

## Vegetable Oil Stability at Elevated Temperatures in the Presence of Ferric Stearate and Ferrous Octanoate

ALINE R. COSCIONE<sup>†</sup> AND WILLIAM E. ARTZ<sup>\*,‡</sup>

Institute of Chemistry, The State University of Campinas, Campinas, São Paulo, Brazil and  
The Department of Food Science and Human Nutrition, University of Illinois,  
382 Agricultural Engineering Science Building, 1304 West Pennsylvania Avenue,  
Urbana, Illinois 61801-4726

The thermoxidative stability of partially hydrogenated soybean oil (PHSBO) was examined after addition of ferric stearate and ferrous octanoate, and then heating the samples at 120, 160, 180, and 200 °C. In a second experiment, the effect of iron concentration (ferric stearate) on PHSBO stability was examined at 180 °C, and at concentrations of approximately 0.5 and 1.2 mg of added iron/kg PHSBO. Oil samples were heated continuously for 72 h and sampled every 12 h. The acid value, *p*-anisidine value, color, dielectric constant and the triacylglycerol polymer content of oil samples were compared to oil samples containing no added iron. Generally, the value of each oxidative index increased with (1) an increase in temperature, (2) an increase in heating time, and/or (3) an increase in iron. The results demonstrate that low concentrations of iron will substantially increase the rate of oxidation for vegetable oil samples heated to temperatures of 120 °C to 200 °C.

**KEYWORDS:** oil stability; thermo-oxidative stability; iron; soybean oil; deep-fat frying

### INTRODUCTION

Vegetable oils remain a popular cooking medium in many parts of the world. Despite the problems associated with the consumption of excessive calories and the health concerns regarding the ingestion of trans fatty acids, the flavor and textural attributes of fried food continue to be greatly desired. As a result of consumer preferences for fried food, the thermal stability of vegetable oils and fats remains important.

Considerable research effort has been expended on improving oil stability. This has been achieved in different ways, primarily by reducing the percentage of unsaturated fatty acid, which is commonly done by partial hydrogenation. However, other methods have been used successfully, such as the hybridization program used to produce NuSun oil, interesterification and genetic modification of oilseed crops. The performance of those products has been evaluated using oil stability tests under various heating conditions, but it can provide conflicting results at times. Neat oil heating experiments (without food samples) can be informative, since many of the complex reactions dependent upon the type of food sample fried are eliminated, and this facilitates comparisons between oil samples. The degradation rates obtained can provide some insight on the oxidation reactions involved (1–3).

Transition metals, such as iron and copper, occur naturally in food, including crude vegetable oil, frequently in the low

ppm range and these metals can decrease the stability of the oil. This detrimental effect makes oil purification important and is the reason chelating agents (e.g., citric acid) are added in an effort to reduce the activity of these metals in the oil (4, 5). Despite such measures, there can be a decrease in oil stability during storage (6, 7). Such observations have motivated researchers to examine various thermal instrumental methods in an attempt to describe degradation rates and kinetic parameters for oil oxidation or degradation in the presence of different metallic species (8, 9).

A potential source of transition metal accumulation in vegetable oil is meat, which contains substantial amounts of iron. Meat products could theoretically cause an increase in the iron content in a vegetable oil during extended use in a fast food restaurant, increasing the rate of oil degradation. There has been a multitude of studies examining the effect of transition metals on food oil oxidation under various conditions. The studies have included a wide variety of model systems (emulsions, bulk oils, various food systems), iron forms (iron palmitate, heme iron, and heating equipment fabricated from iron) and conditions (from room temperature to ~100 °C, in the absence/presence of light, etc.). The following list is only a small portion of the published reports on the topic (6, 7, 10–12). While there are a large number of studies examining vegetable oil stability at high temperatures, and a substantial number of studies in the literature demonstrating that transition metals accelerate oxidation at ambient and elevated temperatures including the temperatures encountered during the OSI analysis, there appears to be few studies quantifying the effect of oil soluble iron compounds on oil degradation at the temperatures

\* Author to whom correspondence should be addressed: [phone: 217-333-9337, fax: 217-333-9329, e-mail: wartz@uiuc.edu].

<sup>†</sup> Institute of Chemistry, The State University of Campinas.

<sup>‡</sup> The Department of Food Science and Human Nutrition, University of Illinois.

in the range of 160 °C to 180 °C. A study on the catalytic effect of solid metals on the thermal stability of vegetable oil at temperatures ranging from 220 °C to 320 °C was reported (8), but it is not clear how this might be extrapolated to the effect of soluble iron compounds in vegetable oil at the temperature range normally encountered, ~160 °C to 180 °C.

A complicating factor is that although some direct measurement of oxidation (e.g., peroxide value, oxygen consumption, triacylglycerol destruction) would be best, it is not feasible to directly monitor oxidation at high temperatures. The quantitation of the primary oxidation product, hydroperoxides, does not provide an estimate of the oxidation that has occurred in used frying oils, since hydroperoxides do not accumulate during frying since they are rapidly destroyed at temperatures near or above 100 °C or in the presence of low concentrations of transition metals. Likewise, it is not feasible to monitor oxygen absorption, another direct measurement of oxidation, at frying temperatures. A determination of the change in the substrate concentration (unaltered triacylglycerols) as a function of heating time would be an option, although there are no published methods using HPLC for this particular application. Therefore, indirect methods of measurement must be used, such as quantitation of the polymer content.

