HEAT EFFECTS OF THE OXIDATION AND PYROLYSIS OF TOTAL LIPIDS EXTRACTED FROM VARIOUS HOG AND CATTLE TISSUES

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SUMMARY: The total heat effects of the oxidation and pyrolysis of lipids extracted from various hog and cattle tissues (muscle and fatty tissues, brain, spinal cord and liver) were studied by differential scanning calorimetry (DSC Du Pont 9900).

The obtained results indicate that the endothermal effects of total lipids pyrolysis is 480 to 620 J/g which is comparable to the determined values of 860 and 960 J/g for triolein and tristearin as standards respectively. The exothermal oxidation effects range from 930 J/g (brain lipids) to 2400 to 2600 J/g (spinal cord, fatty and muscle tissue lipids), while the values for triolein and tristearin are 3740 and 5420 J/g. The obtained results were successfully interpreted on the basis of the content of polyunsaturated (PUFA) and monounsaturated (M) fatty acids in the acid composition of total lipids.

INTRODUCTION: In recent years the DSC analysis of different oils and lipids was successfully applied for the determination of various characteristics of natural substances. It has been shown that thermal methods can be applied in the determination of polymorphic transformations of lipids which strongly depend on the chemical structure of the key components present in lipids and on other compounds constituents of neutral lipids mostly on the content of phospholipids and glucolipids (1-4).

Investigation of the thermal oxidation of lipids and oils mostly involved the analysis of oxidation rates, formed products and mechanisms of complex oxidative reactions in bulk lipids. However, there are no published data on the total heat effects of lipid oxidation determined by DSC methods. Several data were presented in literature related to the oxidation of different substances (crude oil, heavy oil, coal, oil shale, tar sand, etc) (5).

An attemp was made in the past to broaden the potential of the thermal method for the study of oils and oil product composition by analysis of the shapes of DSC curves (6). Recently, we started to investigate the total heat effects of pyrolysis and oxidation processes of different lipids extracted from animal tissues using DSC techniques. In spite of the different composition of the analysed lipids (7,8) one can expect a great influence of the content of phospholipids, free fatty acids, mono- and diglycerides on the total heat effect of oxidation. Finaly, the objectives of the present work were, on the one hand, to show that DSC techniques can be used as a suitable method to identify specific lipid composition (5) by using only the total heat effect of the oxidation and pyrolysis process and, on the other hand, to compare the heat effects of the oxidation of lipid originating from tissues of different animals (cattle and hog).

MATERIALS AND METHODS: The preparation of samples of total lipids from different hog and cattle tissues is given in detail elsewere (8). DSC analysis in oxidizing and inert atmosphere was performed using lipid samples held at + 4°C for 2 years after their preparation. The total lipids from muscle and fatty tissues were fractionated to neutral lipids, glucolipids and phospholipids by Johnston's procedure (9). Triglyceride fractions were separated by column chromatography from the corresponding neutral lipids which were further also analysed by DSC.

DSC experimental investigations of oxidation and pyrolysis were performed using a Du Pont DSC 9900 pressure cell unit. The heating rate was always 1o K/min in the temperature range 3o-4oo°C for oxidizing atmosphere (air, 5 bar, 5 ccm/min) and 3o-6oo°C for inert atmosphere (Argon, 1 bar, 5 ccm/min). The aim of using air under pressure was to suprpess as much as possible the evaporation of light compounds (e.g. hydrocarbons, free fatty acids) as well as some oxidation products. The initial sample weight was always app. 5 mg, and after each experiment the residue mass was measured with the aim to determine the total quantity of samples pyrolysed or oxidized during thermal treatment.

RESULTS AND DISCUSSION: Typical DSC curves for some of the five different hog and cattle tissues obtained under the same thermal treatment are shown in Figure 1 (spinal cord, fatty tissue and liver total lipids), while,the corresponding DSC curves for the oxidation of standard substances (tristearin and triolein) are presented in Figure 2.

