A Rapid Instrumental Method for the Evaluation of the Stability of Fats

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A rapid instrumental method for evaluation of stability of fats has been proposed. Acceleration of oxidation is accomplished by vigorous mixing of a heated sample with oxygen at atmospheric pressure. The volume of absorbed oxygen determined directly by means of a special manostatic device constitutes the measure of the course of the reaction. Experimental results are recorded on a strip-chart plot of the volume of oxygen absorbed as a function of time. The start of rapid absorption of oxygen at the end of the induction period is taken as the end point. Samples of commercial low-erucic rapeseed oil, soybean oil and lightly hydrogenated soybean oil had end points in the range of 50 to 100 at a temperature of 120 C.

Stability of fats during storage can be anticipated on the basis of special tests called stability tests. Standard tests are based on storage of fats under normal conditions and determination of changes in odor, peroxide content, ultraviolet absorption or carbonyl content. The basic disadvantage of such tests is their very long duration. Due to this, accelerated tests were introduced. They are based on reduction of the induction period by elevation of temperature, UV irradiation, intensive oxygenation, etc. Among the most commonly used methods are the classic Active Oxygen Method (1) and its automated versions (2-4). The rate of pressure changes caused by absorption of oxygen by fats under standard conditions constitutes the measure of the rate of oxidation reaction in Warburg's test. It is necessary to observe the apparatus and the pressure readings closely in order to determine oxygen absorption as a function of time. The oxygen bomb test is based on a similar principle; this method, however, is not very sensitive, especially at small pressure changes. A dynamic method was patented (5) recently, in which the amount of oxygen absorbed during oxidation is measured continuously by a detection system identical to the one used in gas chromatography (6,7).

This paper presents a rapid method for evaluating the oxidative stability of fats. Acceleration of oxidation is accomplished by vigorous mixing of a heated sample with oxygen at atmospheric pressure. The volume of absorbed oxygen, determined directly, continuously and automatically, constitutes a measure of the course of the reaction (8).

EXPERIMENTAL

The process of accelerated oxidation of fats was carried out in a laboratory model of an apparatus for investigating the kinetics of reactions proceeding with evolution or absorption of gases (8). The prototype of this apparatus was developed in our laboratory; it is shown in Figure 1.

The most essential part of the apparatus is the manostatic device (Fig. 1, No. 2) equipped with a hydraulic seal which is placed in a thermostat. The manostatic device is connected via a tube with a steel cylinder (Fig. 1, No. 1), containing oxygen and with a reactor (Fig. 1, No. 4) for accelerated oxidation of oil. The cylinder-shaped glass reactor, 200 mm high and 50 mm in diameter, is equipped with a high-speed rotary paddle stirrer made of stainless steel (Fig. 1, No. 4_1); a temperature sensor (Fig. 1, No. 4_2); a heating element (Fig. 1, No. 5); a side tube for introduction of catalyst (Fig. 1, No. 4_3), and a side tube for sample drawing (Fig. 1, No. 4_4). The movable part of the manostatic device is

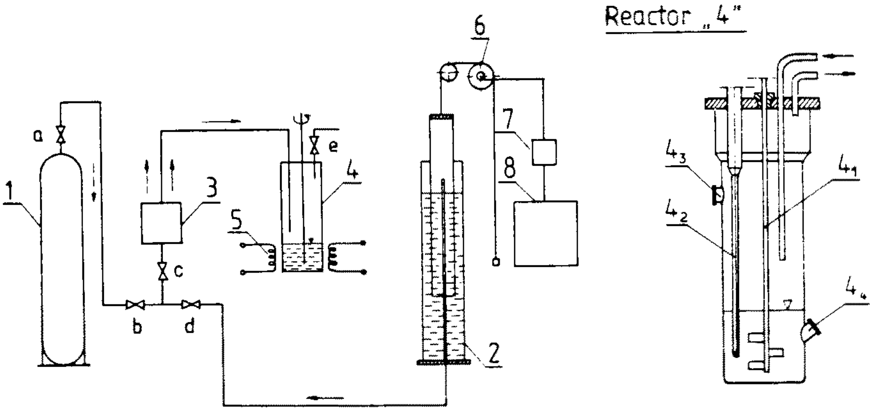

FIG. 1. Schematic diagram of the apparatus for the determination of the kinetics of oxidation of fats. 1, Steel cylinder containing oxygen; 2, manostatic device; 3, drying system; 4, reactor equipped with a stirrer (4_1), a temperature sensor (4_2) and side tubes (4_3, 4_4); 5, heating element; 6, transducer; 7, power supply; 8, strip-chart recorder, and a-e, valves.

connected to a transducer (Fig. 1, No. 6) changing mechanical variables into electrical ones. The transducer, equipped with a power supply (Fig. 1, No. 7), is connected to a continuous-record strip-chart recorder (Fig. 1, No. 8). The strip-chart record, illustrating the course of absorption of oxygen by the investigated oil as a function of time, characterizes the kinetics of the oxidation reaction. When valves "a" through "e" are open, oxygen from the cylinder flows to the manostatic device and through the reactor, purging the system. Due to a small overpressure in the system, the movable part of the manostatic device moves up. The level of this part is controlled with the "d" valve. When the manostatic device is set in its upper position the "d" valve is closed and the pen of the strip-chart recorder draws the base line. The oil in the reactor is heated to the desired temperature. The stirrer remains switched off during heating. When the preset temperature is reached, the "a," "b" and "e" valves are closed and the reactor is connected to the manostatic device by opening the "c" and "d" valves. The moment of switching the stirrer on is assumed to be the beginning of the reaction.

