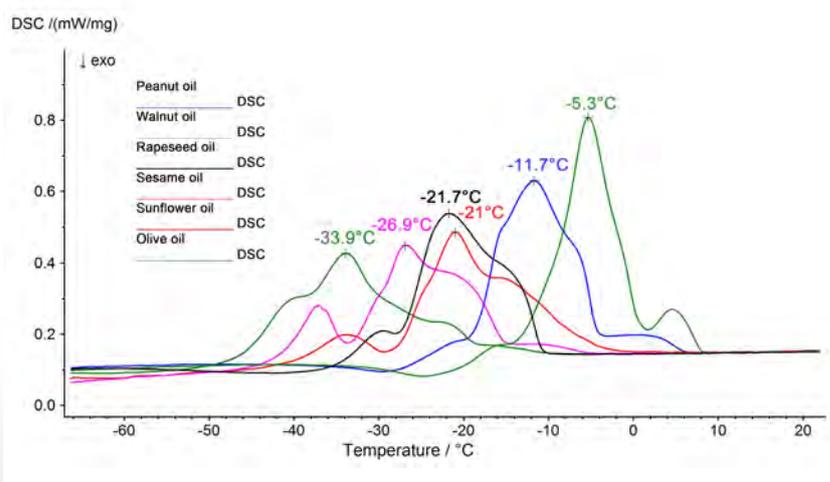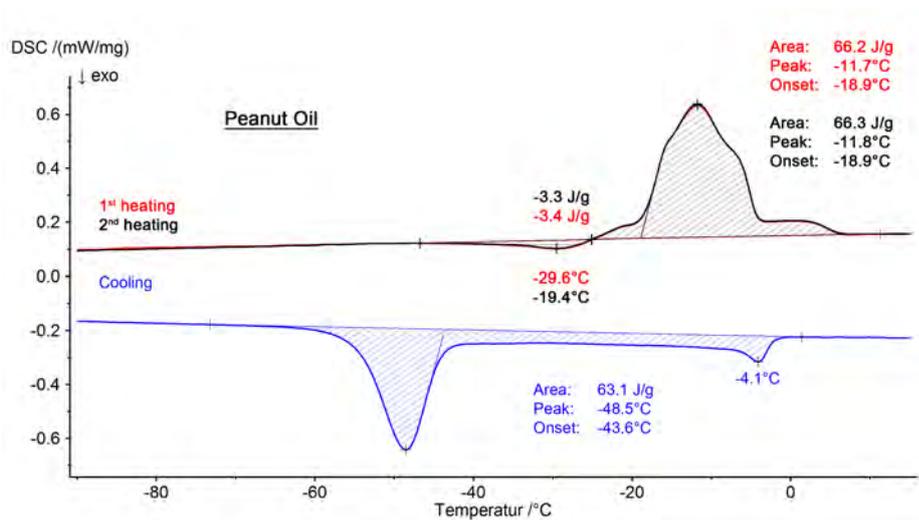

2 Comparison of the melting behavior for all of the cooking oils investigated

NETZSCH

Presented in figure 3 are the results for peanut oil, consisting of two heating segments and the cooling segment in between. Beyond that, the beginning of the melting process (extrapolated onset) and the peak temperature of the main component are assessed for each sample. A comparison of these results is summarized in table 3. The values shown are mean values calculated from six measured values. A consistent trend toward lower temperatures can be seen in both the onset and the peak temperatures in the following order: olive oil, peanut oil, sesame oil, rapeseed oil, sunflower oil, walnut oil.

In comparing the content levels shown in table 4 for saturated (column 1), monounsaturated (column 2) and polyunsaturated fatty acids (column 3) in the cooking oils analyzed, in the order listed from olive oil to walnut oil, no trend can initially be seen for any of columns 1 to 3. Not even the total unsaturated fatty acid content listed in column 4 (sum of columns 2 and 3) shows a trend fitting directly to the selected sequence of the cooking oils in table 4. The relationship between the fatty acid content and the melting temperature is more clearly illustrated in figure 4. Here, it can be seen that the melting temperature increases as the saturated and monounsaturated fatty acid contents increase, and decreases as the polyunsaturated fatty acids increase.

3 Melting and crystallization behavior of peanut oil

Tab. 3 Extrapolated onset and peak temperatures of the melting processes [°C]

	Olive Oil	Peanut Oil	Sesame Oil	Rapeseed Oil	Sunflower Oil	Walnut Oil
Producer	**A**	**B**	**C**	**C**	**D**	**B**
Extrapolated Onset	-10.1	-18.9	-28.3	-28.0	-31.5	-44.9
Peak Temperature	-5.1	-11.8	-21.0	-21.4	-26.7	-34.0

NETZSCH

Tab. 4   Compilation of the cooking oils and their content levels [4]