The obtained results show a similar shape of the DSC curves for lipids originating from the same tissues of different animals but with larger total heat effects of oxidation in the case of lipids

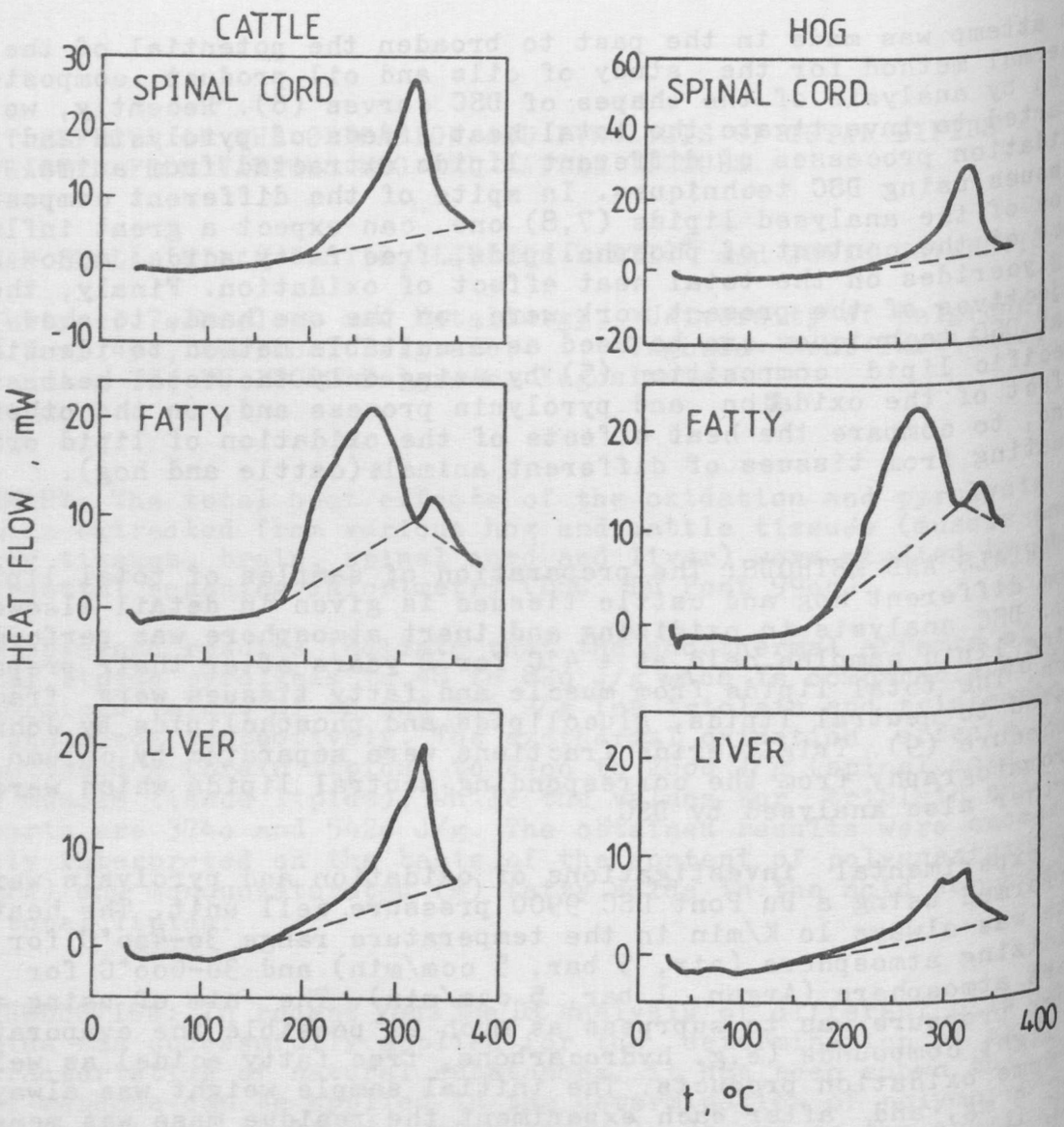

Figure 1. DSC curves of the oxidation of total lipids extracted from different animal tissues (3o-4oo°C; air 5 bar; 5 ccm/min; heating rate 1o K/min).

extracted from cattle tissues. All the curves are characterized practicaly by two maxima; the first at a temperature of about 25o°C followed by a second one above 3oo°C.Only in the case of total lipids from fatty tissues of cattle and hog the peak at about 25o°C is dominant, while that at the higher temperature is the major one in the case of all other investigated samples.