In this study, ferric stearate and ferrous octanoate were used as model compounds to evaluate the stability of a partially hydrogenated soybean oil (PHSBO) in the presence of iron, under continuous heating conditions at temperatures encompassing the range encountered during deep fat frying (120 °C, 160 °C, 180 °C, and 200 °C). In a second experiment, using only ferric stearate, the effect of two iron concentrations (approximately 0.5 and 1.2 mg Fe per kg of PHSBO) on PHSBO stability at 180 °C was studied.

## MATERIALS AND METHODS

A sample of commercial liquid vegetable shortening consisting of partially hydrogenated soybean and cottonseed oils (PHSBO) was obtained from ADM Packaged Oils (Decatur, IL). The oil contains TBHQ (40 ppm), citric acid (20 ppm), and the anti-foam agent dimethylpolysiloxane (4 ppm). The iodine value was determined according to AOCS Official Method Cd 1d-92 and the fatty acid profile was determined by FAME (fatty acid methyl esters) analysis according to AOCS Official Method Ce 2-66 (13). The GLC standard 15a (Nu-Chek Prep, Inc., Elysian, MN), suitable for soybean and cottonseed oils was used as a fatty acid reference. The column used was a DB-1701 (J&W Scientific, CA, 60 m, 0.25 mm i.d.,  $d_f = 0.25 \mu\text{m}$ ) for the fatty acid separation. The initial column temperature was 190 °C (2 min), then the temperature was ramped at 0.5 °C/min to a final temperature of 225 °C (70 min). Helium was used as the mobile phase (1 mL/min). The injector split ratio was 1:100.

Ferric stearate and ferrous octanoate (Pfaltz & Bauer, Waterbury, CT) were used as purchased, and dissolved in PHSBO oil as suggested in AOCS Official Method Ca 15-75 for the preparation of metal standards. Samples of 5.00 g of the resulting oil standard containing iron and the unmodified oil sample were diluted with xylene and the actual iron content was determined in triplicate directly with atomic absorption spectrophotometry (AAS) (model 2380, Perkin-Elmer, CT) according to the procedure described in AOCS Official Method Ca 15-75 (13). The iron content of the PHSBO was <0.01 mg/kg, prior to iron addition.

**Heating.** Aliquots of the iron in the oil standards described above were diluted with the proper amount of the unmodified oil to prepare 350.0 g oil samples with the desired concentration of transition metal, in 500 mL round-bottom flasks. The flasks were covered with aluminum foil and heated continuously for 72 h with heating mantles. Preliminary experiments indicated that the TAG polymer content exceeded 20% after 72 h of heating at 200 °C. The iron content of each oil sample was confirmed with AAS after heating.

**Table 1.** Fatty Acid Composition of the Unheated Oil Used in Each Experiment

fatty acid	fatty acid percentage
C16:0	10.2 ± 0.1%
C18:0	4.8 ± 0.1%
C18:1	28.0 ± 0.1%
C18:2	53.3 ± 0.1%
C18:3	3.0 ± 0.0%

The temperature of the oil samples was monitored with copper–constantan thermocouples encased in stainless steel probes and recorded every 10 min with a data logger system. A 12 g oil sample was removed every 12 h and placed in a dark brown glass vial. After cooling, the headspace was purged with argon and stored in the freezer until the physical-chemical and chromatographic analysis was performed.

The stability of the PHSBO at different temperatures (120 °C, 160 °C, 180 °C, and 200 °C) was studied with samples containing ferrous octanoate (2.21 ± 0.41 mg of added Fe per kg of PHSBO) or ferric stearate (1.02 ± 0.12 mg of added Fe per kg of PHSBO). The effect of the added iron was studied using only ferric stearate, at zero; 0.49 ± 0.05 and 1.22 ± 0.12 mg Fe/kg PHSBO at a single temperature of 180 °C. A sample of unmodified oil sample (no iron added) was heated under each set of conditions for comparison. The sampling began after the oil reached the desired temperatures.

**Physicochemical Analysis.** The acid value (AV) and the *p*-anisidine value (*p*-AV) were determined, in triplicate, for each sample as described in AOCS Official Methods Cd 3d-63 and Cd 18-90, respectively. The color intensity changes were determined using a Lovibond Tintometer (AOCS Official Method Cc 13b-45) (13). The dielectric constant of the oil was measured with a Food Oil Sensor (FOS), model NI-21A (Northern Instruments Corp., Lino Lakes, MN), zeroed with the unheated PHSBO.

