myristic acid both the methyl and ethyl esters yielded cetane indexes of 48.

It is evident that the ASTM method produced cetane indexes which were lower for the shorter chain esters and higher for the polyunsaturated esters than those produced by equation 6. This difference can also be seen in the cetane indexes for the transesterified oils, Table II. The ester mixtures which are higher in shorter chain acids or low in polyunsaturated acids show cetane indexes which are low compared to the experimentally determined indexes (6) when the ASTM-calculated indexes for constituent esters are used. On the other hand, cetane indexes for these mixed esters agree within the stated limits for determination of cetane number (8) when the cetane indexes for the constituents of the mixtures calculated according to equation 6 are used. Close agreement might be expected here since the cetane indexes for the individual esters were derived from these experimentally determined cetane numbers. However, the fact that the agreement was close for all of the vegetable oil-derived ester mixtures which have quite wide variations in their fatty acid compositions lends credence to the cetane indexes estimated for the fatty acid esters. The minor differences observed may be attributable to one or more of the following sources: (a) precision of the cetane number determinations; (b) use of fatty acid composition data which might not match the fatty acid compositions of the ester mixtures on which the cetane number data were obtained; and (c) possible nonlinearities of cetane index with chain length and unsaturation.

The method described above provides a convenient means of estimating the cetane indexes for methyl ester mixtures containing the ordinary range of fatty acids. Recently, the cetane number for the ethyl esters prepared from soybean oil has been reported to be 50.0 (9) and 48.2 (10), both on samples obtained from the same source. Since the cetane number for the methyl ester prepared from soybean oil was reported to be 45 (6) and the cetane index calculated in this study was 45.7, it appears that ethyl esters have cetane indexes between two and five units higher than the corresponding methyl esters.

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A Gas Chromatographic Reactor to Measure the Effectiveness of Antioxidants for Polyunsaturated Lipids[1]

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ABSTRACT

A method and apparatus consisting of a gas chromatographic reactor was developed to study the effect of antioxidants on lipid-containing systems. The oxygen uptake during the oxidation tests was continuously measured. The relative efficiencies, expressed as protective index, for butylated hydroxytoluene (BHT), propyl gallate (PG), α-tocopherol, citric acid, and ascorbic acid on the oxidation of linoleic acid at 85 C and 55 mmHg were determined. The effect of increasing the concentration of BHT (0.025, 0.05, and 0.1%) on the oxidation of safflower oil at 70 C and 45 mmHgO_2 was observed. The method was found to be a rapid and reproducible approach to investigate the effect of antioxidants on polyunsaturated lipids.

INTRODUCTION

Modern methods of food processing and handling require the addition of antioxidants in lipid-containing foods to ensure high storage stability. The most common antioxidants in food processing are the free radical scavengers (Type 1) which can donate a hydrogen to a radical and the free radical production preventors (Type 2) which inhibit oxidation by chelating trace metals normally present in foods (1). Examples of the Type 1 include butylated hydroxytoluene (BHT), tertiary butylhydroquinone (TBHQ), propyl gallate (PG), and tocopherols. Citric acid, ascorbic acid, phosphoric acid, and ethylene diaminetetraacetic acid (EDTA) are examples of the Type 2 which are also classified as synergists (1-2). Because of possible toxicity of the synthetic antioxidants, other natural compounds have been reported. For instance, the active antioxidant component in the extracts of rosemary and sage has been shown to improve the flavor stability of soybean oil and of fried food such as potato chips (3). In addition, antioxidant activity of amino acids (4,5) and of caffeic acid and its esters (6) are other examples of natural inhibitors of lipid oxidation.

The mechanism of protection given by an antioxidant is postulated to occur at the initial stage of autoxidation (1, 2,7,8). The free radicals formed by an initiator (light, metals) or by chain reaction are inhibited or interrupted by the free radical acceptor (phenolic structure), thus stopping the chain reaction. Such protection mechanism leads to an increase in the induction period of antioxidation and therefore a longer

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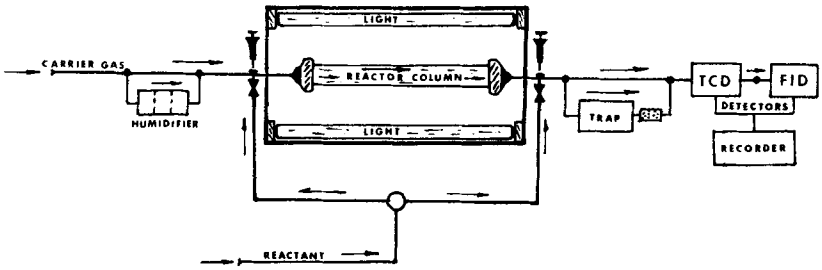

FIG. 1. Diagram of the gas chromatographic reactor showing the pulse and continuous designs. Patent pending by J.A.F. Faria, 1981.

shelf life of a packaged fatty foods is achieved.