Absorption of oxygen by oil results in a lowering of the movable part of the manostatic device. The changes in position of this part are recorded by the strip-chart recorder. The glass reactor also is equipped with a side connector, enabling drawing of the samples of the oxidized oil, e.g. by means of a syringe, for simultaneous chemical analyses.

The curves of absorption of oxygen as a function of time, called the kinetic curves of oxidation, are obtained as a result of the reaction. These curves allow for determination of the induction period and for continuous observation of the course of absorption of oxygen by the investigated oil in the entire measuring range.

The stability of oil can be evaluated on the basis of the length of the induction period. The induction period is determined graphically by extrapolating the upward portion of the curve to the time axis. The point where these lines intersect is taken as the induction period.

CONTROL TESTS OF OXIDATION

The following oils were used for testing of the apparatus: soybean and low-erucic rapeseed oils after complete industrial refining, partially hydrogenated soybean oil and partially oxidized oil obtained by accelerated autoxidation of refined soybean oil (9).

The following parameters of the oxidation process were used: mass of oil, 50 g; stirring rate, 2500±200 rpm; oxygen pressure, atmospheric; temperature, 100-140 C.

Depending on the shape and size of the reactor, kind of stirring and design of the stirrer, as well as the amount of oil used, there are critical revolutions of the stirrer at which the oxygen transport resistance is eliminated. This means that further increase of the revolutions does not influence the rate of the reaction and the character of the kinetic curve of oxidation. For the examined apparatus the critical rate of stirring was equal to ca. 2000 rpm.

The peroxide value is expressed as milliequivalents of peroxide/1000 g of sample (10).

Figure 2 presents the kinetic curves of oxidation of a sample of soybean oil at 100, 120 and 140 C. As expected (11), the higher the temperature of the reaction, the shorter the induction period, and the smaller the total amount of absorbed oxygen. In the course of further research the temperature equal to 120 C was set as the oxidation temperature, because the induction period is too long at lower temperatures.

Figure 3 depicts the course of changes of the peroxide values in the process together with the curve of absorption of oxygen. A similar course of both curves is observed, viz. after an induction period a rapid increase of the peroxide value and the amount of the absorbed oxygen occurs, and after passing a maximum the peroxide value decreases while no absorption of gas is observed on the oxygen absorption curve. The maximum in the latter case depends, among other things, on the reaction temperature (Compare with Fig.

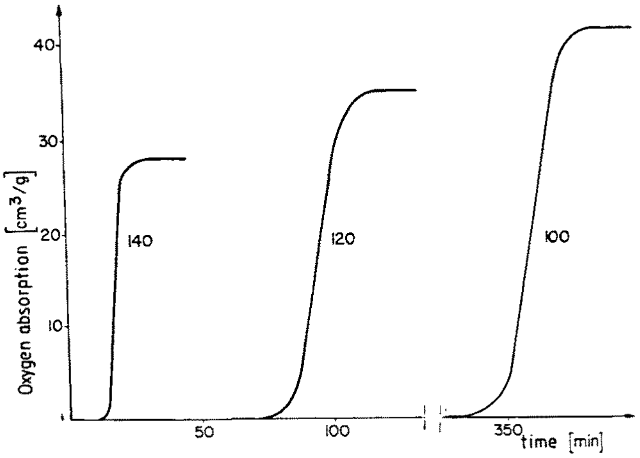

FIG. 2. Kinetic curves of oxidation of soybean oil at various temperatures.

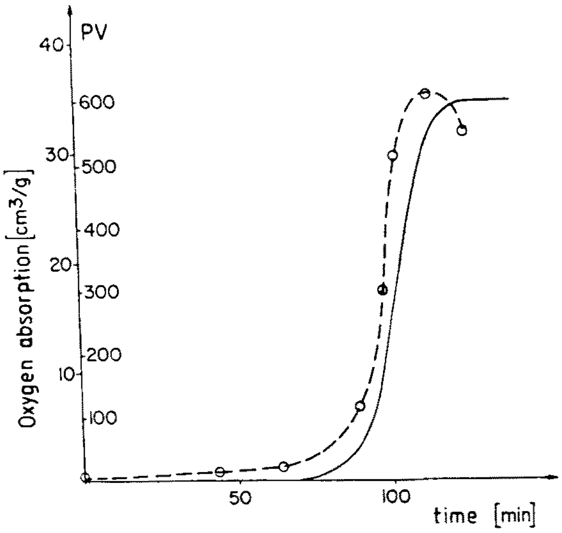

FIG. 3. Changes in the peroxide value of soybean oil during oxidation at 120 C (---) as compared to the kinetic curve of oxidation determined by means of the apparatus (———).