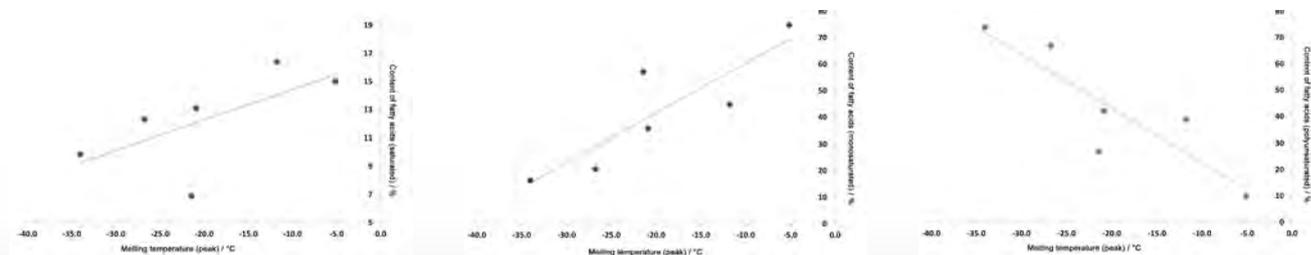| Fatty Acid Content Levels [%]				
	saturated (S)	monounsaturated	polyunsaturated	unsaturated total (P)	P:S
Walnut oil[1]	9.87	16.3	73.9	90.2	7.49
Sunflower oil[2]	12.3	20.7	66.9	87.6	5.44
Rapeseed oil[1]	6.9	57.1	26.9	84.0	3.90
Sesame oil[1]	13.1	35.8	42.0	77.8	3.21
Peanut oil[2]	16.4	44.8	38.8	83.6	2.37
Olive oil[1]	15.0	74.7	9.89	84.6	0.66

[1]Manufacturer-provided data
[2]Values according to [4]

Also, in determining the quality of oils for food analysis, it is not so much the absolute values for the different fatty acid content levels as their relationships to each other that are key. Namely, if one creates a set of ratios using columns 4 and 1 – i.e., the ratio of total unsaturated fatty acid to saturated fatty acid content (P:S) – a consistent trend emerges, since the values decrease from 7.49 for the walnut oil to 0.66 for the olive oil (compare to column 5). The coloring in table 4 illustrates two groups of samples. The values marked in green describe the oils with a higher polyunsaturated than monounsaturated fatty acid content. The values marked in red, on the other hand, designate oils with a

higher monounsaturated than polyunsaturated fatty acid content.

It must be taken into consideration that the information on the fatty acid content levels for the sunflower oil and peanut oil samples only reflect mean values taken from literature. Experience dictates that a fluctuation range of approximately 5% should be assumed for each value. Also, in evaluating the DSC results, only the peak temperatures of the main components were taken into consideration, which certainly only constitutes a reference point in analyzing the melting behavior of a mixture and can explain

4   Left: Melting temperature as a function of saturated fatty acid content
Middle: Melting temperature as a function of monounsaturated fatty acid content
Right: Melting temperature as a function of polyunsaturated fatty acid content

NETZSCH
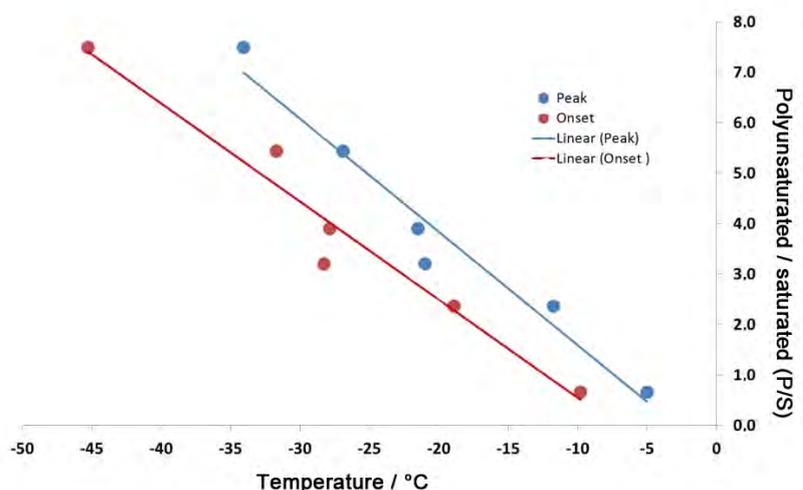
5 Relationship of the overal polyunsaturated to saturated fatty acid content (P:S) as a function of the peak temperature detected during the melting process

the existing deviations in the correlation diagram (figure 5). The value for the sesame oil with a P:S of 3.21 is the one which lies farthest from the trend line in figure 5. This might have something to do with the fact that this is the only oil in this set to which the seed was subjected to an additional roasting process. The influence of the roasting process on crystallization is not known at this point in time.

Although this study fundamentally confirmed that a higher polyunsaturated fatty acid content means a lower melting temperature for an oil, it can also be seen in figue 4 that concentration is not the only deciding factor. Figure 5 shows that it is rather the P:S ratio – i.e., the concentration of polyunsaturated to saturated fatty acids – which exhibits a consistent trend.

Conclusion

This application note demontrates that the melting and crystallization behavior of different cooking oils can be characterized by means of differential scanning calorimetry (DSC). Easy sample preparation and a standard temperature program allow for rapid measurement results on values for melting and crystallization behavior. Evaluation based on peak temperatures make a meaningful comparison of the cooking oils simple to obtain.

Literature

[1] Wikipedia: „Speiseöl", Mai 2013
[2] Lebensmittellexikon, www.lebensmittellexikon.de
[3] Deutsche Gesellschaft für Ernährung, www.dge.de
[4] Landesanstalt für Pflanzenbau Forchheim, "Informationen für die Pflanzenproduktion" Sonderheft 1/2001, ISSN 0937 6712

NETZSCH