SOYA OIL—Round table discussions

Metals in Soybean Oil

F.J. FLIDER and **F.T. ORTHOEFER**, A.E. Staley Manufacturing Company,
2200 E. Eldorado St., Decatur, IL 62525

ABSTRACT

Certain metals often produce deleterious effects when present in soybean oil. Trace quantities of copper, iron and manganese dramatically reduce the oxidative stability of edible oils. The presence of calcium and magnesium in crude oils reduces the efficiency of degumming and refining operations. Sodium soaps reduce bleaching efficiency by inactivating adsorption sites on bleaching earth. Phosphatides or phosphorous containing lipids exert a poisoning effect on hydrogenation catalysts. Nickel, an artifact of hydrogenation, must be removed from the oil for health, stability and safety considerations. This paper provides an overview of the various effects of metals on processing and stability, describes how to inhibit or diminish their activity, and discusses various analytical techniques for identification and quantitation of the metals present in soybean oil.

INTRODUCTION

Throughout oil refining operations, metals can be encountered, many of which reduce the efficiency of the process or cause deterioration of product quality. The most notable of these metals are copper, iron, calcium, magnesium, sodium and nickel. Other metals which may affect the oil from a health and safety standpoint are the heavy metals lead and cadmium. Phosphorous, although classified as a metalloid, also adversely affects soybean oil during processing and, therefore, will be discussed.

PROOXIDATION

Certain metals, particularly copper and iron, exhibit a prooxidant effect in soybean oil. The manifestations of oxidation are flavor, odor and color deterioration. Copper, which is perhaps the most potent oxidation catalyst of these metals, exhibits a noticeable oxidative effect at concentrations as low as 0.005 ppm. Iron exhibits a noticeable effect at 0.03 ppm. Other metals that reduce the oxidative stability of soybean oil are cobalt (II), manganese (II) and chromium (III).

Table I gives the concentrations of various metals necessary to reduce the keeping time of lard by 50% at 90 C. Because of compositional differences, these values do not directly correspond to soybean oil. However, the values are a good comparison of the relative prooxidant effects.

The effects of prooxidant metals can be diminished by using chelating agents before and after deodorization. The most commonly used chelating agents are citric acid, phosphoric acid and soybean lecithin. Citric acid is metered into the oil as an aqueous or alcoholic solution at levels of 50-100 ppm. It is important to add citric acid during the cooling phase of deodorization, as its decomposition temperature is 175 C. Citric acid added prior to deodorization, although ultimately decomposed at typical deodorization temperatures, affords a certain degree of protection, as trace quantities of oxygen may be present during preheating. Also, the preponderance of fatty acids in an undeodorized oil solubilizes the metals, thus magnifying the problem. An early study compared peroxide values of soybean oil with and without 100 ppm citric acid spiked with 3 ppm of a prooxidant metal and held at 100 C for 8 hr (Table II). Except for the sample containing copper, the peroxide values of the oils containing citric acid were much lower than those without citric acid. As copper is the most potent prooxidant metal, the addition of 3 ppm may be too great a concentration for citric acid to adequately accomodate. Phosphoric acid is added to the deodorized oil in aqueous solution to a final concentration of 10 ppm. Lecithin may be added to a final concentration of 5 ppm.

Most of these metals are naturally present in soybean oil (albeit at extremely low concentrations) but can be kept to a minimum with proper handling. Without exception, copper and its alloys should not be allowed to contact fats and oils. It is not possible to eliminate oil contact with iron, because much of the industry uses black iron equipment. With proper treating and cleaning, iron contamination can be kept to a minimum. Gavin (7) prepared a table from data presented by Beal and Lancaster (Table III) of the relative catalytic activities of metal encountered in processing equipment toward soybean oil oxidation. Assigning a value of 100 to Type 304 stainless steel, copper has a relative catalytic activity of 389 and the commonly used mild steel, 140.

Crude oils from field-damaged soybeans have been found to contain up to five times the amount of iron found in oils

TABLE I

Concentration of Metal Required to Reduce the Keeping Time of Lard by 50% at 98 C (1)

Metal	Concentration (ppm)
Copper	0.05
Manganese	0.6
Iron	0.6
Chromium	1.2
Nickel	2.2
Vanadium	3.0
Zinc	19.6
Aluminum	50.0

TABLE II

Effect of 100 ppm Citric Acid on Oil Containing 3 ppm of a Prooxidant Metal (8)

Metal as chloride (3 ppm)	PV (after 8 hr at 100 C) Without citric acid	PV (after 8 hr at 100 C) With citric acid
Control	46.6	10.7
Cu (II)	294	291
Co (II)	239	9.1
Mn (II)	85.4	13.1
Fe (III)	293	125
Cr (III)	153	17.8

TABLE III

Activity of Metals toward Soybean Oil Oxidation (100 C)

Metal	Activity
Copper	389
Mild steel	140
Stainless steel (t. 304)	100
Stainless steel (t. 316)	85
Nickel	75
Hastelloy B	66
Inconel	60
Aluminum	45

from sound beans, and processing may be insufficient to remove iron to levels acceptable for high quality salad oils. Possibly, the poor flavor of salad oils often obtained from damaged beans is a result of iron-catalyzed oxidation.

