Methods for Stability and Antioxidant Measurement[1]

E. R. SHERWIN, Eastman Chemical Products Inc.,
Subsidiary of Eastman Kodak Company, Kingsport, Tennessee

Abstract

A great variety of books and technical papers has been published dealing in detail with the basic chemistry of rancidity in fats and oils and the techniques which have been investigated as a means of determining the stability characteristics of fats and oils as well as the effectiveness of various agents, such as antioxidants, in improving those stability characteristics. This review of methods for stability and antioxidant measurement is intended to serve as a relatively brief outline of that particular area of fat and oil technology.

Introduction

Other papers on processing and quality control of fats and oils have covered many facets of producing from animal and vegetable raw materials the highly refined, attractive fats and oils available on the market today. These commercial fats and oils, by virtue of the modern-day processing techniques, have a variety of built-in characteristics which make them especially suitable for many diverse applications. Also, considerable time has been devoted to discussing means of controlling production of fats and oils so that the presence of these desirable characteristics in the finished product will be assured. In reviewing the methods for stability and antioxidant measurement, which are extremely important in quality control of fats and oils, primary concern will be with understanding the nature of the rancidity problem in fats and oils and then with making a detailed inspection of various means available for determining rancidity in a fat or oil and the stability or storage life until rancidity occurs.

Stability, or the resistance to the development of rancidity, is a factor or characteristic which, to a major extent, must be built into fat or oil through the use of proper raw materials, by application of sound processing techniques, and possibly by the addition of chemical agents (antioxidants) at the appropriate time during production. Possibly no other single bit of technology has had a more widespread impact on the processing and marketing of fats and oils than that of antioxidant technology since the inherent stability of many fats and oils is not adequate to meet the needs. Stability of fats and oils tends to be a rather elusive thing in that it is so readily affected by a wide variety of factors commonly encountered during manufacture, storage, shipment, and consumption. Herein lies the source of many difficulties and even misunderstandings associated with attempts to improve the stabilities of fats and oils through the use of antioxidant agents and to measure the effect of antioxidant treatment on the stability of the fat or oil. Possibly adding to this confusion is the lack of complete agreement on the actual nature of the oxidation mechanism and the function of antioxidants (23,24).

Scanned in this paper will be the current state of the science of evaluating fats and oils from the standpoint of rancidity development, estimation of stability, and evaluation of antioxidant effectiveness. To do this, it will be necessary first to review the more commonly accepted theories accounting for fat and oil structure and rancidity development, then to examine the methods of rancidity, stability, and antioxidant measurement in the light of these theories.

Development of Rancidity

Fats and oils of commerce are fundamentally esters of glycerol, a trihydric alcohol, and various of the many fatty acids found in nature (39). It is important to remember that pure triglycerides are essentially odorless, colorless, and tasteless. Odor, color, and flavor characteristics (desirable and undesirable) of commercial fats and oils stem mainly from nonglyceride components which are present naturally, or through contamination, or as a result of decomposition of the basic triglyceride structure. Components that can be found in fats and oils aside from the basic glycerides are fat-soluble vitamins, pigments, moisture, dissolved gasses, metals, phospholipids, free fatty acids, and various products of rancidity development (5,9,14,15,20,23,24,33–35,39). In consideration of stability and antioxidant measurement, concern will be mainly with products which result from the two principal types of decomposition of the basic fat and oil structure, hydrolysis at the ester linkage and oxidation at the double bond linkage.

These hydrolytic and oxidative reactions result in the formation of a variety of decomposition products which can have significant effects on odor, flavor, and other characteristics of a fat or oil. More specifically, the decomposition products can be identified as free fatty acids, peroxides or hydroperoxides, carbonyls (aldehydes and ketones), and fatty alcohols, which can cause, in addition to the off-odors and off-flavors of rancidity, lowered smoke point, foaming in frying oils, destruction of vitamins, and even possible toxic effects under extreme conditions.

In addition to recognizing that certain hydrolytic or oxidative decomposition products are responsible for the rancid condition in fats and oils, one should also recognize that certain factors or agents in the environment or in fats and oils themselves are responsible for accelerating or promoting the development of rancidity. Some of these factors which not only have a significant bearing on storage life of fats and oils under commercial conditions but play important roles in the various stability tests are: hydrolytic rancidity—enzymes (particularly lipases or fat-splitting enzymes), moisture, and heat, and oxidative rancidity—oxygen, light (especially ultraviolet), heat, metals (especially copper and iron), other oxidized fats, salt, acids and anything that might inactivate antioxidants. Obviously the development of rancidity in fats and oils can be minimized by the elimination or reduction of these "pro-rancidity" factors.

Methods for Rancidity Measurement

Through the years a wide variety of techniques for determining rancidity in fats and oils has been investigated and reported in the literature. However relatively few of these techniques have been found suitable for use in day-to-day quality control and product development work. Clearly the measurement or detection of rancidity is dependent upon techniques suitable for determining the products of rancidity found in fats and oils. Some of the more commonly used rancidity measurement techniques will be examined in detail (26).

Free Fatty Acid Value (1). Hydrolytic rancidity occurs as a result of a splitting of the glyceride molecule at the ester linkage with the formation of fatty acids which can contribute objectionable odor, flavor, and other characteristics. The free fatty acids will react with alkali, in a simple neutralization reaction, and this is used as the basis for measuring the amount of free fatty acid in a fat or oil.

In determining the free fatty acid value, a small weighed portion of the fat or oil is dissolved in alcohol, to which

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