Study of the Thermooxidative Behavior of Edible Oils by Thermal Analysis[1]

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ABSTRACT

The complex thermoanalytical investigation of oil stability has been made by means of the Derivatograph using dynamic and static programs. TG, DTG and DTA curves have been registered simultaneously. The aim of the experiments was to determine the optimum conditions for examination of oxidative stability and oxidation state of edible oils. Results show that the study of thermal decomposition under dynamic conditions allows the detection of thermal and oxidative degradation. Storability can be investigated under static (isothermal) conditions by modeling the oxidation processes. Oxidative changes can be followed quantitatively with thermogravimetry (TG) and derivative thermogravimetry (DTG) curves, while differential thermal analysis (DTA) measurements show exothermic enthalpy changes. A novel method has been developed for rapid indication of the oxidative stability using isothermal conditions.

INTRODUCTION

A number of methods have been developed to estimate the deterioration of edible fats and oils during storage, thermal and oxidative treatment, (e.g., frying). The majority of these procedures are based on subjecting the sample to conditions accelerating the normal oxidation process (1-3).

There is a possibility to estimate the oxidative changes of fats and oils and their tendency to further deterioration by studying the thermooxidative behavior by thermal analysis, a widely used method for the investigation of aging processes.

Only a few papers have been published on the application of thermoanalytical methods to evaluate the oxidative stability of fats and oils. C.K. Cross (4) used the differential scanning calorimeter (DSC) to characterize different oils and shortenings. The exothermic enthalpy change during the rapid oxidation process which follows the induction period has been detected by a baseline shift under isothermal conditions. Good correlation was found between the results obtained by standard tests and DSC data. Nieschlag et al. (5) suggested micro thermogravimetric (TG) method; Hassel (6) introduced pressure differential calorimetric (PDC) procedure for the estimation of oil stability, using both static (isothermal) and dynamic programs (determination of the changes as a function of temperature).

EXPERIMENTAL PROCEDURES

The aim of our experiments was to develop a simple, fast method suitable for routine evaluation of the storability, i.e., oxidative stability and oxidation state of edible oils. For this purpose, fresh and aged oils were compared. The experimental models were sunflower and rapeseed oils, the most important edible oils in Hungary. Aged samples were obtained from fresh oils either by aeration at 100 C for two days, or by storing at room temperature for six months. In a few cases fried samples were also investigated. Fresh oils were used for frying potatoes at 180 C, modeling household frying, until samples were foaming and found very rancid. Decomposition of the oils was characterized by peroxide and acid values determined according to the standard tests (7) (Table I).

Oxidation results change both in the enthalpy and weight; therefore, in our investigation a complex thermoanalytical instrument was used (Derivatograph, manufactured by Hungarian Optical Works, MOM), which combines methods of thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA). Investigations of the oxidative stability of fats and oils by complex thermoanalytical methods have been published (8).

For the study of both oxidative and thermal changes, samples were dispersed as a thin film on a ceramic block, which was a fire-brick with considerably large surface (1 m^2/g measured by argon adsorption). It has been proved that this sample holder can be heated up to 1600 C without change in its specific surface. A similar block was the reference material for DTA measurements. Investigations were carried out under air flow (20 l/h). Sample weight was 400-450 mg.

The weight change (TG), its rate (DTG) as well as the temperature difference between the sample and the reference material (DTA) were registered simultaneously. The thermoanalytical curves were recorded as a function of temperature (dynamic program) and also as a function of time under isothermal conditions (static program).

RESULTS AND DISCUSSION

Figure 1 shows the thermoanalytical curves of fresh sunflower and rapeseed oils obtained under dynamic conditions at a heating rate of 5 C/min. Decomposition of the samples proceeded in three steps. With increasing temperature, weight gain started at 140 C due to oxidation and reached its maximum rate at 150 C (sunflower oil) and 165 C (rapeseed oil), as the DTG curves show. This process was followed by degradation from 175 C to 260 C, with

TABLE I

Peroxide and Acid Values of Fresh and Rancid Samples

Sample	POV mval oxygen / kg oil	AV mg KOH / g oil
Sunflower oil		
fresh	1.0	0.1
stored at room temperature	12.0	0.1
oxidized at 100 C	120.0	0.3
fried used 10 times	5.0	0.6
fried used 20 times	5.0	0.9
Rapeseed oil		
fresh	2.0	0.1
stored at room temperature	15.0	0.1
oxidized	90.0	0.3