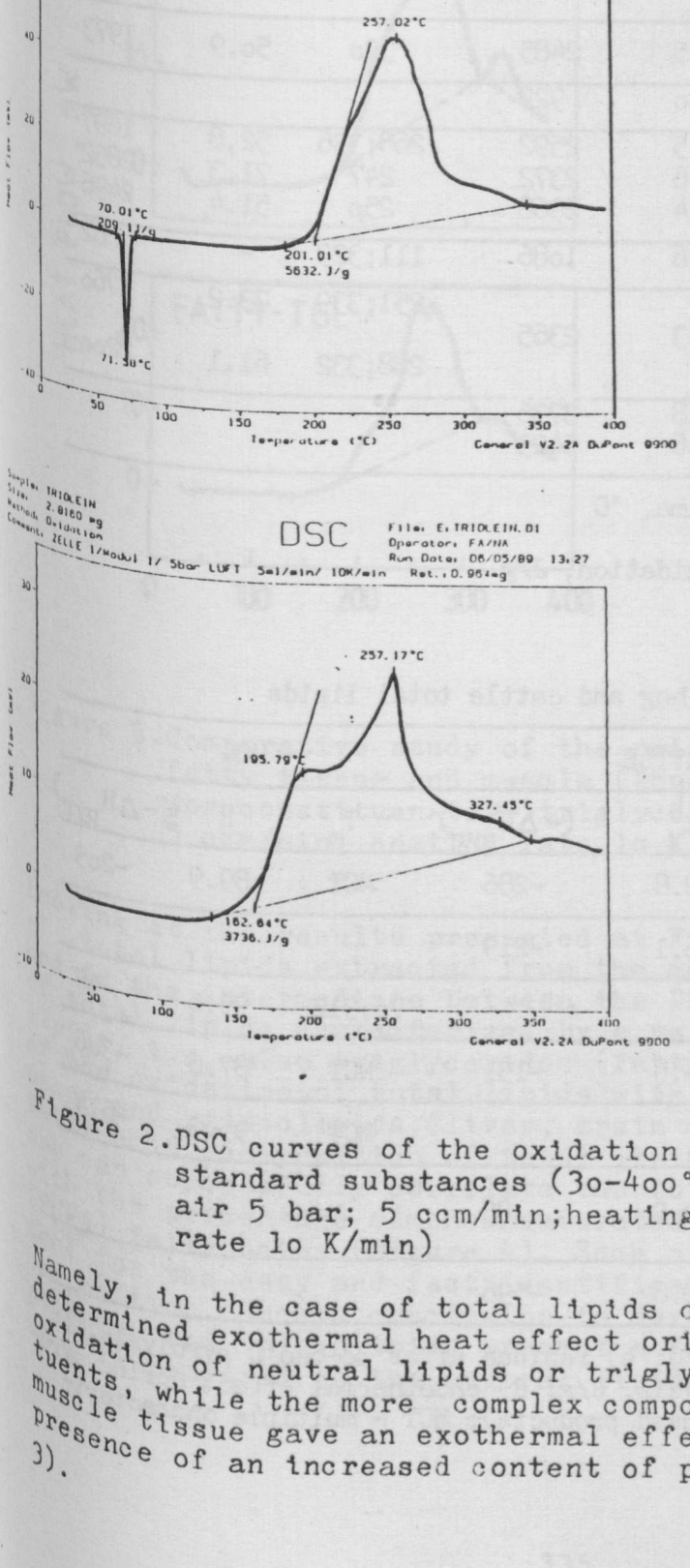

Figure 2. DSC curves of the oxidation of standard substances (3o-4oo°C; air 5 bar; 5 ccm/min; heating rate lo K/min)

Such a shape of the DSC curves could be explained by using the results of oxidation of saturated and monounsaturated triglycerides (tristearin and triolein) where the maximum heat flow or DSC-maxima were expressed at 257°C (Figure 2).

