Thermooxidative degradation of dried milk studied by non-isothermal thermogravimetry

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Summary

Thermooxidative degradation of three samples of powder dried milk with various fat content was studied by simultaneous DTA/thermogravimetry technique under air. The oxidation onset temperatures were determined from the thermogravimetric records by using a non-isothermal approach. Contrary to the isothermal measurements, the peak of oxidation is distinct in the nonisothermal measurements and the oxidation onset temperature can be read accurately and unambiguously. From the dependence of the onset temperature on the heating rate the kinetic parameters characterizing the length of induction period of oxidation have been obtained. The parameters appeared the same for all the dried milk samples. The lengths of induction periods decrease exponentially with temperature. A sinusoidal modulation of temperature leads to a considerable decrease of thermooxidative stability of the dried milk.

Keywords

dried milk; thermooxidative stability; induction period; thermogravimetry

Dried milk powder is an important ingredient in many foods such as chocolate, infant formula or coffee whiteners. Lipid oxidation is among the main reasons of the loss of shelf life and, consequently, the oxidation of dried milk is intensely studied as reviewed in [1-4] and the citations therein.

Monounsaturated and nonconjugated polyene fatty acids are those of significance in milk fat [1]. The initial step in the autoxidation of unsaturated fatty acids and their esters is the formation of free radicals. The resulting radicals or the radical products formed in the subsequent reactions with oxygen can be studied by electron paramagnetic resonance (EPR) [2]. Although EPR is a very efficient method, its application in monitoring the extent of autoxidation is quite rare. Various titration and colorimetric methods have been employed to determine the extent of autoxidation in lipids and lipid-containing food products, residing principally in the determination of peroxide concentration. The methods, however, are cumbersome and are not suited for routine analysis [1].

Oxidation in condensed phase exhibits an induction period, in other words, the stage preceding the main process, where seemingly no chemical reaction takes place. At the end of induction period, a sudden change in physical, physico-chemical or sensory properties of the material mostly takes place so that the length of induction period is often considered as a relative measure of material stability. The oxidation is an exothermic process and the reaction heat evolved makes it possible to employ the differential scanning calorimetry (DSC) or differential thermal analysis (DTA) for its study. Thermogravimetry (TG) can be also used since the oxidation is accompanied by a change of the sample mass. All the techniques mentioned, i.e. DSC, DTA and TG, belong to the category of thermoanalytical methods. The end of induction period is determined as the time/temperature of a sudden increase in the rate of the main oxidation stage, i.e. as the oxidation induction time (OIT) in the case of isothermal measurements and the oxidation onset temperature (OOT) in the case of measurements with linear heating [5]. Thermoanalytical methods are generally very efficient in the study of oxidation stability of edible oils [6], methyl esters of fatty acids [7], pharmaceutics [8] or other organic matter such as polymers [5].

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To our knowledge, there is no paper published on the thermoanalytical study of dried milk. Hence, the aim of this paper is to study the thermooxidative stability of three samples of dried milk powder by simultaneous DTA/TG thermal analysis.

THEORETICAL PART

Oxidation in the condensed phase is a very complex process exhibiting the induction period. The theory of induction periods is presented in [5]; only a very brief outline of the theory will be given here.

Rate of a complex multi-step condensed-state process can be formally described as [9]

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where $k(T)$ and $f(\alpha)$ are the temperature and conversion functions. The temperature function $k(T)$ is most frequently expressed by the Arrhenius-like relationship:

$$k(T) = A_k \exp\left[-\frac{B}{T}\right] \tag{2}$$

where A_k and B are parameters and T is absolute temperature. Eq. (1) can also be used to describe the kinetics of the reactions occurring during the induction period. The existence of those reactions is undetected by the experimental technique used; however, they have to occur as a preparatory stage preceding the main oxidation process.

The separation of variables in Eq. (1) and substitution of Eq. (2) gives after some manipulations

$$\int_0^{\alpha_i} \frac{d\alpha}{f(\alpha)} = \int_0^{t_i} A_k \exp\left[-\frac{B}{T}\right] dt \tag{3}$$

where α_i is the conversion of the reactions occurring during the induction period and corresponding to the end of the induction period and t_i stands for the length of induction period. Eq. (3) can be rearranged as follows:

$$1 = \int_0^{t_i} \frac{dt}{A \exp\left[\frac{B}{T}\right]} \tag{4}$$

Eq. (4) enables to calculate the induction period for an arbitrary temperature/time regime. The parameter A is given as

$$A = \frac{F(\alpha_i) - F(0)}{A_k} \tag{5}$$

where F is the primitive function of the inverted conversion function $1/f$. For isothermal conditions, the temperature is constant. Then, the denominator in Eq. (4) is also a constant and the numerator after integration is equal to t_i. In this case, t_i is the oxidation induction time:

$$t_i = A \exp\left[\frac{B}{T}\right] \tag{6}$$

For the linear heating program, the furnace temperature can be expressed as

$$T = T_0 + \beta t \tag{7}$$

where T_0 is the starting temperature of the measurement and β stands for the heating rate. After carrying out the transformation between time and temperature, from Eqs. (4) and (7) can be obtained [5]:

$$\beta = \int_0^{T_i} \frac{dT}{A \exp\left[\frac{B}{T}\right]} \tag{8}$$

T_i in the upper integration limit stands for the temperature coresponding to the end of induction period, i.e. the oxidation onset temperature. From Eq. (8) it can be seen that the oxidation onset temperature increases with increasing the heating rate.