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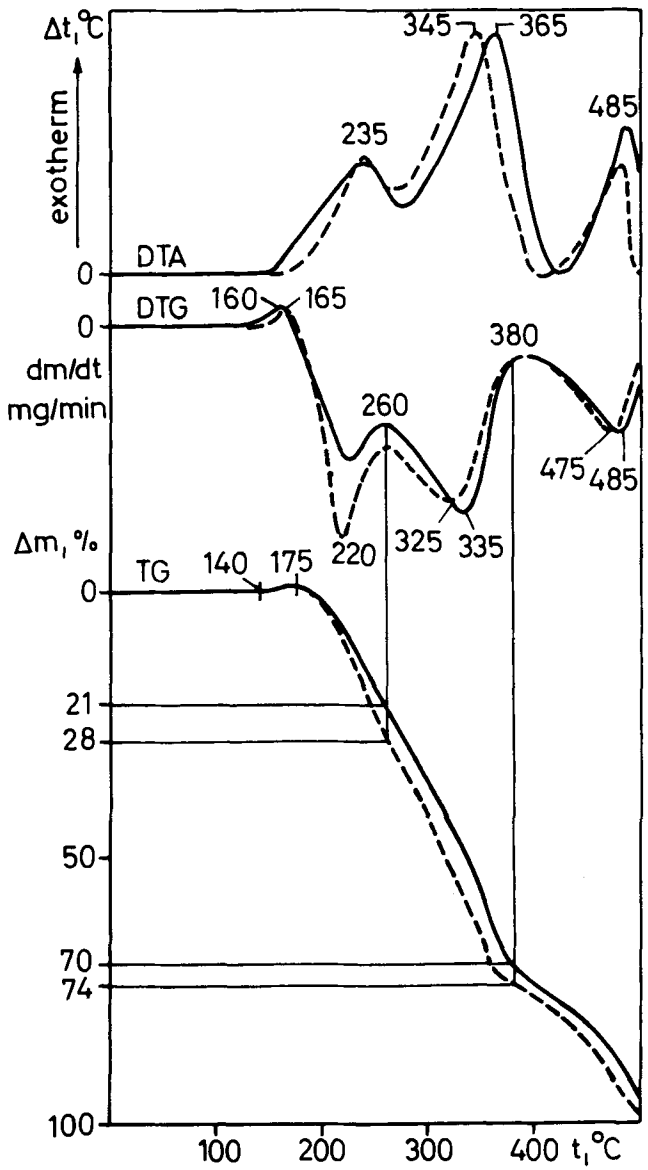

FIG. 1. Decomposition of fresh sunflower and rapeseed oils under dynamic conditions (as a function of temperature); heating rate 5 C/min: —— Sunflower oil, —— rapeseed oil.