It is not the purpose of this work to review the extensive literature available on the measurement of lipid oxidation, but rather to discuss the most common methods used to evaluate the efficiency of antioxidants, especially in vegetable oils. In general, lipid oxidation is measured by objective and subjective methods. Subjective methods involve the testing of a prepared food by organoleptic means, i.e., relying upon the individual judgment of trained persons. There is no ideal chemical method which correlates well with changes in organoleptic properties of oxidized lipids throughout the entire course of autoxidation (9). Although widely used, subjective methods for assessing the stability of prepared foods are time consuming, and taste panels are difficult to maintain (10). In a lipid system undergoing oxidation, the lipid composition, the oxygen uptake, the intermediate products of peroxide formation, and the final products of reaction or peroxide decomposition have been considered in developing objective methods for determining lipid stability (10). However, it should be emphasized that the oxidation process in a lipid system is dynamic, i.e., a continuing series of reactions; thus, any one means of measurement is subject to errors related to this dynamism (11).

Objective methods may be either static or dynamic. Static methods are defined as those which measure the extent of oxidation at a certain moment in time. Dynamic methods, commonly used for testing antioxidants, refer to the assessment of oxidation of a sample which is submitted to a kind of accelerated oxidative test. Examples of accelerators are high temperature, light, and metals.

Oxygen-absorption methods measure the oxygen uptake during a dynamic oxidation test. Some of these methods include the oxygen bomb method (OBM), the Barcroft-Warburg method, the Ekey method, and the weight-gain technique. Methods which measure lipid oxidation by directly or indirectly determining the peroxide value (PV) include the active oxygen method (AOM) and the Schaal oven test (12). The AOM of the AOCS has been employed extensively to evaluate the relative stability of vegetable oil systems. It measures the time (in hours) required for a sample of oil to attain a predetermined PV under specific conditions (9, 12).

Antioxidant effectiveness as monitored by the above mentioned methods has been questionable because of the high temperatures (65 and 100 C) used to accelerate the reactions. Tests conducted at high temperatures are subject to secondary reactions other than lipid oxidation. Moreover, the degree of protection or effectiveness of primary antioxidants decreases as the temperature increases (12).

The present work reports a new method to determine the efficiency of antioxidants in lipid-containing systems. It is a dynamic method which measures the amount of oxygen reacted during the oxidation. The high sensitivity of the detector system enables the assessement of low extents of reaction at the early stage of the induction period. The method consists of a gas chromatographic reactor (GCR) which has been found to be fast and reproducible for monitoring oxidation reactions at a broad range of temperatures and reactant concentrations (13).

EXPERIMENTAL

Description of the Apparatus

Figure 1 is a diagram of the apparatus which was developed to perform accelerated shelf life test where temperature, oxygen concentration, relative humidity, and light can be adjusted to different levels (13). The apparatus, a GCR, consisted of the following parts: the reactor chamber, the

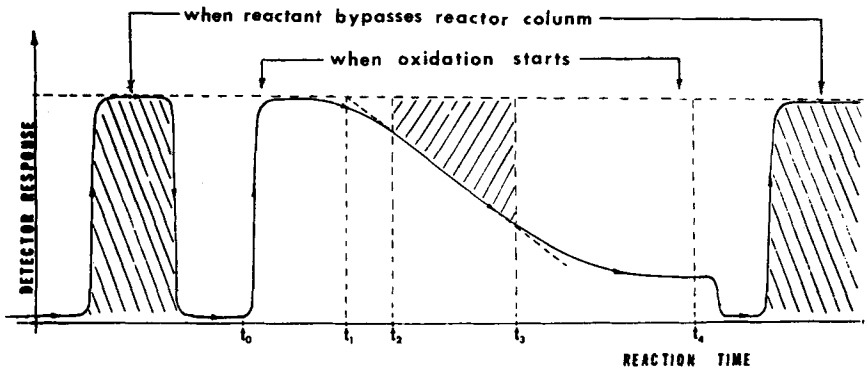

FIG. 2. Chromatogram profile obtained when the reactant is continuously introduced. A constant detector response indicates a steady state partial pressure of the reactant in the system; a decrease in response indicates uptake of reactant, when the reaction starts.