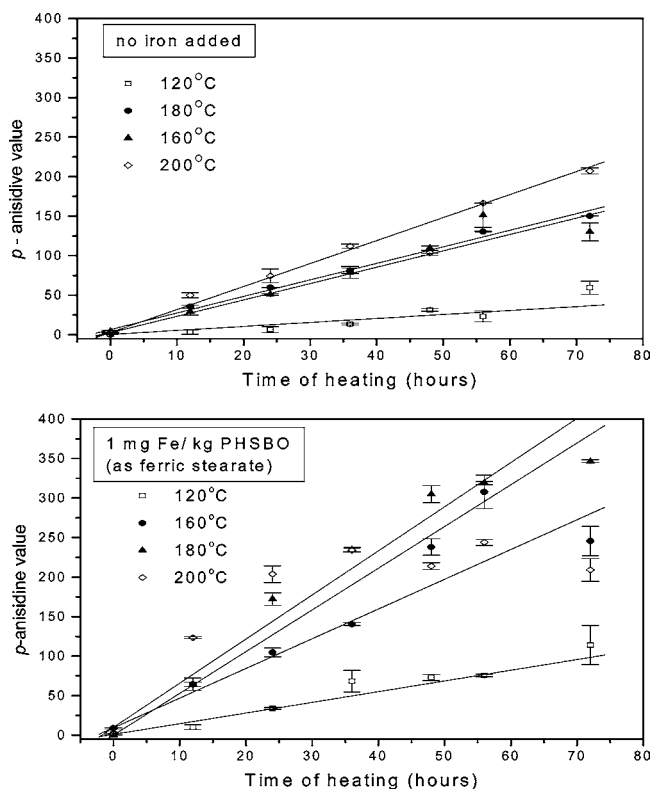
**Chromatographic Analysis.** HPSEC analyses were completed as described by Artz et al. (14). The HPSEC system consisted of five (5) Phenogel columns that contained 5  $\mu\text{m}$  diameter particles. The particles in the first column had a pore size of 500 Å (600 mm in length, 7.8 i.d.), the particles in the next three columns had a pore size of 100 Å, while the fifth and last column had particles with a pore size of 50 Å (the last 4 columns were 300 mm in length with a 7.8 mm i.d.) (Phenomenex, Torrance, CA) connected to an evaporative light scattering detector, model ELSD IIA, (Varex Corp., Burnstone, Maryland). Tetrahydrofuran (THF) was used as the mobile phase.

**Statistical Analysis.** The values presented in the figures and tables represent an average of 3 replicate analyses. The averages and the respective standard deviations are represented as the average ± standard deviation. The relationship of mean FOS values and percent polymer vs time, for the samples without iron added and the oil containing ferric stearate or ferrous octanoate, was determined by statistical regression analysis and correlation coefficient analysis using Origin software, v. 5.0 (Microcal Software, Inc., 1997). For comparison of treatment means Analysis of Variance and the Duncan's multiple range test with an acceptance at a significant level of 95%, were used. The temperature, the time of heating and the type of sample (iron added or unmodified oil) were considered as treatments.

## RESULTS AND DISCUSSION

Substantial oxidation occurred due to the added iron, even in the presence of an antioxidant and a chelating agent. TBHQ can protect frying oil during storage and citric acid can reduce the catalytic effects of low concentrations of iron. However, it was considered important to demonstrate that even in protected oils small concentrations of iron can be pro-oxidative at elevated temperatures (120 °C to 200 °C).

The iodine value of the unmodified PHSBO was 113 ± 3. The fatty acid composition of the oil, obtained from the gas chromatographic analysis of the FAMES, is in **Table 1**.

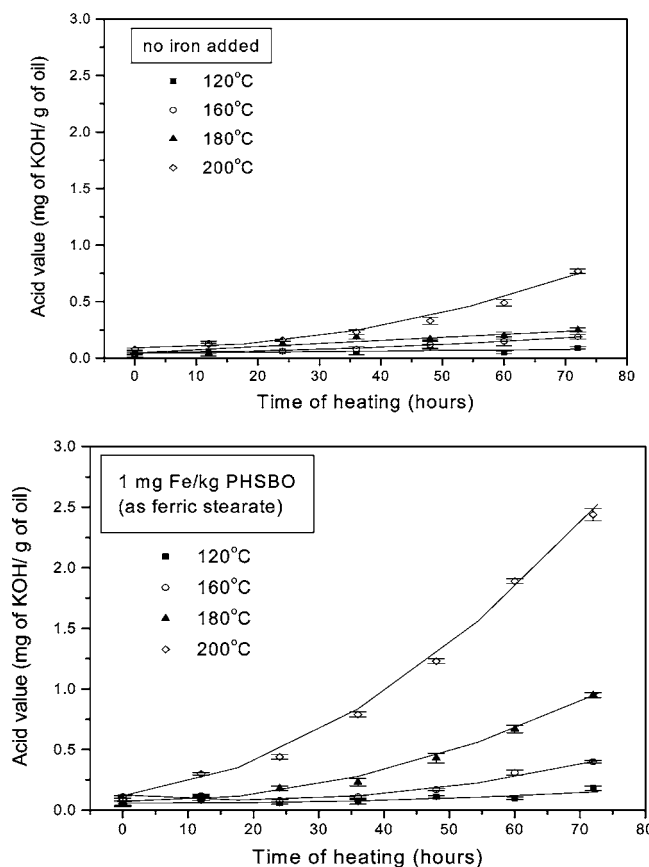


**Figure 1.** (a,b) Effect of temperature on partially hydrogenated soybean oil (PHSBO) stability as a function of heating time, with and without added ferric stearate, as indicated by the *p*-anisidine values. The *p*-anisidine ferric value is equal to 100 times the optical density. The individual data points represent average values, the error bars represent  $\pm$  the standard deviation, while the lines represent the equations generated by linear regression analysis.