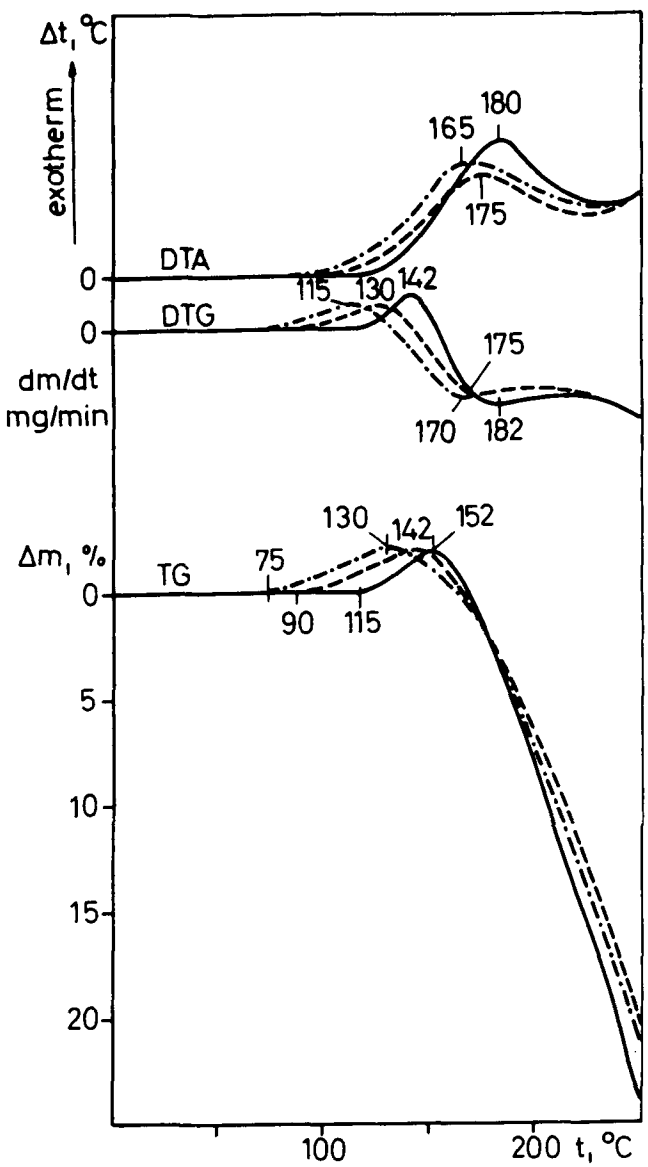

FIG. 2. Decomposition of fresh and thermally treated (fried) sunflower oils under dynamic conditions (as a function of temperature); heating rate 2.5 C/min: —— fresh (POV = 2.0; AV = 0.1) —— fried: used 10 times (POV = 5.0; AV = 0.6) -.-.-. fried: used 20 times (POV = 5.0; AV = 0.9).

DTG maxima 220 C in both cases. The second step of decomposition took place between 260 and 380 C, and then the oils decomposed quantitatively. DTA curves showed exothermic enthalpy changes. Since total degradation of the triglyceride molecules and combustion occurs above 260 C, the first step of decomposition is decisive in the study of oxidative changes. Only slight differences could be observed between the curve of sunflower and rapeseed oils, in spite of the fact that rapeseed oil is more resistant to oxidation than sunflower oil due to its fatty acid composition. This phenomenon is in agreement with the fact that there is no significant difference between the smoke-points of the two kinds of oils (3).

When thermal and oxidative stability of the samples was lowered by frying, significant differences could be detected between the thermooxidative behavior of fresh and fried oils. It could be better observed at a lower heating rate (2.5 C/min), as is seen in Figure 2. According to the results, initiative and maximum temperatures of weight gain as well as DTG maxima are characteristic of the stability of the oils. The results are in agreement with data in the literature (5,6).

To study the effect of mild oxidation (storage, aeration), we compared the degradation of fresh and aged samples in the similar way. There was no significant difference between the thermoanalytical curves of fresh and oxidized samples registered under dynamic conditions.

Isothermal (static) conditions proved to be suitable for evaluating storability and detecting autoxidative changes (8). In this case temperature was raised rapidly (ca. 10 min) to the reaction temperature, and TG, DTG and DTA curves were studied as a function of time.

Figures 3 and 4 present the thermoanalytical curves of fresh, stored and aged sunflower oils. Ninety-eight C was first chosen for the reaction temperature, similarly to the standard stability test. In this case a remarkable difference could be observed between the thermooxidative behavior of fresh and aged samples.

Evaluation of the TG curves was based on classical methods. The technique of following the oxidation of edible oils by weighing samples at intervals has been used for a long time. Olcott and Einset standardized the method for the investigation of the initial stages of autoxidation (9,10). According to this procedure, the length of the