A reason should be mentioned why a simpler way of obtaining the parameters A and B is not employed, i.e. from the temperature dependence of OIT using Eq. (6). The determination of induction periods from isothermal thermoanalytical measurements is often quite problematic mainly at lower temperatures since the corresponding peak is flat and its onset can hardly be read unambiguously. On the other hand, at higher temperatures where the induction periods are below 1 min, the periods are comparable with the time of establishing the steady state of the apparatus and an accurate determination of the induction period cannot be carried out. Contrary to the isothermal measurements, the peak of oxidation is distinct in the nonisothermal measurements and the oxidation onset temperature can be read accurately and unambiguously. The parameters A and B, characterizing the induction period, are obtained from nonisothermal measurements by treating the dependence of T_i on β using Eq. (8). Then, the OIT for a given temperature can be calculated using Eq. (6).

EXPERIMENTAL METHODS

DTA/Thermogravimetry

Simultaneous DTA/thermogravimeter Shimadzu DTG-60 (Kyoto, Japan) was employed to study the thermooxidative stability of the samples. The temperature scale was calibrated using the standards In and Zn. The samples of 2–4 mg were placed in crimped standard aluminium pans. In order to facilitate the contact of the samples with air, the lid of each pan was perforated by ten pinholes. The measurements were carried out in the temperature interval 50–300 °C with heating rates 1, 2, 3, 5, 7, 10 and 15 °C.min^{-1}. The purge gas, forming also the oxidation atmosphere, was air with flow rate of 50 ml.min^{-1} supplied from a cylinder. In the DTA records, the exothermic peaks are oriented upwards.

Materials

Three samples of dried milk powder (PML joint stock company, Nový Bydžov, Czech republic) were subjected to the study. The samples were marked as MILK 1, MILK 2 and MILK 3; the content of individual components declared by the producer is given in Table 1.

Fig. 1. Simultaneous DTA/TG records of the sample of powder dried whole milk (MILK 1) measured in air at the heating rate 10 °C.min^{-1}.

Tab. 1. Composition of the samples of dried milk powder.

Component [wt %]	MILK 1	MILK 2	MILK 3
Albumin	25	31	34
Lactose	39.5	45	53.2
Fat	26	14	1.3
Water	5	5	5

RESULTS AND DISCUSSION

An example of the simultaneous DTA/TG records is shown in Fig. 1 for the oxidation of dried whole milk (sample MILK 1) at the heating rate 10 °C.min^{-1}. It can be seen from the DTA record in Fig. 1 that the oxidation begins at about 170 °C.
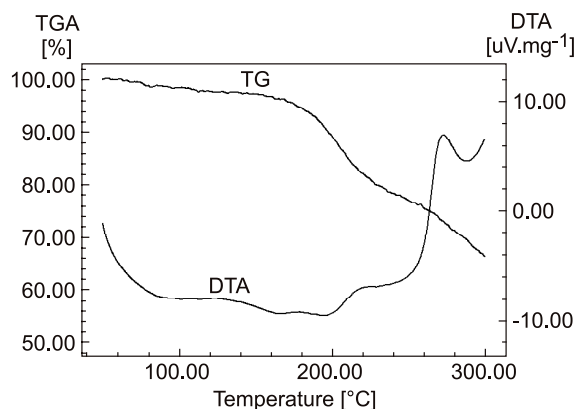
Between 170–290 °C three exothermic peaks are observed indicating that the oxidation is a multistep process. The first endothermic peak is too small to be observed when the measurement is carried out at lower heating rates. Therefore the determination of the oxidation onset temperature from the DTA record could be inaccurate. From the TG record it is seen that the sample mass begins to decrease simultaneously with the appearance of the first small exothermic peak at the DTA record. Moreover, the onset temperature from the TG record can be read more clearly than from the DTA record. Therefore, the end of the oxidation induction period was determined from the TG record as the onset temperature of the oxidation peak. The oxidation onset temperature as a function of the heating rate for the three dried milk samples is given in Table 2.