The percentage of polar compounds is commonly used as a criteria for determining when to discard a used oil (15). Investigators have correlated the percentage of polar compounds to the concentration of polymeric material in the heated oil, and they have found that  $\sim 27\%$  to  $28\%$  polar material corresponds to a polymer content of approximately  $20\%$  (16, 17). Since the polymer content of the heated oil provides a good indication of the degree of oxidation in the oil and since accurate values were easily determined, oil samples were heated until a target end-point of  $20\%$  polymer was obtained, which occurred in samples containing added iron after approximately 72 h of heating at  $200^\circ\text{C}$ . All the tested samples were, therefore, heated for 72 h in the present study.

At the iron concentrations examined ( $1.02 \pm 0.12$  mg of Fe/kg of oil for ferric stearate and  $2.21 \pm 0.41$  mg of Fe/kg of oil for ferrous octanoate), there was generally an increase in the value of each index of oil oxidation with either; (a) an increase in temperature, or (b) an increase in the heating time for the samples with iron added or for the samples that did not contain added iron (Figures 1 and 2). This was confirmed by the ANOVA with significant differences at different temperatures and heating times. The treatment levels (specifically heating time and temperature) were significantly different from each other (e.g., samples heated at  $160^\circ\text{C}$  were significantly different from samples heated at  $180^\circ\text{C}$ , etc. and samples heated for 24 h were significantly different from samples heated for 36 h, etc.).

The results indicated that the oil samples with added iron had significantly more oxidation than the oil samples heated under the same conditions without added iron. This was



**Figure 2.** (a,b) Effect of temperature on partially hydrogenated soybean oil (PHSBO) stability as a function of time, with and without added ferric stearate, as indicated by the acid values. The individual data points represent average values, the error bars represent  $\pm$  the standard deviation, while the lines represent the equations generated by polynomial regression.

**Table 2.** Duncan's Average Comparison Test for "Temperature" Effects on the Oxidation Parameters Analyzed<sup>a</sup>

<i>T</i> ( $^\circ\text{C}$ )	acid value	<i>p</i> -anisidineFOS value	FOS readings	% TAG polymer	color	
					yellow	red
120	c	b	c	c	c	b
160	bc	b	c	bc	b	b
180	b	b	b	b	a	a
200	a	a	a	a	a	a

<sup>a</sup> Within the same column, different letters indicate that the average values are statistically different by Duncan's test, at a 5% confidence level.

confirmed by the ANOVA, indicating that the results from the three different oil sample types (ferric stearate added oil, ferrous octanoate added oil, and oil samples without added iron) were statistically different for all the oxidative indexes tested in this study. The means of each oxidation index for the samples with iron added was compared to the samples of oil without added iron using Duncan's multiple range test (Tables 2 and 3).

For each oil oxidation index measured (FOS, polymer, acid, *p*-anisidine and color), for the temperatures examined and during the entire 72 h heating period, the ferric stearate and ferrous octanoate added samples were not statistically different from each other, although both of these samples were statistically different from the oil sample that contained no added iron, based on the ANOVA. Although a difference between ferric stearate and ferrous octanoate was expected, due to the differences in iron concentration, the absence of a difference does not seem

**Table 3.** Duncan's Average Comparison Test for "Time" Effects on the Oxidation Parameters Analyzed<sup>a</sup>

heating time (hours)	acid value	<i>p</i> -anisidine value	FOS readings	% TAG polymer	color	
					yellow	red
0	d	f	e	d	e	c
12	cd	e	e	d	de	c
24	cd	d	de	d	cd	c
36	cd	cd	cd	cd	c	a
48	bc	bc	bc	bc	bc	a
60	ab	ab	ab	ab	ab	b
72	a	a	a	a	a	a

<sup>a</sup> Within the same column, different letters indicate that the average values are statistically different by Duncan's test, at a 5% confidence level.

to be due to any increase in error, since no statistical difference was obtained for indexes with smaller relative errors (such as the percent polymer), as well as for indexes with larger relative errors (such as the *p*-anisidine values and the FOS values). A portion of that data is presented in **Table 6** (values for each index after 72 h of heating). Despite the unexpected results, some investigators have also reported the absence of a significant difference in the rate of oxidation when different iron concentrations and iron forms were used (8, 9).