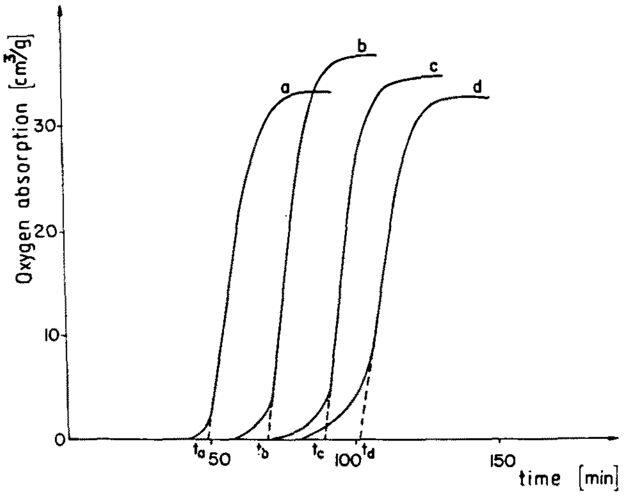

FIG. 4. Kinetic curves of oxidation of natural and modified soybean oils. Line a, partially oxidized oil (IV = 125.1; PV = 22.7); line b, partially oxidized oil (IV = 129.0; PV = 7.1); line c, initial oil (IV = 131.5; PV = 1.0), and line d, partially hydrogenated oil (IV = 107.8; PV = 0.7).

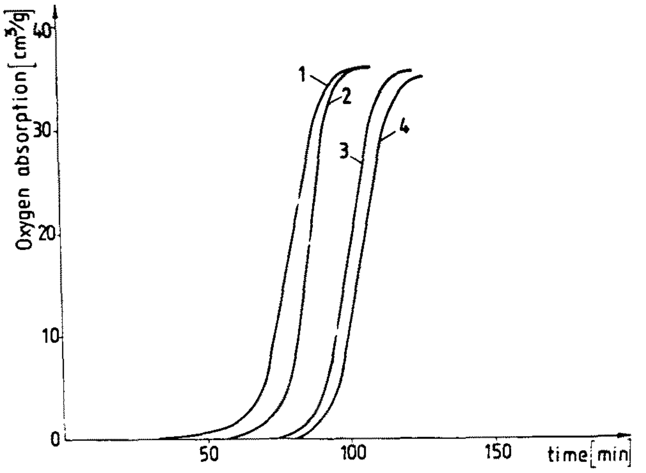

FIG. 5. Kinetic curves of oxidation of commercially refined low erucic rapeseed oils.

TABLE 1

Initial Iodine Values and Peroxide Values of Low-Erucic Rapeseed Oils Subjected to an Oxidation Test and the Obtained Lengths of the Induction Periods

Sample no.	Iodine value	Peroxide value	Induction period (min)
1	116.7	0.9	67.0 ± 0.8
2	119.9	0.2	77.0 ± 0.9
3	118.3	0.5	90.5 ± 1.0
4	117.7	0.6	93.5 ± 1.0

2). This can be related to establishing of an equilibrium between the evolving gaseous products of destruction of hydroperoxides and oxygen drawn from the manostat. The problem has not been examined extensively because for practical purposes, viz. determination of the stability of fats, this part of the oxidation curve is unimportant.

Figure 4 illustrates the effect of modification of oil on its behavior in the oxidation process. As could be expected, hydrogenation of oil increases its resistance to oxidation ("d" curve), while oils characterized by an increased peroxide value at the beginning of the examination reveal that, the shorter the induction period, the higher the peroxide value ("a" and "b" curves).

Figure 5 presents the kinetic curves of oxidation of four samples of low-erucic, refined rapeseed oil originating from industry. Fatty acid compositions of these oils were almost the same. Table 1 lists the iodine values (IV) and peroxide values (PV) of these oils and the lengths of their induction periods, together with the confidence intervals. The confidence intervals were determined for five measurements of the induction period assuming Student's distribution at chosen confidence level equal to 0.95.

Analysis of the results in Table 1 and the course of the curves in Figure 5 indicates large differences in the lengths of the induction periods (from 67 to 93.5 min) of the samples of low-erucic oils of similar initial peroxide and iodine values. This means that the above mentioned oils differed significantly in their oxidative stability.

The analysis of the course of the kinetic curves of oxidation allows for anticipation of the behavior of the investigated oil during storage. The course of these curves illustrates the total effect of all the factors responsible for both acceleration and inhibition of the process. The method is a rapid one, and the course of the oxidation process can be determined in a wide range of changes of the peroxide value. The proposed method can be used for investigation of the kinetics of oxidation of fats and for evaluation of their oxidative stability. It can be applied for both fundamental research and routine industrial analyses.

In case of application of the proposed method for a routine analysis, steady-state conditions of carrying the oxidation process — the manner of stirring, the design of the reactor and the size of the oil sample, among others— must be strictly observed, because only in such a case can comparable results of tests carried out in various laboratories be obtained.

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[Received October 25, 1985]