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THERMOGRAVIMETRIC ANALYSIS: DETERMINATION OF THE RATE OF VOLATILE COMPOUND FORMATION FROM BOAR M.SEMIMEMBRANOSUS INTRAMUSCULAR LIPIDS

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SUMMARY

The rate of volatile compounds formation from boar M.Semimembranosus total intramuscular lipids was investigated on the basis of nonisothermal thermogravimetric (TG) analysis. The investigation were performed at different heating rate (q, K/min) in oxygen and nitrogen atmosphere. Comparative analysis in N_2 and O_2 was made in order to compare the rates of volatile compounds formation with and without the chemical reaction of oxidation. TG analysis was always done with the same initial sample mass and in the temperature interval 30-250°C. The rate of formation of volatile compounds was derived only for temperatures greater than 130°, when significant mass change occurs.

The results of comparative DSC analysis, which was performed in the same temperature interval in inert atmosphere and in air, confirmed the increasing rate of formation of volatile compounds above 130° as well as starting point of oxidation in air.

The proposed method for determination of the rate of volatile compounds formation using TG analysis could serve as a standard procedure in the quantitative analysis of the rate of creation of compounds mostly responsible for odor and flavors from different sources.

INTRODUCTION

Thermal analysis is increasingly used for investigating the stability of various materials, not only in research laboratories, but also as a standard quality control procedure for raw materials and final products. The results of such an analysis indicate the optimum storage and production means of various pharmaceutical products, as well as food, mostly products containing lipids (Cross,1970; Mackenzie,1979). The application of TG analisis as an alternate method for measuring the stability of edible oils is presented in the work of Hassel (1976) which was recently confirmed by Mikula and Khayat (1985). Problems concerning the estimation of edible oil oxidation stability by TG analysis were also studied in the works of Cross (1970) and Buzás et al.(1979). Hagemann and Rothfus(1979) recommend TG analysis as a convenient method for determining oxidative changes in sperm whale oil and in the natural and synthetic esters of some waxes.

Investigation of the composition of white meaty hog M.Semimembranosus intramuscular lipids (Bastić Ljubica,1986) as well as literature data concerning the direct correlation between the amount of volatiles and the content of unsaturated compounds (Mottram et al. 1982; Sinclair et al.,1982; Mottram and Edwards,1983), indicated the possibility of efficiently following the rates of oxidation and volatiles formation during the heating of intramuscular lipids in an oxygen stream by TG analysis.

The purpose of this paper was to give more complete information on the volatile formation rate of boar M.Semimembranosus intramuscular lipids.

MATERIALS AND METHODS

Boar M.Semimembranosus intramuscular lipids of white meaty hogs (6-7 months old, 95-105 kg) were extracted according to Folch et al.(1957). The muscle was removed 24 h upon slaughtering and cooled in the carcass at +4°C; before extraction it was cleaned of fatty and connective tissue.

Thermogravimetric Analysis

All the investigations were performed on a Perkin Elmer TGS-2 instrument. The sample was heated from 30° to 280°C at heating rates of 2.5, 5 and 10°/min. under controlled oxygen or nitrogen flow (15 cm^3/min). All the investigations were performed with approximately the same initial sample mass (10 mg).

DSC Analysis

The experiments were performed using a Perkin Elmer DSC-2 instrument in order to indicate the effects of oxidation and evaporation during the heating of the sample of intramuscular lipids in an oxygen or nitrogen stream. DSC analysis was performed with about 50 mg of substance at a heating rate of 5 °/min and a gas (N_2 or O_2) flow of 33 cm^3/min.

RESULTS AND DISCUSSION

Kinetics of the Oxidation Process

Figures 1 and 2 present the cumulative mass changes of boar intramuscular lipids during heating up to 250°C at various heating rates.

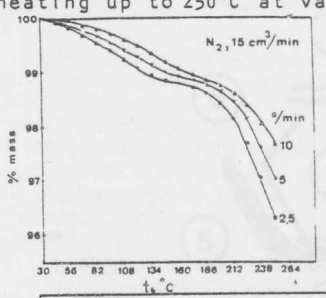

Fig.1. Cumulative mass changes obtained by TG analysis of boar intramuscular lipids at various heating rates in N_2 stream.

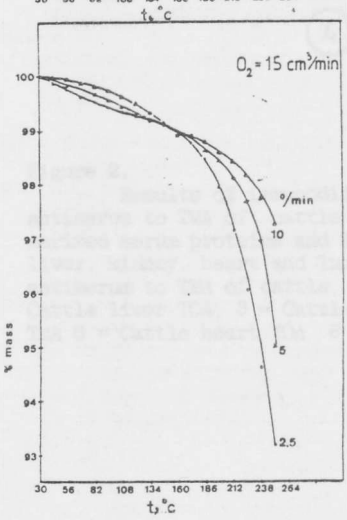

Fig.2. Cumulative mass changes obtained by TG analysis of boar intramuscular lipids at various heating rates in O_2 stream.