**Figure 1a** contains the *p*-anisidine values for the unmodified PHSBO, while **Figure 1b** is for the oil sample with added ferric stearate (1.02 ± 0.12 mg of Fe/kg of PHSBO). The *p*-anisidine values increased with an increase in heating time and with the addition of iron (**Figure 1a,b**). Generally, the *p*-anisidine value for the sample with added iron was approximately twice the value for the sample heated for similarly without added iron. For the *p*-anisidine value, Duncan's multiple range test indicated that the results obtained for samples heated at 160 °C, 180 °C, and 200 °C were significantly different (greater) only from the sample heated at 120 °C. In addition to the increases in the *p*-anisidine values that occurred with an increase in time (**Figure 1a,b**), the means comparison for the ferric octanoate and ferrous stearate added samples and the unmodified oil sample indicated that those samples were significantly different only after 12 h of heating. For the oil sample without added iron, there was a substantial increase in the *p*-anisidine value initially (first ~36 h), then the values increased only slightly after that, which was similar to results reported by other investigators (1). For the oil sample with added ferric stearate heated at 200 °C, there was a rapid increase in the *p*-anisidine values only for the first 24 h of heating. The *p*-anisidine values for all of the samples with added iron were much greater for each time period than the *p*-anisidine values in the sample with no iron added for all four temperatures.

The *p*-anisidine values after 72 h of heating were approximately the same for the samples heated at 160 °C and 180 °C, which was much greater than for the sample heated at 200 °C, possibly due to additional losses due to the greater reactivity and volatility of the aldehydes at the higher temperature.

The acid values for the oil sample without added iron and the oil sample with added ferric stearate (1.02 ± 0.12 mg of Fe/kg of PHSBO) are shown in **Figure 2a,b**. There is a much larger increase in the acid value due to iron addition, as compared to the samples without added iron for the samples heated at 180 °C and 200 °C. There is a systematic trend in the rate of oil degradation for both types of samples (with and without added iron), with a greater rate of change for the sample with added iron. The degradation rates can best be described by second order polynomial equations (highly correlated  $r^2 > 0.98$  and significant  $P > 0.001$ ). This same trend was observed

**Table 4.** Lovibond Color Readings ( $Y + 10R$ ) for Partially Hydrogenated Soybean Oil (PHSBO) without Iron Added and for Samples Containing Added Ferric Stearate, Heated Continuously for 72 h at Various Temperatures

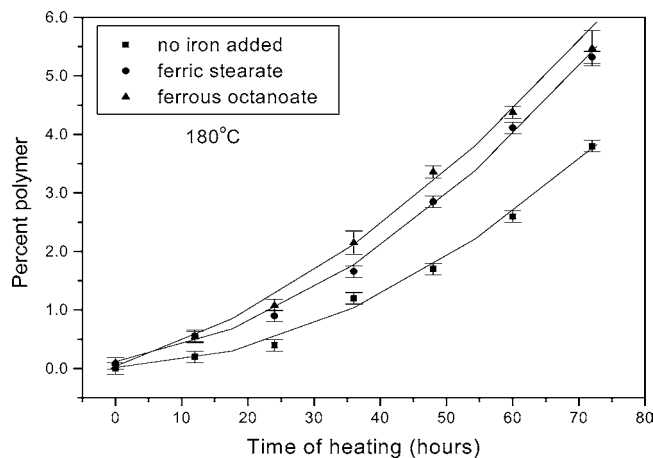
time of heating (h)	no added iron					~1 mg Fe/kg PHSBO (as ferric stearate)		
	120 °C	160 °C	180 °C	200 °C	120 °C	160 °C	180 °C	200 °C
0 hours	2	1	1	1	3	2	6	1
12 hours	2	1	2	1	4	10	13	16
24 hours	2	5	2	1	4	12	18	18
36 hours	4	5	3	3	5	14	18	30
48 hours	6	7	4	10	8	16	30	50
60 hours	6	7	10	18	8	18	45	80
72 hours	6	9	15	20	8	20	65	80

for the FOS values and the triacylglycerol polymer content. Although the acid values have not been reported elsewhere, the data collected for FOS and percent polymer from these experiments are consistent with those reported for the percentage of total polar material and the polymerized triacylglycerol content obtained under discontinuous heating experiments (190 and 204 °C) using a soybean shortening (2).

For the results of the triacylglycerol polymer analyses, the effect of temperature on the increase in the rate of degradation was similar to the effect on the acid value. However, for the FOS values, the samples heated at 120 °C were significantly different (lower) from the samples heated at the other temperatures examined (160 °C, 180 °C, and 200 °C), although the values for the samples heated from 160 °C, 180 °C, and 200 °C were not significantly different from each other. The samples containing added iron were significantly greater than the sample containing no added iron, but only after 24 to 36 h of heating.

For all of the heating experiments completed, the same profile and similar values were obtained for the oxidation indexes evaluated, whether the iron was added as ferric stearate (1.02 ± 0.12 mg of Fe/kg PHSBO) or as ferrous octanoate (2.21 ± 0.41 mg Fe/kg PHSBO). When ferrous octanoate was added to the oil, the *p*-anisidine value increased from 0.7 to 114.8 at 120 °C; 8.2 to 340.4 at 160 °C; 6.5 to 349.9 at 180 °C and 9.4 to 218.6 at 200 °C after 72 h of continuous heating. The acid value, for the ferrous octanoate experiments, increased from 0.02 to 0.14 at 120 °C, 0.12 to 0.53 at 160 °C; 0.05 to 1.28 at 180 °C, and from 0.07 to 3.06 mg of KOH/g of sample at 200 °C, after 72 h of heating, respectively.