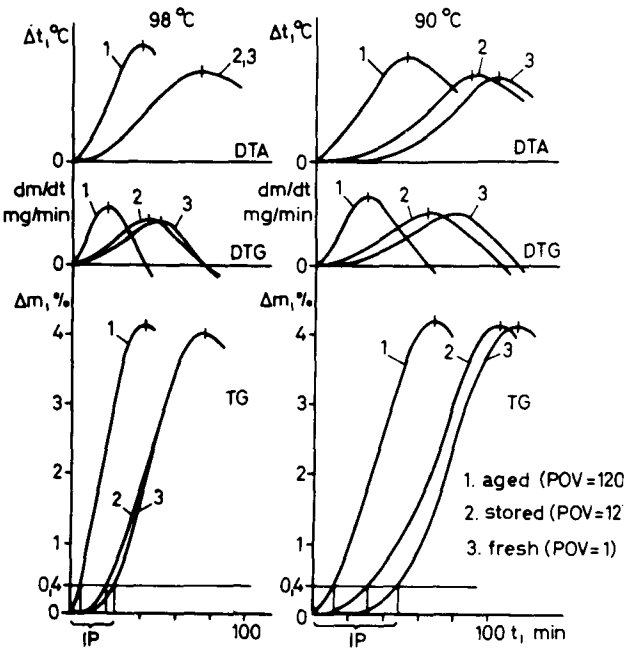

FIG. 3. Thermoanalytical curves of fresh, stored, and aged sunflower oils at 98 C and 90 C.

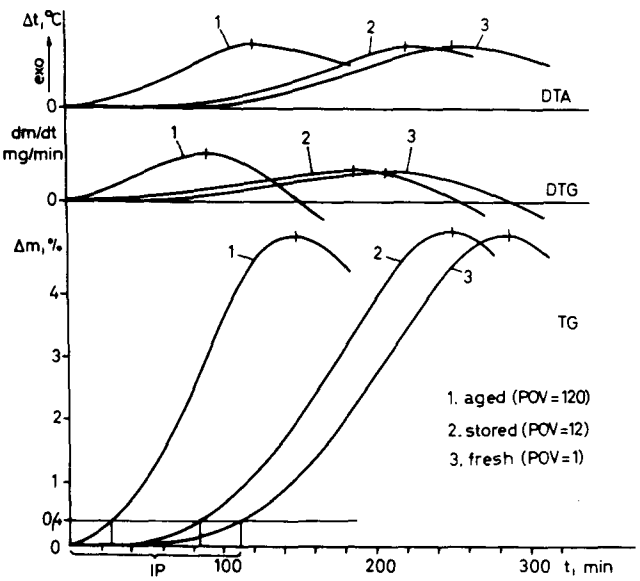

FIG. 4. Thermoanalytical curves of fresh, stored, and aged sunflower oils at 80 C.

induction period is taken as the time elapsed from the start of the experiment to the point the samples have gained 0.4% in weight.

As can be seen, the oxygen uptake of oils at 98 C is too fast to distinguish between fresh and slightly oxidized samples. In order to model autoxidation more properly and to find optimum conditions for the study of the initial phase, we have lowered the temperature. At 90 C and especially at 80 C, greater differences can be found in the length of the induction periods, the slope of the TG curves and the time of TG, DTG, and DTA maxima. The changes occurred still within a reasonable time.

Thus, oxidative stability of the oils can be characterized with the following data:

- length of induction period (IP, min)
- time of maximum weight gain (TG_{max}, min)

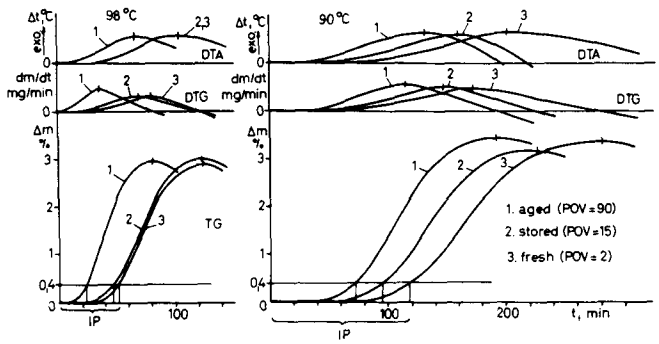

FIG. 5. Thermoanalytical curves of fresh, stored, and aged rapeseed oils at 98 C and 90 C.