However, the peak above 3oo°C can be related to the oxidation of a more complex structure of total lipids, namely its constituents which contain to a larger percent polyunsaturated fatty acids. Such a conclusion is derived on the basis of the known content fatty acids in phospholipids and glucolipids which were extracted from total lipids, indicating an increased content of polyunsaturated fatty acids (7,8). The complete results of DSC investigations of total lipids oxidation are given in Table 1, while those corresponding to the results of DSC pyrolysis are present in Table 2.

Thus once again, now also in the case of DSC results of total lipids oxidation this study confirms the assumption postulated in some of our previous papers, that the total exothermal heat effect could be related to the composition of total lipids.

Namely, in the case of total lipids oxidation from fatty tissue, the determined exothermal heat effect originated dominantly from the oxidation of neutral lipids or triglycerides as their major constituents, while the more complex composition of total lipids from muscle tissue gave an exothermal effect more influenced by the presence of an increased content of phospho- and glucolipids (Figure 3).

Table 1. DSC oxidation of different hog and cattle lipids

tissue	CATTLE			HOG		
	T_m^a	R^b	$(-\Delta H^c_{oxs})$	T_m	R	$(-\Delta H_{oxs})$
SPINAL CORD	31o	74.5	2485	32o	5o.9	1973
BRAIN	316	49.o	929			
FATTY	265;332	68.5	2592	268;336	52,8	1697
- triglycerides	255;335	63.6	2372	247	71.3	2852
- neutral lipids	244	61.4	2968	25o	51.4	2496
LIVER	12o;324	54.6	1o86	111;323	-	862
MUSCLE (Longisimus dorsi)				251;339	73.2	176o
-neutral lipids	257	59.3	2365			
-triglycerides				288;332	61.1	22oo
TRIOLEIN	196;257	65.8	3736			
TRISTEARIN	257	18.6	5423			

a- temperature of DSC peak maxima, °C
b- residue after oxidation, %
c- exothermal heat effect of oxidation, J/g

Table 2. DSC pyrolysis of different hog and cattle total lipids

tissue	CATTLE			HOG		
	T_m^a	R^b	$(-\Delta H^c_{pyr})$	T_m	R	$(-\Delta H_{pyr})$
SPINAL CORD	MCT	89.8	-286	MCT	89.9	-2o5
BRAIN	295	86.1	-219			
FATTY				7o;312	99.6	-48
LIVER	MCT	86.6	-131	MCT	87.6	-3o6
MUSCLE				MCT	95.3	-614
TRIOLEIN	175-18o[d]	99.8	- 86			
	41o-412					
TRISTEARIN	73;416	99.8	-596			

a) temperature of DSC peak maxima, °C; b) residue after 3o-6oo°C pyrolysis,%; c) endothermal heat effect of pyrolysis, J/g; d) endothermal effect during pyrolysis (possible formation of condensed products); MCT - multiple characteristic temperatures of peak maxima.