DEGUMMING AND REFINING INEFFICIENCY

When divalent metals such as calcium and magnesium are present in crude oil, degumming efficiency is reduced, leaving some phospholipids in the degummed oil. Divalent metals depress the hydration of phospholipids by competing with water for the same sites. These divalent metal phosphatidates, along with β-phospholipids, are known as nonhydratable phosphatides. Nonhydratable phosphatides are removed by many refiners by pretreating the degummed oil with ca. 0.1% concentrated phosphoric acid prior to the alkali refining step. This pretreatment decreases refining losses, helps prevent the formation of "off" flavors in a refined soybean oil, and reduces phospholipids, which are known hydrogenation catalyst poisons. When calcium is present in sufficiently high levels, a hard precipitate believed to be predominantly $Ca_3(PO_4)_2$ is formed which tends to block the soap-separating centrifuges. This problem has been studied by a number of researchers. However, to our knowledge, a commercially feasible solution to this problem has not been found.

Removing the preponderance of phospholipids during degumming will result in a more efficient alkali refining step. Treating crude oil with an acid anhydride prior to degumming will dissociate the divalent metal phosphatides, thus increasing degumming efficiency. The resulting degummed oil contains 25 ppm phosphorous or less, is break-free and requires little more than neutralization during the alkali treatment step.

BLEACHING AND POST-BLEACHING INEFFICIENCY

Bleaching removes residual soaps left from alkali refining, polar materials, and color bodies, all of which damage flavor and stability in refined soybean oil. Adequate bleaching of hydrogenation feedstocks is imperative because of the notorious catalyst poisoning effect of sodium soaps.

Sodium, and especially its corresponding soaps, tend to inactivate adsorbent sites on the bleaching substrate, resulting in less-than-optimal bleaching efficiency. This probably is more of a problem to refiners who use neutral bleaching clay rather than acid-activated clay; however, bleaching efficiency can be optimized by removing as much of the soap as possible during the water washing step of alkali refining. One refiner advocates the use of up to 0.1% citric acid during bleaching to dissociate and chelate sodium from soaps, thereby improving overall efficiency.

Hydrogenated oils require a special posttreatment to remove traces of nickel from the finished product. During hydrogenation, nickel soaps are formed and are sufficiently oil-soluble to remain in the oil during filtration. Citric acid (100 ppm) added prior to final filtration will chelate the remaining nickel and leave a residual nickel level of less than 1.5 ppm. According to the industry, a residue of 0.1-1.5 ppm nickel may be present in hydrogenated oils.

METHODOLOGIES

The determination of trace metals in vegetable oil has always been a formidable problem. As the metals found in oil are usually present in parts per million or less, the traditional gravimetric and volumetric methods often are unsatisfactory for quantitative purposes. Colorimetry, polarography and emission spectroscopy have been used, and, in recent years, atomic absorption spectrophotometry (AAS) has gained wide acceptance.

The older methods and certain AAS methods require destroying the organic material by ashing. There is no universal ashing procedure for all metals because of the differing reactivities and volatilities. It is not the intent of this presentation to give specific procedures for the determination of various metals, but to briefly review the methods that are employed.

Emission spectroscopy has been successfully employed in the determination of iron, copper, manganese and tin. These same metals also can be quantitated by line-width spectroscopy.

The nickel content of oil can be quantitated colorimetrically using dimethylglyoxime as the color developing reagent and measuring the transmittance at 445 μm. Nickel sulfate is employed as a standard; standard solutions are quite stable, enabling the analyst to semiquantitatively determine the nickel content from a series of known standards, rather than by actually measuring transmittance.

Iron is determined colorimetrically with hydroquinone and 1,10-phenanthroline. Copper is determined with dithizone or diethyldithiocarbamate reagents.

Although methods have been developed and successfully used, polarographic techniques are not easily done to fats and oils due to the possibility of volatizing the metals or converting them to an indeterminable form. Before the advent of AAS, however, polarography was perhaps the best method for the determination of tin.

Phosphorous content is indicative of phospholipid concentration, and is thus a good measure of how well soybean oil is refined. Phosphorous color is developed with molybdic acid and quantitated by reference to a standard curve. AOCS Method Ca 12-55 is a reliable and accurate procedure for phosphorous determination (13).

As previously mentioned, AAS techniques have gained wide acceptance in recent years for the determination of trace metals in fats and oils. Three common sample preparation techniques were compared by Black (11) for the analysis of cadmium, calcium, chromium, copper, iron, lead, magnesium, manganese, nickel, potassium, sodium and zinc. These techniques were char ashing, direct aspiration of the oil diluted with methyl isobutyl ketone and carbon rod atomization. Results were the same for many metals regardless of the technique, however, zinc, cadmium, chromium, lead and calcium results depend on the technique used.

