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protective effects of polydimethylsiloxane in soybean oil at frying temperatures

Jose Arnaldo Gerde
Iowa State University

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Protective effects of polydimethylsiloxane in soybean oil at frying temperatures

by

Jose Arnaldo Gerde

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Co-majors: Food Science and Technology; Biorenewable Resources and Technology

Program of Study Committee:
Pamela White, Co-major Professor
Lawrence Johnson, Co-major Professor
Tong Wang
Buddhi Lamsal
Thomas Brumm

Iowa State University

Ames, Iowa

2010

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To my father, my mother, and my brother

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Abstract

The impact of polydimethylsiloxane (PDMS) on oxidation of soybean oil at frying temperatures was investigated. At concentrations of PDMS greater than that calculated to be necessary for a compact monolayer on the oil surface, the rates of degradation of linoleate (18:2) and γ - and δ -tocopherols were slower than in untreated oil. Degradation rates of 18:2 increased after a certain time at frying temperatures, likely caused by a reduction of the tocopherols and/or the PDMS to levels at which they were no longer protective. PDMS decreased oxygen transfer to the oil at temperatures close to frying temperatures. The concentration of 4-hydroxynonenal (HNE), a toxic product of 18:2 oxidation, was affected by PDMS concentration. In general, PDMS retarded HNE formation when used at concentrations greater than the monolayer concentration. PDMS concentrations capable of forming multilayers were more effective than a monolayer, and the protective effect lasted for a longer time. The results strongly suggest that PDMS decreases the oxygen transfer rate into the oil, thus decreasing the degradation of 18:2, tocopherols, and the formation of oxidation products, such as HNE.

CHAPTER 1. GENERAL INTRODUCTION

Rationale and Overview

The food industry utilizes hydrogenation to extend the frying life of oils. This process increases the saturation of the oil, but also isomerizes part of the naturally present *cis* double bonds in the fatty acids into the *trans* geometric isomer. Consumption of *trans* fatty acids has been linked to increased low-density lipoprotein cholesterol and decreased high-density lipoprotein cholesterol in human blood serum, and coronary vascular disease (1,2). Also during frying, polyunsaturated fatty acids oxidize and form degradation products with proven toxicity, such as 4-hydroxy-2-(E)-nonenal (HNE) (4). Starting January 2004 it became mandatory to label the content of *trans* fats in foods if they contain more than 0.5 g/serving (3). Thus, the industry is seeking ways to increase oil stability during frying without using partial hydrogenation and its consequential formation of *trans* fatty acids.

Polydimethylsiloxane (PDMS) has been used as an antifoaming additive by the food industry; but, it can also protect oils at frying temperatures (180°C) when used at very low concentrations (7-9). Extensive work has been done to try to understand the mechanism by which PDMS exerts its protective effect (7, 10-13); however, the mechanism of action for PDMS is not yet fully understood.

In this dissertation, understanding the protective mechanism of PDMS was approached by studying the influence of the PDMS concentration on the kinetics of the degradation of linoleate (18:2), the major fatty acid in soybean oil, and the degradation of the

tocopherols in soybean oil. Tocopherols, antioxidants naturally present in the oil, help to prevent oil degradation. Also, the influence of PDMS on oxygen uptake by the oil at different temperatures was evaluated. Finally, the formation and degradation of the potentially toxic HNE under different PDMS concentrations was studied.

Dissertation Organization

This dissertation contains a general introduction, which includes the research rationale and the literature review, followed by three papers and a general conclusion. The papers are presented in the required journal format (Journal of the American Oil Chemists' Society).

Literature Review

Introduction

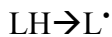
Frying is a widely used process in the food industry. The fast and efficient heat transfer to the food and the unique flavors and texture developed by the food are reasons why this process is so popular. The type of oil used as frying medium is very important, especially because most of the flavor and aroma compounds are breakdown products formed during the heating of the oil.