The results indicate that the process of thermal decomposition is considerable at temperatures above 170°C. The temperature interval up to 130°C is also interesting when, at low heating rates, oxidation can be observed. Increase in the sample mass indicates formation of the corresponding peroxides which are the basic cause of the formation of larger amounts of volatiles at higher temperatures. Figure 3 presents the corresponding DTG curves or rates of volatiles formation (r_{vc}) at various heating rates.

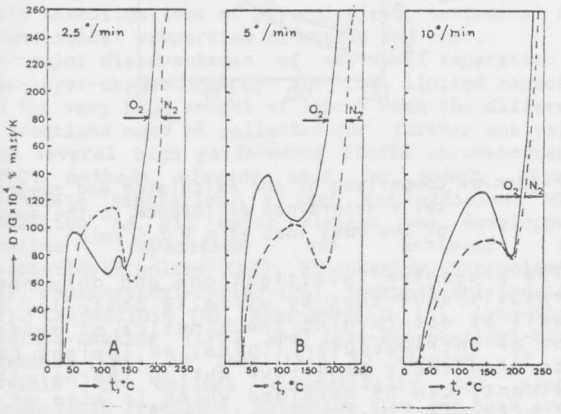

Fig. 3: DTG curves obtained by analysis of boar intramuscular lipids at various heating rates in O_2 and N_2 streams.

The effect of hydrogen bonding is clearly noted in the first phase only at heating rates which at temperatures higher than 160°C leads to accelerated thermal decomposition (Fig. 2 and 3A)

As can be seen from the experimental data, the thermal decomposition of boar intramuscular lipids is a two-step complex mechanism. Characteristic mass changes up to the beginning of intensive decomposition, i.e. the second step, can best be noted from the corresponding TG and DTG curves (Fig. 2 and 3).

In the case of freshly extracted intramuscular lipids, the mass change in the first phase, regardless of heating in O_2 or N_2, is very small (about 1%). In order to determine the kinetic equations of the intensive process of thermal decomposition, it is necessary, among other things, to define its beginning on the basis of corresponding TG and DTG curves (Fig. 1, 2 and 3). These results are presented in table 1.

Table 1. Analysis of the beginning of intensive thermal decomposition

q (°/min)	Gas, 15 (cm^3/min)	Characteristic end temperature of the first phase*, °C	Mass change at the end of the first phase, %
2.5	N_2	140	1.12
5.0	N_2	160	1.15
10.0	N_2	180	1.20
2.5	O_2	110	0.66
5.0	O_2	130	0.97
10.0	O_2	170	1.22

*In the characteristic temperature region it is noted that in a narrow temperature interval of 10-20° there is no relevant mass change.

Determination of the Kinetic Parameters of the Rate of Intensive Thermal Decomposition

As mentioned earlier this paper presents a detailed analysis of the thermal decomposition of boar intramuscular lipids but only in the temperature range 130-250°C.

Although a corresponding mass decrease is noted in the temperature interval up to 130°, it is less intensive (table I). The rate of oxidation and formation of volatiles at higher temperatures is defined by the following equation:

$$r_{vc} = r_{oxid.} = -\frac{dm}{dt} = DTG = k(T).m \qquad (1)$$

In analogy to homogeneous chemical reactions in the gas and liquid phase which behave according to the kinetic law of a first order reaction. In this equation $k(T)$ is the rate constant of the formation of oxidized products defined by the Arrhenius equation, while m is the actual sample mass at temperature T. Adonyi and Vajta (1966) and Adonyi and Körösi (1972) analysed in the same way, by means of TG, the evaporation of pure liquids and corresponding mixtures.

The nature of the complex thermal decomposition process is denoted by the performed DSC analysis. Typical exothermal oxidative processes are clearly visible during heating in an oxygen stream. They are reprosented in the first phase of the process. In the region of intensive thermal decomposition the exothermal process overlaps with the endothermal reactions of decomposition of the oxidized products and evaporation of the formed volatiles.

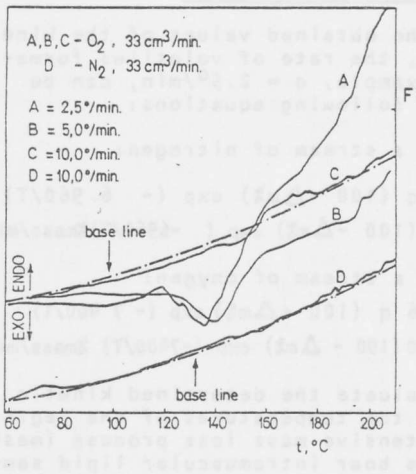

Fig. 4. DSC analysis of boar intramuscular lipids at various heating rates in O_2 and N_2 streams.