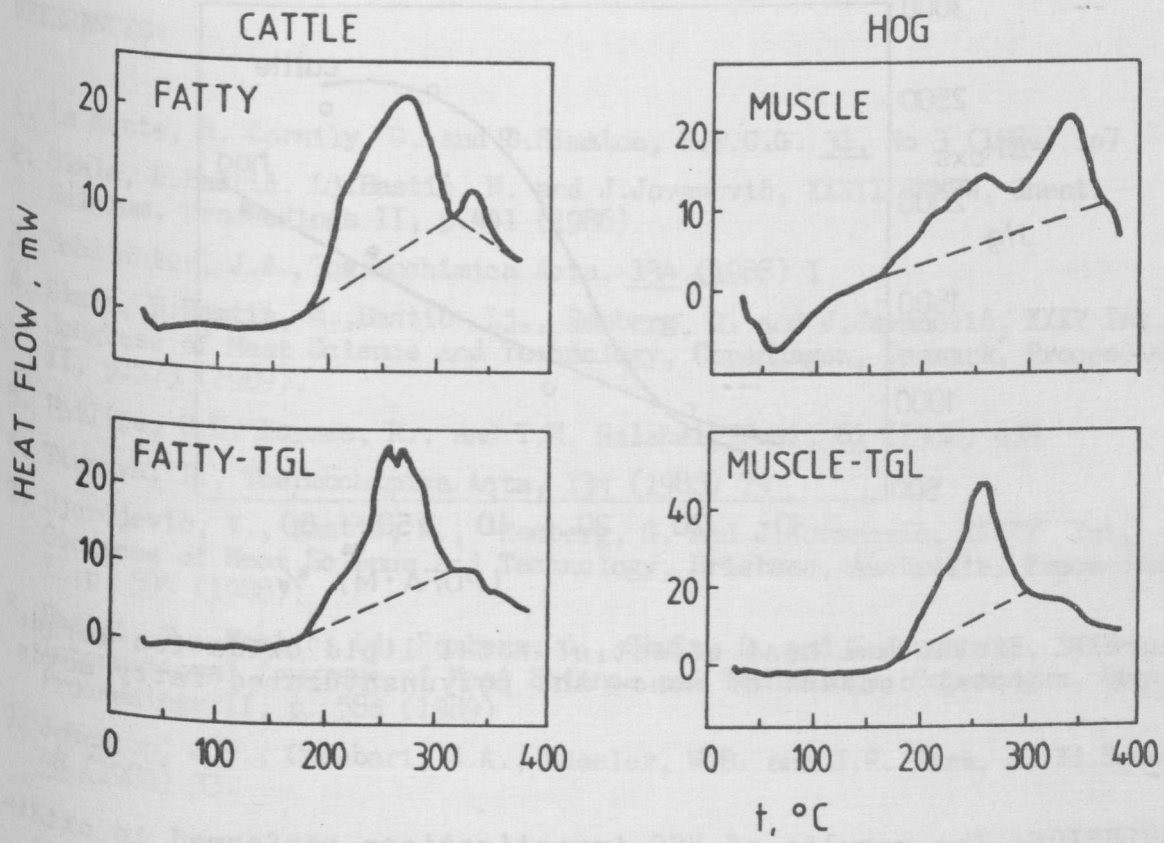

Figure 3. Comparative study of the oxidation of total lipids from fatty tissue and muscle (Longisimus dorsi) and their major constituents - triglycerides (3o-4oo°C; air 5 bar; 5 ccm/min; heating rate lo K/min).

Looking at the results presented at Figures 1 and 3, the oxidation of total lipids extracted from the muscle tissue of cattle and hog is the intermediate between the DSC results of the oxidation of total lipids characterized by a very large content of neutral lipids, i.e. also triglycerides (fatty tissue) and the DSC results of the oxidation of total lipids with an increased content of phospho- and glucolipids (liver, brain and spinal cord). Knowing the fatty acid composition of total lipids from our earlier work (8), one can successfully correlate the total heat effect of oxidation with the percentage ofmonounsaturated (M) and polyunsaturated (PUFA) fatty acids (Figure 4). Such a correlation is a very useful tool for the easy and fast identification of complex total lipids composition. Such a conclusion is derived on the fact that both phospho- and glucolipids present a fraction with a larger content of PUFA compared to the neutral lipids fraction.