Oxidation and polymerization during frying

Heating the oil in the presence of oxygen results in oxidative reactions and polymerization of the unsaturated fatty acids. When food is introduced into the hot oil, other reactions, such as hydrolysis, also occur as the result of the interaction between the oil and the food components at high temperature. Oxidation typically comprises three stages: initiation, propagation, and termination (14)

During initiation, an external factor (light, preexistent peroxides, redox metals) produces a free radical. In the case of frying oils, the main factor is the action of the temperature in the pre-existent lipid hydroperoxides (14).

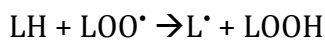
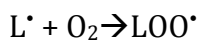
I



Initiation

Where LH is an unsaturated lipid and I is the initiator.

The second stage of the oxidation process is propagation. At this point, the radicals formed during the initiation stage combine with oxygen to yield peroxy radicals. These peroxy radicals can attack other unsaturated fatty acids to form more free radicals or they can extract a hydrogen from a fatty acid and yield a hydroperoxide. The hydroperoxide can break into two free radicals, which can propagate the reaction (peroxide decomposition):



Propagation

The last stage is termination. At this point, the free radicals formed during previous stages react with each other to form non-radical products. Several types of products are formed: alcohols, aldehydes, ketones, hydrocarbons, dimers, trimers, and epoxides. Some

of them, such as aldehydes and ketones, can be further oxidized to acids (14).

Many of these non-radical compounds have sensory properties and contribute to the fried flavor and aroma of the food. Depending on their concentration, however, they may also impart obnoxious flavors, typical of oxidized or rancid oil. The type of compound is directly linked to the structure of the precursor fatty acid. Some of these compounds are hexanal, *trans*, *trans*-2, 4-decadienal, *trans*-2-hexenal, *trans*-2-nonenal, *trans*-2-heptenal, furfural, 4-hydroxy-*trans*-2-nonenal, and nonanal (14). In general, the greater the proportion of unsaturated fatty acids, the more susceptible the oil is to oxidation. The relative rates of oxidation for the main fatty acids present in vegetable oil are oleic acid, 1 (1 double bond); linoleic acid, 10.3 (2 double bonds); and linolenic acid, 21.6 (3 double bonds) (15).

During frying, isomerization leading to the formation of conjugated double bonds and *trans* double bonds may occur. Cyclization also is possible, yielding five- or six-carbon cyclic compounds (16). The formation of polymers may occur independently of the presence of oxygen. If oxygen is present, cyclic compounds are usually formed during the termination stage of the autoxidation. If the radicals that originated the polymer contained oxygen, the polymer will contain oxygen in its structure. The presence of oxygen in the structure of a polymer increases its polarity. Polymerization also can occur as the result of heating through the Diels-Alder condensation mechanism as depicted by Figure 1 (17).

Frying oils

When choosing a frying oil one must consider several aspects, such as the type of fried product, consumer acceptance, nutritional factors, price and availability, oil stability, and

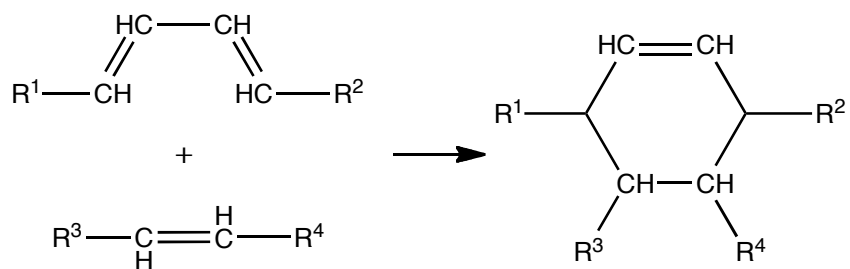


Fig. 1. Polymer formation through Diels-Alder condensation mechanism

sensory characteristics (18). In the past, partial hydrogenation of polyunsaturated oils was an economically feasible solution to increasing the stability of frying oils. Because of the negative health effects associated with *trans* fatty acids (1, 2) produced during the hydrogenation process, however, the food industry has tried to replace partially hydrogenated oils with more healthful products. The major seven vegetable oils produced in the world in the 2008/2009-crop season were palm oil (42.00 Mt), soybean oil (38.79 Mt), rapeseed oil (18.71 Mt), sunflower oil (11.33 Mt), palm kernel oil (5.05 Mt), cottonseed oil (4.96 Mt), and peanut oil (4.94 Mt) (19). Their typical fatty acid compositions are presented in Table 1 (20).