Although color change alone is not a useful method to monitor oil oxidation, color is an important parameter associated with consumer acceptance. The oil samples with added ferrous octanoate and the oil samples with added ferric stearate were not statistically different from each other, but they were significantly darker than the oil samples containing no added iron. In addition, the means comparison test revealed that there were significant differences in yellow color intensity for samples heated at 200 °C, as compared to samples heated at lower temperatures. There were also significant differences in red color intensity between two groups of samples (group one—samples heated at 120 °C and 160 °C; and group two—samples heated at 180 °C and 200 °C). The rate of change was also different for the two color components, samples became different after 12 h of heating for the yellow color intensity, while it took 36 h for the differences to become significant for the red color. The increase in color ( $Y + 10R$ ) was greater for the oil samples containing added iron than for the oil samples containing no iron added, with greater increases in the red, than in the yellow color intensity (**Table 4**).



**Figure 3.** Effect of either added iron octanoate or iron stearate on partially hydrogenated soybean oil (PHSBO) stability as a function of time for oil samples heated at 180 °C, as indicated by the amount of triacylglycerol polymer formed during heating. The individual data points represent average values, the error bars represent  $\pm$  the standard deviation, while the lines represent the equations generated by polynomial regression.

The data and polynomial regression curves obtained from samples heated at 180 °C (percent polymer and FOS readings) are shown in **Figures 3** and **4**. From the data presented, one can compare the samples without iron added, with the samples containing added ferric stearate ( $1.02 \pm 0.12$  mg Fe/kg oil) and ferrous octanoate ( $2.21 \pm 0.41$  mg Fe/kg oil). From the percent polymer data presented in **Figure 3**, the equations obtained by polynomial regression are as follows

$$Y = 4.9 \times 10^{-4} X^2 + 4.3 \times 10^{-2} X - 7.6 \times 10^{-3} \quad (r = 0.995; P < 0.001)$$

for the sample without added iron (eq 1)

$$Y = 4.2 \times 10^{-3} X^2 - 6.3 \times 10^{-2} X + 0.25 \quad (r^2 = 0.995; P < 0.001)$$

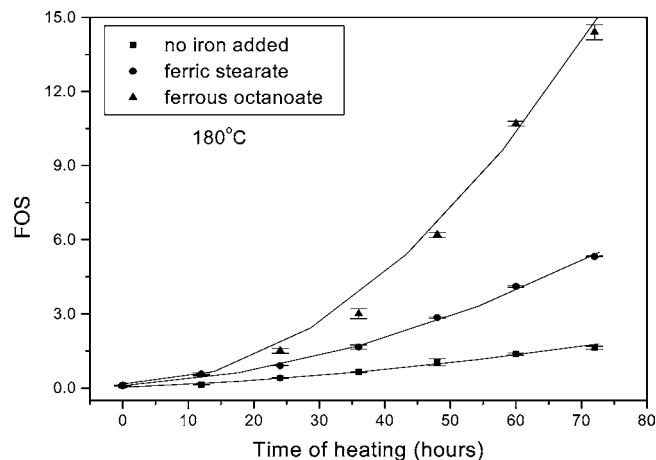
for the sample with added ferric stearate (eq 2); and

$$Y = 6.44 \times 10^{-4} X^2 + 5.8 \times 10^{-3} X - 3.1 \times 10^{-3} \quad (r^2 = 0.996, P < 0.001)$$

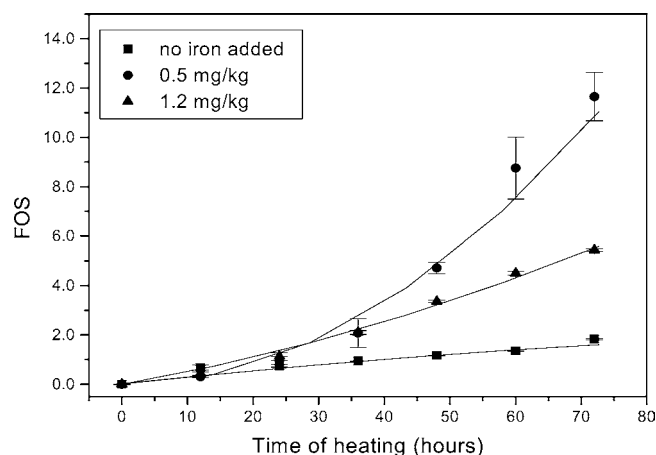
for the sample with added ferrous octanoate (eq 3); where  $Y$  = percent polymer and  $X$  = the heating time.

From these equations, one can calculate the heating time needed to reach a target endpoint of 20% polymer, which is an estimate of the relative stability of the oil as affected by temperature and added iron. For example, at 180 °C, 177.8 h would be required for the oil sample to attain 20% polymer without added iron, while 82.6 h would be needed for the sample with added ferrous octanoate and 76.5 h for the sample with added ferric stearate, respectively. Each of the heating times needed to reach the target endpoint of 20% polymer are listed in **Table 5**.

The results in **Table 5** indicates that iron plays an important role on the thermo-oxidative stability of vegetable oils, and that there is a moderate and significant temperature effect. For example, an increase in temperature from 120 °C to 180 °C resulted in a reduction of approximately 40 to 60% in the thermal-oxidative stability of the oil. At 200 °C, the oil degrades at a much greater rate than at 160 °C to 180 °C, and it appears that the iron effect is slightly less.