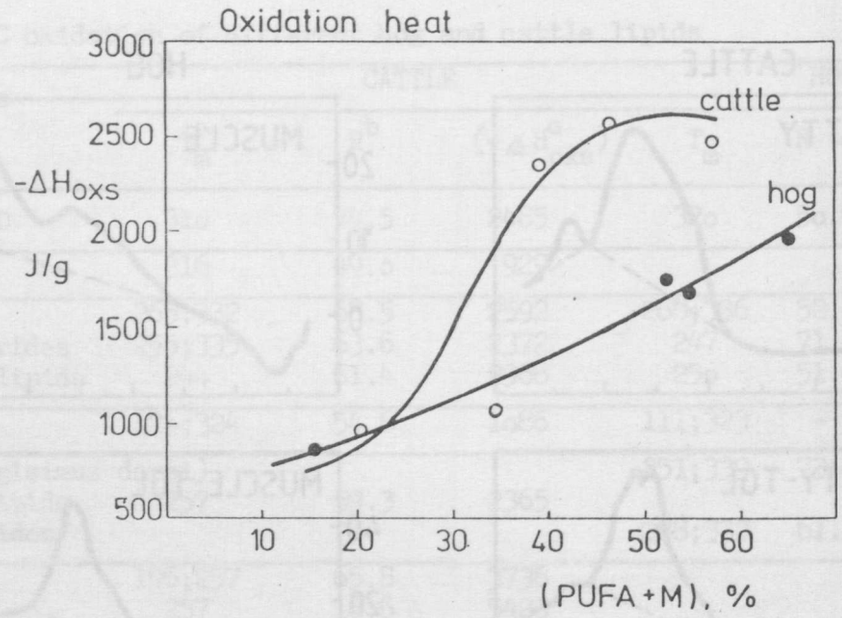

Figure 4. Exothermal heat effect of total lipid oxidation versus total content of mono- and polyunsaturated fatty acids

CONCLUSION: The results of DSC investigations performed in oxidizing and inert atmosphere indicate that the exo-effect of total lipids oxidation increases in the series: brain (900 J/g), liver (1100), muscle (2300-2400), spinal cord (2500), fatt (2500-2900), while the endo-effect of pyrolysis was much smaller (50-600 J/g) followed by a very complex shape of the DSC curves characterized by multiple characteristic temperatures where the maximum of heat flow occurred. The endothermal heat effect of total lipids pyrolysis increases in the series: fatty tissue (-48 J/g), liver (-130), brain (-219), spinal cord (-300) and muscle (-614).

Only in the case of total lipids extracted from the liver, the oxidation process was observed at a lower temperature (110-120°C) with a small heat effect; in all other samples the maximal rate of oxidation was in the temperature range 245-360°C.

Quite a good relation between the total exothermal effect of lipids and their compositions was represented using values of the total content of unsaturated fatty acids present in total lipids. In such a derived correlation, about 40% larger values of the exothermal heat effect of oxidation were registered in the case of lipids extracted from cattle tissues.

REFERENCES:

1. Le Meste, M. Cornily, G. and D.Simatos, R.F.C.G. 31, No 3 (1984) 1o7
2. Skala, D.Bastić, Lj.Bastić, M. and J.Jovanović, XXXII EMMRW, Ghent, Belgium, Proceedings II, p.441 (1986).
3. Schlichter, J.A., Thermochimica Acta, 134 (1988) 1
4. Skala, D.Bastić, M.,Bastić Lj., Remberg, G. and J.Jovanović, XXXV Int. Congress of Meat Science and Technology, Copenhagen, Denmark, Proceedings II, p.573 (1989).
5. Phillips, C.R, Luymes, R., and T.M. Halahel, Fuel, 61 (1982) 639
6. Tiunova, I., Thermochimica Acta, 134 (1988) 79
7. Djordjević, V., Bastić, M., Remberg, G. and J.Jovanović, XXXIV Int. Congress of Meat Science and Technology, Brisbane, Australia, Proceedings II,p. 595 (1988).
8. Bastić, M., Bastić, Lj. Remberg, G., Skala, D. and J.Jovanović, XXXV International Congress of Meat Science and Technology, Copenhagen, Denmark, Proceedings II, p. 58o (1989)
9. Johnston, J.J., Chaubari, H.A., Wheeler, W.B. and J.R. Kirk, J. Fd.Science, 48 (1983) 33.