Palm oil is widely used in frying operations in industrial scale. Palm fatty acid composition is low in polyunsaturated fatty acids (9-12% 18:2 and <0.5% linolenic acid, 18:3) making it very stable in high temperature applications (21). However, its high concentration of palmitic acid (16:0) (39.3- 47.5%) has raised concerns about consuming it because the intake of high amounts of 16:0 has been associated with hypercholesterolemia in humans (22).

Palm oil can be fractionated into palm olein and palm stearin. Palm olein is the liquid fraction and palm stearin the high-melting point fraction (20). Palm olein is used as the main cooking oil in household applications in Malaysia (21). During frying, palm olein had stability similar to hydrogenated soybean, hydrogenated cottonseed, and hydrogenated sunflower oils (23) and better than corn and soybean oils (24).

Typical commodity soybean oil is rich in polyunsaturated fatty acids (18:2 and 18:3), with some contributions from saturated and monounsaturated fatty acids (Table 1) (20).

Table 1. Typical Fatty Acid Compositions of the major oils produced in the World in 2007/2008 (20)

Fatty Acid	Palm	Soybean	Rapeseed	Rapeseed (low 22:1)	Sunflower	Palm kernel oil	Cottonseed oil	Peanut oil
Hexanoic (6:0)	-	-	-	-	-	<0.8	-	-
Octanoic (8:0)	-	-	-	-	-	2.4-6.2	-	-
Decanoic (10:0)	-	-	-	-	-	2.6-5.0	-	-
Dodecanoic (12:0)	≤0.5	≤0.1	-	-	≤0.1	45.0-55.0	≤0.2	≤0.1
Tetradecanoic (14:0)	0.5-2.0	≤0.2	≤0.2	≤0.2	≤0.2	14.0-18.0	0.6-1.0	≤0.1
Hexadecanoic (16:0)	39.3-47.5	8.0-13.5	1.5-6.0	2.5-7.0	5.0-7.6	6.5-10.0	21.4-26.4	8.0-14.0
Hexadecenoic (16:1)	≤0.6	≤0.2	≤0.3	≤0.6	≤0.3	≤0.2	≤1.2	≤0.2
Heptadecanoic (17:0)	≤0.2	≤0.1	≤0.1	≤0.3	≤0.2	-	≤0.1	≤0.1
Heptadecenoic (17:1)	-	≤0.1	≤0.1	≤0.3	≤0.1	-	≤0.1	≤0.1
Octadecanoic (18:0)	3.5-6.0	2.0-5.4	0.5-3.1	0.8-3.0	2.7-6.5	1.0-3.0	2.1-3.3	1.0-4.5
Octadecenoic (18:1)	36.0-44.0	17-30	8.0-60.0	51.0-70.0	14.0-39.4	12.0-19.0	14.7-21.7	35.0-69
Octadecadienoic (18:2)	9.0-12.0	48.0-59.0	11.0-23.0	15.0-30.0	48.3-74.0	1.0-3.5	46.7-58.2	12.0-43.0
Octadecatrienoic (18:3)	≤0.5	4.5-11.0	5.0-13.0	5.0-14.0	≤0.3	≤0.2	≤0.4	≤0.3
Eicosanoic (20:0)	≤1.0	0.1-0.6	≤3.0	0.2-1.2	0.1-0.5	≤0.2	0.2-0.5	1.0-2.0
Eicosenoic (20:1)	≤0.4	≤0.5	3.0-15.0	0.1-4.3	≤0.3	≤0.2	≤0.1	0.7-1.7
Eicosadienoic (20:2)	-	≤0.1	≤1.0	≤0.1	-	-	≤0.1	-
Docosanoic (22:0)	≤0.2	≤0.7	≤2.0	≤0.6	0.3-1.5	≤0.2	≤0.6	1.5-4.5
Docosenoic (22:1)	-	≤0.3	>2.0-60.0	≤2.0	≤0.3	-	≤0.3	≤0.3
Docoasdienoic (22:2)	-	-	≤2.0	≤0.1	≤0.3	--	≤0.1	-
Tetracosanoic (24:0)	-	≤0.5	≤2.0	≤0.3	≤0.5	-	≤0.1	0.5-2.5
Tetracosenoic (24:1)	-	-	≤3.0	≤0.4	-	-	-	≤0.3