The experimental data were treated by the procedure described in [5] using the program KINPAR written in our laboratory (its DOS version is available on request). In the program, the parameters A and B are obtained by minimising the sum of squares between the experimental and calculated values of oxidation onset temperatures by the simplex method. The integration indicated in Eq. (8) is carried out by the Simpson method. The

Tab. 2. Oxidation onset temperature in °C as a function of heating rate for the samples of powder dried milk.

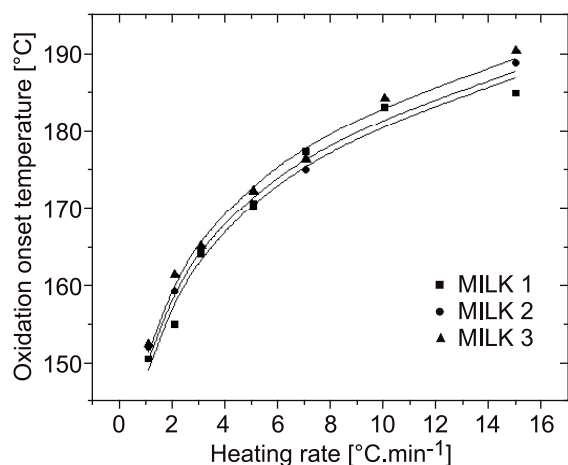| β [°C.min^{-1}]	1	2	3	5	7	10	15
MILK 1	150.5	154.9	164.1	170.6	177.3	183.1	184.9
MILK 2	152.0	159.3	164.5	170.1	175.0	183.1	188.8
MILK 3	152.4	161.4	165.1	172.3	176.4	184.2	190.4

Fig. 2. Experimental (points) and calculated (full lines) values of the onset temperature of oxidation as a function of the heating rate.

Tab. 3. Values of the adjustable parameters A and B obtained from the treatment of the data of Table 2 using Eq. (8).

sample	$10^{13} \times A$ [min]	$10^{-3} \times B$ [K]
MILK 1	4.66 ± 2.30	13.1 ± 0.4
MILK 2	2.87 ± 1.46	13.3 ± 0.1
MILK 3	4.68 ± 0.91	13.1 ± 0.2
average	4.07 ± 1.03	13.2 ± 0.1

experimental and calculated values of the onset temperatures are shown in Fig. 2; it can be seen that the quality of fit is very good.

The parameters A and B resulting from the treatment of experimental data are summarized in Table 3. Table 2 shows that the oxidation onset temperatures for the three samples of the dried milk do not differ much; hence, it is not very surprising that the parameters A and B presented in Table 3 are practically the same and their average values are $A = 4.07 \times 10^{-13}$ min and $B = 13200$ K. In the DTA/TG apparatus, the sample was dried before oxidation and the water liberated was carried away from the apparatus by the purge gas. The values of A and B thus correspond to the ther-

mooxidation of dried milk under air in the absence of moisture.

Eq. (6) shows that the length of the isothermal induction period decreases exponentially with increasing temperature. The length of the induction periods calculated for various temperatures are given in Table 4; it can be seen that the decrease is steep. For temperatures 25 and 50 °C, the calculated lengths of induction periods are obviously not realistic absolute measures of the stability of dried milk. It is recognized that extrapolation of the dependence of the length of induction period on temperature too far from the temperature region of the measurement often leads to unrealistically long values of induction periods [5]. The closer is the temperature to the range of measured oxidation onset temperature, the more realistic are the values of induction periods.

For comparison, for temperatures 25 and 50 °C the length of induction period was calculated by Eq. (4) considering the sinusoidal variation of temperature. The variation is intended to mimic the daily temperature variation so that the angular velocity of the modulation was 1 day^{-1} and the amplitude was 10 °C. The results are shown in Table 4; it can be seen that the modulation brings about a considerable decrease of the induction period of oxidation of the dried milk.

In practice, a pure isothermal regime is rare, the oxidation occurs under nonisothermal conditions. The example with the temperature modulation demonstrates a possibility of modeling the length of induction period for a nonisothermal regime using Eq. (4). Modeling of the processes occurring in foods plays an important role in hazard analysis and ensuring quality during food production, transport and storage. However, it is necessary to bear in mind that the quality of the results of modelling depends on the quality of the kinetic model, i.e. whether the model involves all essential effects, and on the reliability of the input parameters. The sample mass for the TG measurement was very small, the powder particles formed practically a monolayer at the bottom of the sample pan. Consequently, the kinetic parameters A and B obtained by nonisothermal DSC measurements do not convey the effect of oxygen diffusion within the sample. They are transferrable to be used in modeling the oxidation where the effects of reac-

Tab. 4. Length of the induction period as a function of temperature.

T [°C]	25	25 ± 10	50	50 ± 10	75	100	125	150
t_i	13.1 year	8.2 year	5.2 month	3.7 month	8.3 day	16 hour	1.7 hour	14 minute

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tion kinetics, oxygen diffusion, heat transfer and evolution of reaction heat are explicitly involved.

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