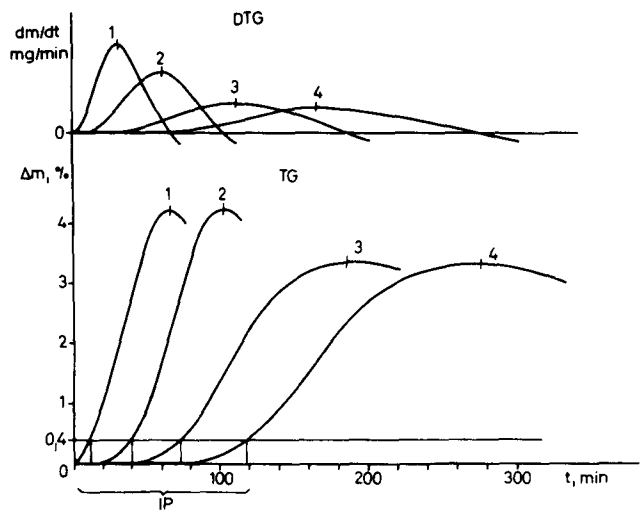

FIG. 6. TG and DTG curves of sunflower and rapeseed oils at 90 C. 1. aged sunflower oil (POV = 120); 2. fresh sunflower oil (POV = 1), 3. aged rapeseed oil (POV = 90); 4. fresh rapeseed oil (POV = 2).

- time of maximum rate of weight increase (DTG_{max}, min)
- time of maximum enthalpy change (DTA_{max}, min).

The total weight gained (Δm, %) depends practically on the experimental conditions.

Fresh, stored and aged rapeseed oils were investigated in the same way (Fig. 5). Rapeseed oil is more resistant to oxidation due to its fatty acid composition; therefore, its oxygen uptake was slower than that of sunflower oil. At 80 C no measurable weight increase could be determined within 3-3.5 hr, as compared to sunflower oil.

In practice, the determination of small differences is generally required. Consequently, sunflower oils can be feasibly studied at 80 C, while 90 C was found to be suitable for the evaluation of the oxidation state (storability) of rapeseed oils.

The thermooxidative behavior of the two kinds of oils can be readily compared at 90 C, as is shown in Figure 6. The difference between the two kinds of oils can be observed: the aged rapeseed oil of high POV oxidized considerably slower than the fresh sunflower oil. It was shown not only by the length of the induction periods but also by the slope of the TG curves and by the time required to reach the highest oxidation rate, i.e., the DTG maxima. It can also be seen that under the same experimental conditions the maximum weight increase depends only on the type of the oil.

The initial phase of the TG curves has been evaluated also by mathematical statistical methods. The weight gain

TABLE II

Sunflower Oils: Coefficients (a) and Exponents (b) of the Power Functions Describing the TG Curves under Isothermal Conditions

Sample	t (c)	a	b
Aged	98	1.2×10^{-1}	1.00
(POV = 120)	90	2.5×10^{-2}	1.21
	80	4.8×10^{-4}	1.95
Stored	98	8.7×10^{-4}	2.06
(POV = 12)	90	5.1×10^{-5}	2.59
	80	2.0×10^{-8}	3.71
Fresh	98	7.2×10^{-6}	3.44
(POV = 1)	90	5.0×10^{-9}	4.69
	80	1.1×10^{-12}	5.75

TABLE III

Rapeseed Oils: Coefficients (a) and Exponents (b) of the Power Functions Describing the TG Curves under Isothermal Conditions

Sample	t (c)	a	b
Aged	98	3.4×10^{-5}	2.97
(POV = 90)	90	1.9×10^{-9}	4.45
Stored	98	8.2×10^{-6}	2.83
(POV = 15)	90	2.4×10^{-10}	4.67
Fresh	98	1.9×10^{-9}	4.95
(POV = 2)	90	8.4×10^{-12}	5.15

(ca. up to 1%) against time can be approached by the power function

$$\Delta m = at^b$$

where Δm is the percentage of weight change measured at t time. The exponents and coefficients of the functions can be determined from the logarithmic function:

$$\lg \Delta m = \lg a + b \cdot \lg t$$

The exponents and coefficients are, thus, the slopes and intercepts of the linearized TG curves. We found the exponents and the coefficients of the function to be in unambiguous correlation with the oxidative stability and oxidative state of the oils (Tables II and III).

TABLE IV

Standard Deviations of Data Obtained from the Thermoanalytical Curves under Isothermal Conditions

Data	Standard deviation (%)
Induction period	± 4.4
Time of DTG_{max}	± 5.3
DTA_{max}	± 3.4
TG_{max}	± 3.4

Good reproducibility of the measurements was assured by the high accuracy of weighing. The standard deviations of the data are summarized in Table IV.

This new method is suitable also for industrial quality control; therefore, we wish to extend our investigations to the study of the correlation with standard methods.

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