The oil is suitable for many industrial and food uses. Based on relative oxidizability of the fatty acids present in soybean oil (15), the large proportions of 18:2 and 18:3 make soybean oil very susceptible to oxidation. Historically, soybean oil for frying applications has been partially hydrogenated to increase its stability.

Soybean cultivars with altered fatty acid composition have been developed in an effort to avoid hydrogenation and subsequent *trans* fats formation. Breeders have targeted several traits to increase the oxidative stability of the oils. The most influential characteristic regarding oil stability is the 18:3 content. When soybean oils from low-linolenic-acid-containing varieties (A16 and A87-191039 with 1.8 and 1.9% 18:3, respectively) were tested during frying of bread cubes, the cubes showed superior oxidative and flavor stability than commodity-type soybean and canola oils containing 5.9-6.8 and 10.3% 18:3, respectively (25). Similarly, potato fries fried in soybean oil containing 1.9 and 2.9% 18:3 (N85-2176 and N89-2009) had equal or better flavor scores than potato fries fried in commodity and partially hydrogenated soybean oils (26). High-stearic (18:0) (A6, 20.2% 18:0 and 5.9% 18:3), low-linolenic (A5, 3.5% 18:3), and commodity soybean oils (Hardin and BSR-101, with 6.9 and 8.1% 18:3, respectively) were compared during intermittent frying of bread cubes. The flavor stability of the bread cubes fried in those oils heated for 40 h was A5 > A6 > Hardin = BSR 101 (27), demonstrating that reducing the 18:3 content had more influence on fried flavor than increasing the 18:0 content. During storage at 28 and 60°C, oils from A5 and A6 cultivars had better performance (lower peroxide values and lower conjugated dienoic acid contents) than commodity soybean oil when

compared by using chemical tests, but sensory evaluation did not show differences (28).

Soybean oil with ~1% 18:3 is commonly referred to as ultra-low 18:3 oil. The beans were being grown and marketed by three companies, Asoyia LLC, Zeeland Farm Services, Inc., and Innovative Growers, LLC (29); however, Asoyia LLC went out of business in 2010 (30) and was bought by Cargill. The oil containing <3% 18:3 is referred to as low-18:3 soybean oil. Companies providing low-18:3 soybean oils with ~3% 18:3 include TREUS™, a brand created from the alliance of Bunge and DuPont/Pioneer Hybrid companies, and Vistive™, an oil brand created from a network of several companies, including Monsanto, Cargill, Zeeland, and Agriculture Grain Processing (AGP).

The soybean industry continues to address the sometimes conflicting issues of soybean oil functionality and nutritional quality, and has been actively producing new cultivars containing oils with new and improved nutritional benefits, yet desirable functional fatty acid profiles. In addition to the low-18:3 soybean oils developed to enhance oxidative and frying stabilities, high-oleic acid (18:1) soybean oils, targeted for development by the “Better Bean Initiative” (31), also enhance oxidative stability. High-18:1 and decreased linolenic acid soybean oil containing 79% 18:1 and 3.8% 18:3 had improved oxidative and frying stabilities compared to commodity soybean oil (32, 33). However, oils containing high levels of 18:1 (around 75 to 80%) produced fried foods with less desirable flavors than more polyunsaturated oils (34). The high 18:1 oils are so stable during frying that they do

not create the desirable flavorful breakdown products of typical or even mid-oleic oils, whose 18:2 levels provide substrate for breakdown to form some desirable (and some undesirable) volatile compounds we associate with good fried-food flavor (35). Oil containing low 18:3 and increased 16:0 concentrations (A17) was more stable than commodity oils during frying and room-temperature storage (25, 36). Screw-pressed soybean oils with 1.5 and 2.6% 18:3 (IA2064 and IA3018, respectively) and physically refined, along with a commodity-type soybean oil processed in the same way, were examined during commercial-like frying of French fried potatoes. Both 18:3-reduced oils performed better than the commodity oil (37).