When the analyses are performed in a N_2 stream only the endothermal processes of thermal decomposition of intramuscular lipids and evaporation of volatiles are registered.

According to equation (1), it is possible to determine the kinetic parameters of the oxidation process (O_2) and thermal decomposition (N_2) according to the equation:

$$\ln (DTG/m) = \ln (A/q) - E/RT \qquad (2)$$

considering that

$$k(T) = (A/q) \exp (-E/RT),\ K^{-1} \qquad (3)$$

The analysis of equation (2) is presented in Fig. 5 , while the analysis of the intercepts of the linear functions and corresponding slopes is given in table II.

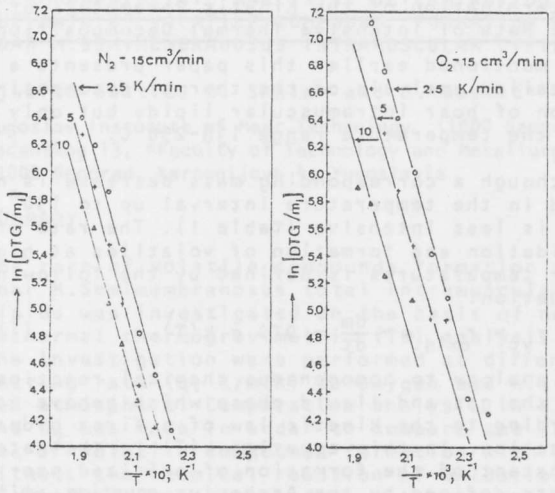

Fig. 5. Graphic interpretation of eq.(2) for the second step of mass loss process of boar intramuscular lipids

Table II. Analysis of the intercept and slope of eq.(2) with various q

Gas, l5 (cm^3/min)	Intercept, ln(A/q) 2.5	5.0	10.0	A, min^{-1} 2.5	5.0	10.0	Slope E, kJ/mol
N_2	5.975	5.632	5.275	983	1395	1953	57.9
O_2	7.839	7.269	6.534	6340	7170	6880	61.5

Check of the Kinetic Parameters

According to the obtained values of the kinetic parameters, the rate of volatiles formation at, for example, q = 2.5°/min, can be defined by the following equations:

TG analysis in a stream of nitrogen:

$$r_{vc}(N_2) = 393\ q\ (100 - \Delta m\%)\ \exp(-6960/T)$$
$$= 982\ (100 - \Delta m\%)\ \exp(-6960/T)\ \%mass/min$$

TG analysis in a stream of oxygen:

$$r_{vc}(O_2) = 2\ 536\ q\ (100 - \Delta m\%)\ \exp(-7400/T)$$
$$= 6\ 340\ (100 - \Delta m\%)\ \exp(-7400/T)\ \%mass/min$$

In order to evaluate the determined kinetic parameters and the temperatures of the beginning of the intensive mass loss process (mass changes) in the boar intramuscular lipid sample at q = 2.5°/min in oxygen and nitrogen streams were calculated and the obtained values compared to experimental data (Figure 6). The mass loss was calculated by the numeric integration of eq.(1). For this calculation the initial conditions defining the beginning of intensive thermal decomposition (Table I) were used.

Good agreement between the calculated and experimental values of $\Delta(\Delta m_{O_2} - \Delta m_{N_2})$ was obtained. This agreement is optimal at a heating rate of 5°/min. The determined activation energy of ~60 kJ/mol is in agreement with the activation energy of the thermal oxidation of oils (Mikula and Khayat, 1985).

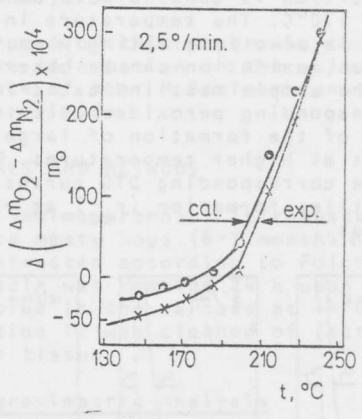

Figure 6. Comparison of the calculated and experimentally determined difference in the amount of the mass loss at q = 2.5°/min

The presented investigations and obtained results show that by using TG analysis, as well as determining the kinetics of oxidation of intramuscular lipids, an insight concerning their behaviour during thermal treatment, can be obtained which is also of definite practical interest. The proposed method of determining the rates of volatiles formation by TG analysis can be used as a standard procedure for the quantitative analysis of the rate of formation of compounds which influence the formation of aromas of various materials (lipids of animal and plant origin, etc).

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