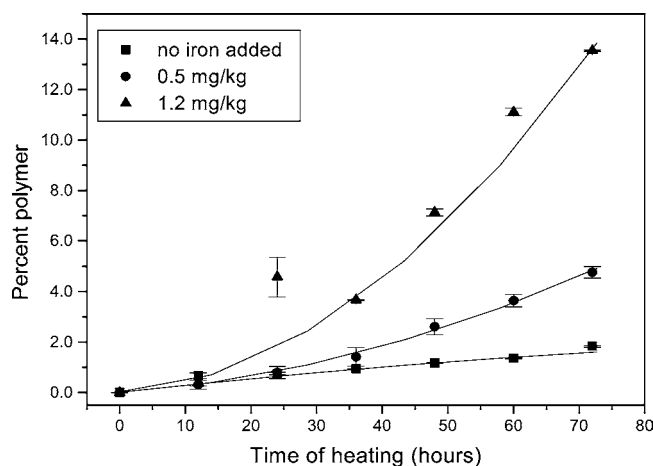
**Figure 4.** Effect of either added iron octanoate or iron stearate on partially hydrogenated soybean oil (PHSBO) stability as a function of time for oil samples heated at 180 °C, as indicated by the changes in the food oil sensor (FOS) readings. The individual data points represent average values, the error bars represent  $\pm$  the standard deviation, while the lines represent the equations generated by polynomial regression.



**Figure 5.** Effect of added ferric stearate (at 0.49 mg and 1.22 mg of iron per kg of oil) on the percent polymer formation during heating at 180 °C, as a function of time. The individual data points represent average values, the error bars represent  $\pm$  the standard deviation, while the lines represent the equations generated by polynomial regression.

The effect of ferric stearate and ferrous octanoate on oil thermo-oxidative stability was examined by the regression analysis for the TAG polymer data obtained from the heating experiments at 180 °C. This index was chosen because it is thought to provide a good estimate of the triacylglycerol degradation rate. The slope of the resulting equation  $d(\text{index})/dt$  (change in the measured parameter vs time) is the rate-specific constant ( $k$ ) for the formation of TAG polymer at the temperatures studied, in the presence and absence of iron. The plots of  $\ln k$  for the temperatures tested vs the reciprocal of the absolute temperature ( $1/T$  in K) produces a straight line via linear regression analysis from which the activation energy  $E_a$  and the frequency factor  $A$  from the Arrhenius equation can be obtained. The frequency factor  $A$  was obtained by extrapolation of the fitted curve, while  $E_a$  was obtained from the slope ( $-E_a/R$ ), where  $R$  is the gas constant. Statistically, there was no difference between the ferric stearate and ferrous octanoate samples and both are significantly different from the samples containing no added iron.

For the activation energy, a value of 63.1 kJ/mol was obtained for the sample without added iron; while 43.8 kJ/mol and 34.5



**Figure 6.** Effect of added ferric stearate (at 0.49 mg and 1.22 mg of iron per kg of oil) on the food oil sensor (FOS) readings during heating at 180 °C, as a function of time. The individual data points represent average values, the error bars represent  $\pm$  the standard deviation, while the lines represent the equations generated by polynomial regression.

**Table 5.** Estimated Time for Oil Samples to Reach 20% Polymer and the Percent Reduction in Frying Oil Life to Reach 20% Polymer Due to the Addition of Iron Compounds

T (°C)	oil w/o added Fe	octanoate (2.21 mg Fe/kg PHSBO)		stearate (1.02 mg Fe/kg of PHSBO)	
	discard point <sup>a</sup> (h)	discard point <sup>a</sup> (h)	est. frying life reduction (%)	discard point <sup>a</sup> (h)	life reduction (%)
120	460.8	230.3	50.0	236.3	42.9
160	176.8	104.8	40.7	105.0	40.6
180	177.8	82.8	53.4	76.5	57.0
200	91.3	56.0	38.7	58.9	35.5

<sup>a</sup> Estimated time to obtain a triacylglycerol polymer content of 20%, as calculated by regression analysis.

**Table 6.** FOS, Polymer, Acid Values, *p*-Anisidine Values and Color for Oil Samples Heated for 72 h without and with Added Ferric Stearate (1.02  $\pm$  0.12 ppm) or Ferrous Octanoate (2.21  $\pm$  0.41 Ppm)