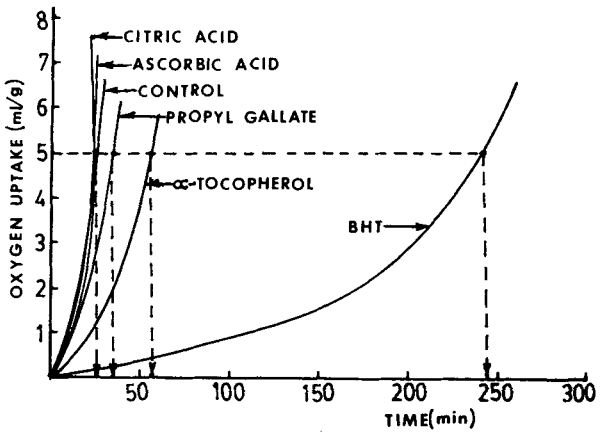

FIG. 3. Effect of antioxidant on the oxidation of linoleic acid. Concentration of antioxidant, 0.1%; 85 C, 55 mmHgO_2.

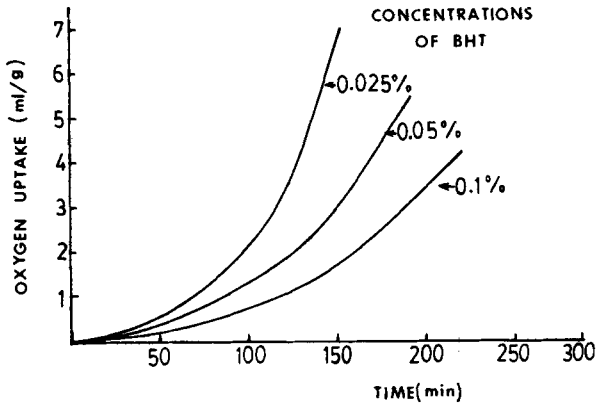

FIG. 4. Effect of the increase in the concentration of BHT on the oxidation of safflower oil. Oxygen partial pressure, 45 mmHg; 70 C.

condenser or trap, the humidifier, the detectors, and the recorder.

Materials

Linoleic acid and antioxidants were obtained from Fisher Scientific Co., Springfield, NJ. Vegetable oils were purchased from local supermarkets. High purity helium, the carrier gas for the GCR, and oxygen as the reactant were supplied by the Union Carbide Corp., Linde Division, NY.

Test Procedures

The sample (linoleic acid or vegetable oil) was packed into a quartz glass column (30 cm length, 1 cm id) which contained cotton as the inert support. The ratio of sample to inert support was 1:2 (w/w).

Experimental tests were begun only after the packed oxidation column had reached thermal equilibrum, i.e., after conditioning for about 1 hr before introducing the reactant (oxygen). The total pressure (helium plus oxygen) was a little higher than one atmosphere. Oxygen partial pressure, as reported in the results, was calculated by considering its mole fraction given by the detector response and the total pressure related by Dalton's Law. The volatiles formed during oxidation were condensed at about -78 C when the carrier gas leaving the reactor column was led through a trap containing dry ice and acetone as the cooling medium. Operation without a trap is possible when gases eluting from the reactor column are sampled and conducted to the detector systems. A thermal conductivity detector (TCD) was used to measure oxygen uptake. When volatiles were also measured, the gases leaving the reactor column were automatically sampled and analysed by a flame ionization detector (FID). Oxygen uptake was calculated by relating the area of the TCD response for a standard by passing the oxidation column and the response of the eluted oxygen during the time of oxidation. Figure 2 shows a typical chromatogram profile obtained during an oxidation test.

RESULTS AND DISCUSSION

The efficiency of antioxidants to protect against the oxidation of linoleic acid at 55 mm HgO_2 is shown in Figure 3.

Antioxidant effectiveness at a given concentration was expressed as protective index (PI), as follows:

$$PI = \frac{\text{time for uptake of 5 mL } O_2\text{/g by sample + antioxidant}}{\text{time for uptake of 5 ml } O_2\text{/g by sample}}$$

When added at a level of 0.1% (w/w), the PI for citric acid, ascorbic acid, PG, α-tocopherol, and BHT were 1.0, 1.0, 1.2, 1.5 and 7.0, respectively. Because the linoleic acid was purified, presumably free of trace metals, the lack of protection by citric acid and ascorbic acid (PI = 1.0) was expected, as they function as chelating agents in protecting against oxidation (1). The high efficiency of BHT compared to PG may be explained by the low solubility of the latter in linoleic acid. Some degree of protection was afforded by α-tocopherol, a natural antioxidant.

Figure 4 shows the effect of increaseing the concentration of BHT on the oxidation of safflower oil. By using this method and apparatus one can determine accurately the amount of antioxidant for a lipid system without overprotecting by excessive addition of antioxidants.

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