Black reported that cadmium and possibly zinc are lost due to volatilization during char ashing. Sensitivity of cadmium, nickel and lead analyses are adversely affected when direct aspiration methods are used. Direct aspiration and carbon rod atomization are unsuitable for chromium analysis, as chromium must be in the hexavalent state for successful analysis. Calcium was run most successfully with the carbon rod technique. However, if a releasing agent such as lanthanum or strontium is used, the other two techniques should give adequate results. Because of the high levels of magnesium and potassium present in soybean oil, the carbon rod technique is not as reliable for these elements as the direct aspiration or char ashing techniques. It was concluded that copper, iron, manganese and sodium can be determined with equal success using any of these three methods.

Farhan and Pazendeh (10) report that direct and simultaneous determinations of iron, copper, nickel, lead, silver, aluminum, magnesium, calcium and manganese can be obtained using arc spectrography. This method has a reported repeatability of ± 10% based on spectra from three replications of a given sample.

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Measurements of Frying Fat Deterioration: A Brief Review

C.W. FRITSCH, General Mills, Inc., James Ford Bell Technical Center, 9000 Plymouth Ave. North, Minneapolis, MN 55427

ABSTRACT

Many factors affect the rate of deterioration of a fat used for deep fat frying. Because of the complexity of the problem, there is no single procedure which will yield reliable results in all situations. Determination of total polar materials in a frying fat provides the most reliable measure of the extent of deterioration in most cases. For monitoring a frying operation in which there is no dilution of the frying fat by the fat in the food being fried, the change in the dielectric constant is the simplest of the methods judged reliable. Free fatty acid determinations by titration and peroxide value are not recommended procedures for measuring frying fat deterioration.

INTRODUCTION

In deep fat frying, a complex series of changes and reactions produce numerous decomposition products. The complexity is illustrated in Figure 1. A list of methods for evaluating fat deterioration is provided in Table I. As these reactions proceed, the functional, sensory and nutritional quality of frying fats are changed and may reach a point where high quality foods can no longer be prepared. The question is, how does one know when the frying fat needs to be dumped? Unfortunately, there is no simple answer. Many different foods are fried in various fats using a choice of fryer designs and operating conditions. The combinations of these variables determines the rate at which the individual reactions take place. For example, in one operation, the rate of hydrolysis may be twice that of the rate of oxidation, whereas in another operation, the reverse may occur. Hence, a specific method may be ideal for one operation but completely useless in another. Determination of the endpoint of a frying fat requires good judgment,'based on knowledge of the particular frying operation, the nature of the deep frying fat, and the advantages and limitations of the analytical procedures employed.

DISCUSSION

The first attempt to define a deteriorated frying fat was made by the German Society for Fat Research in 1973 (1). It was recommended that "a used frying fat is deteriorated if, without doubt, odor and taste are unacceptable; or if, in case of doubtful sensory assessment, the concentration of petroleum ether insoluble oxidized fatty acids is 0.7% or higher and the smoke point is lower than 170 C; or if the concentration of petroleum ether insoluble oxidized fatty

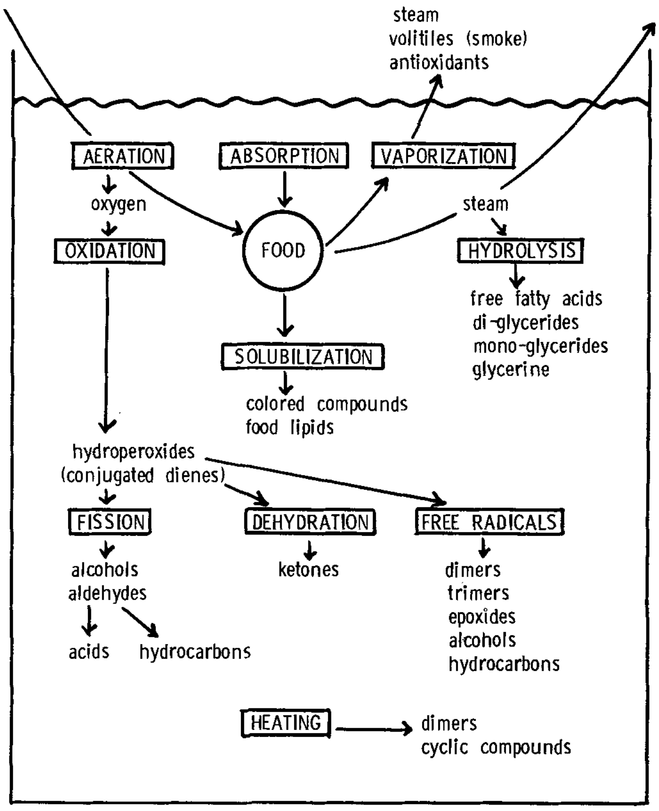

FIG. 1. Changes occurring during deep fat frying.