analysis	T (°C)	no added iron	ferric stearate	ferrous octanoate
FOS	120	0.80 $\pm$ 0.00	1.22 $\pm$ 0.02	0.95 $\pm$ 0.01
	160	1.22 $\pm$ 0.01	3.61 $\pm$ 0.01	3.25 $\pm$ 0.00
	180	1.63 $\pm$ 0.06	5.47 $\pm$ 0.02	5.32 $\pm$ 0.02
	200	3.84 $\pm$ 0.05	7.85 $\pm$ 0.18	7.22 $\pm$ 0.20
polymer	120	0.89 $\pm$ 0.04	1.83 $\pm$ 0.07	1.74 $\pm$ 0.13
	160	3.10 $\pm$ 0.04	8.43 $\pm$ 0.07	8.20 $\pm$ 0.13
	180	3.80 $\pm$ 0.04	14.40 $\pm$ 0.30	17.50 $\pm$ 0.10
	200	12.00 $\pm$ 0.25	29.91 $\pm$ 0.06	26.05 $\pm$ 0.07
acid values	120	0.09 $\pm$ 0.01	0.14 $\pm$ 0.02	0.18 $\pm$ 0.02
	160	0.19 $\pm$ 0.02	0.53 $\pm$ 0.04	0.40 $\pm$ 0.01
	180	0.25 $\pm$ 0.02	1.28 $\pm$ 0.02	0.95 $\pm$ 0.01
	200	0.77 $\pm$ 0.02	3.06 $\pm$ 0.02	2.44 $\pm$ 0.05
<i>p</i> -anisidine	120	59.5 $\pm$ 8.4	114.8 $\pm$ 8.5	114.0 $\pm$ 24.8
	160	130.2 $\pm$ 11.2	340.4 $\pm$ 16.2	245.6 $\pm$ 18.4
	180	150.3 $\pm$ 0.4	349.9 $\pm$ 2.1	346.6 $\pm$ 2.0
	200	207.2 $\pm$ 3.8	218.6 $\pm$ 17.3	209.0 $\pm$ 14.4
color: yellow/red	120	2/0.4	4/0.8	3/0.5
	160	4/0.5	15/2.0	10/1.0
	180	6/0.4	15/5.0	15/3.0
	200	10/0.9	10/7.6	10/7.0

kJ/mol were determined for the samples with added ferric stearate and ferrous octanoate, respectively (figure not shown). In addition, a decrease in the frequency factor was observed from the sample without iron, with  $42.5 \times 10^3 \text{ cm}^3/\text{molecule}$ , to  $0.67 \times 10^3 \text{ cm}^3/\text{molecule}$  and  $0.41 \times 10^3 \text{ cm}^3/\text{molecule}$  for

the ferric stearate and the ferrous octanoate spiked oil samples, respectively. The decrease in both the activation energy and frequency factor for this thermal-oxidative reaction in the presence of transition metals, as compared to the oil samples without added iron, is consistent with data reported on the literature on olive oil samples and metal catalyzed oxidation in homogeneous and heterogeneous phases (8, 9).

In the second part of this study, the effect of iron (added as ferric stearate) was examined at two different concentrations and at 180 °C. Generally, there was a significant increase in the value of each oxidative index with either; (1) an increase in the heating time, and/or (2) an increase in the heating temperature.

The change in the oxidation indexes during heating was the very similar to the experimental results reported in the first experiment discussed above. The amount of oxidation for the samples with added iron ( $0.49 \pm 0.05$  and  $1.22 \pm 0.12$  mg Fe per kg of oil) was significantly different from the oil samples that did not contain added iron. Others have found similar results, although those experiments were done at much lower temperatures (18). However, the increase in oxidation with an increase in concentration for the concentrations studied ( $0.49 \pm 0.05$  and  $1.22 \pm 0.12$  mg Fe per kg of oil) was not significant by the means comparison test at the confidence level used. It should be noted that this comparison was made for all of the heating times, not just at the end of heating when the differences would have been maximum.

For both sets of experiments, the FOS readings, percent polymer values, acid values, *p*-anisidine values and the color changes show that small amounts of can iron substantially increase the rate of oil oxidation upon heating at elevated oil temperatures. However, the differences in the amount of oil oxidation due to the form or amount of iron added (ferric stearate vs ferrous octanoate, at  $1.02 \pm 0.02$  and  $2.21 \pm 0.41$  mg of Fe/kg of vegetable oil, respectively) was not significant. Although the extent of oxidation was greater when more iron was added to the oil as ferric stearate, the respective increase was not statistically significant within the concentration range (0.49 and 1.22 mg Fe/kg oil) examined. It is not clear why the concentration effect was not significant, although this statistical comparison was made for all of the combined heating times, not just the final time where the differences would have been maximum.

As expected, there was an increase in the reaction rate with the addition of an iron catalyst. It is possible that the amount of iron needed to significantly increase the rate of oxidation had been added, and that moderate increases in the catalyst concentration were insufficient to induce a statistically significant increase in the oxidation rate.

It cannot be determined unequivocally whether the absence of a difference is exclusively due to the form of iron added, or if part of the reason for the absence of a significant difference is due to relatively small differences in iron concentration. Further studies are needed to clarify this point.

Finally, the results indicate that there is a substantial increase in the rate of oxidation at elevated temperatures with even small increases in iron concentration. Therefore, it was demonstrated that an increase in the iron concentration will increase the rate of oxidation, that different oxidation states of the iron can induce this degradative effect, and that iron can reduce the oil thermo-oxidative stability of a vegetable oil. Finally, the greater the heating temperature becomes, the greater the effect of iron on the thermo-oxidative stability of the oil becomes.

**ABBREVIATIONS USED**

PHSBO, partially hydrogenated soybean oil; TBHQ, tertiary butyl hydroquinone; FOS, food oil sensor.

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