Rapeseed oil, as many other plants from the *Brassica* genus and the *Cruciferae* family, is rich in erucic acid (22:1). The concentration of 22:1 may be as high as 60% (20). Erucic acid has been related to fat accumulation in heart and skeletal muscles in rodents (38). For food applications, cultivars low in 22:1 (less than 2%) and glucosinolates (compounds that impair the nutritional value of the meal) concentrations were developed by Canadian breeders. The resulting cultivars were called canola (Canadian oil low acid).

Canola oil is rich in 18:3, which makes it very unstable when used in frying applications. Historically canola oil has been partially hydrogenated to increase its stability. Low 18:3 canola cultivars have also been developed to be used in frying applications (38). Canola oil containing 1.7% 18:3 had better frying stability than

unmodified canola oil (39).

The high content of 18:2 in sunflower oil makes it very susceptible to oxidation and to produce shelf-stable fried products. To increase the stability of sunflower oil, partial hydrogenation has been used (18). Sunflower cultivars have been developed with reduced 18:2 and increased 18:1 concentrations: high-18:1 sunflower oil (75-90.7% 18:1) and mid-18:1 sunflower oils (43.1-71.8% 18:1) (20). High-18:1 sunflower oils have not demonstrated improved stability during frying (40, 41). However, French fried potatoes fried in high-18:1 sunflower oil were more stable during storage at 60°C than those fried in normal sunflower oil (42). Mid-18:1 sunflower oil was compared during pan-frying of hash browns with canola oil. Even though canola oil contained 6.5% 18:3, the performances of both oils during frying were similar (43). Mid-18:1, high-18:1 and normal sunflower oils have also been compared during frying of tortilla chips. After 30 h of intermittent frying, there were no differences in the total polar compounds formed during frying; however, the fried flavor was better in mid-18:1 and normal oils than in high-18:1 oil, probably because of the need of some oil degradation to form flavor compounds typical of fried foods. After storing the tortilla chips for 4 mo at 25°C, the overall flavor quality was better in the chips fried in mid-18:1 and high-18:1 oils. As part of the same study, French fried potatoes fried in mid-18:1 and high-18:1 oils were compared to those fried in partially hydrogenated soybean oil. The overall quality scores for mid-18:1 were better than for the other two treatments, especially later in the frying process, after 20 and 30 h frying (44).

Palm kernel oil: palm kernel oil, a co-product of the palm oil production, is rich in laurate (45-55% 12:0) (20). It is highly saturated, however, the high concentrations of laurate and myristate (14:0) and the presence of short chain fatty acids result in low melting points. It is not used for frying applications. It is used in the production of soap and cosmetic products and in the productions of cocoa butter substitutes (45).

Cottonseed oil is rich in 18:2 (46.7-58.2%). In the United States it is considered the “gold standard” for the production of potato chips because of the glossy appearance cottonseed oil imparts(18). The high concentration of 16:0 (21.4-26.4%) and 18:1 (14.7-21.7%) and its <1% 18:3 contribute good oxidative stability of the oil (46). During the extraction process, the seed has to be cooked to bind gossypol, a natural toxin present in the seed. During frying of potato chips, cottonseed oil had stabilities comparable to low-18:3 soybean oil (2% 18:3), although it was less stable than high-18:1, low-18:3 soybean oil (85.2% 18:1 and 2.0% 18:3). However, during storage of the fried product at 25°C, the overall sensory quality of the chips fried in cottonseed oil was better than in chips fried in high-18:1 low-18:3 soybean oil (35).

The major fatty acids in peanut oil are 18:2 (12-43%) and 18:1 (35-69%). Peanut oil contains significant amounts of arachidic acid (20:0, 1-2%), behenic acid (22:0, 1.5-4.5%), and lignoceric (0.5-2.5%) (20). Peanut oil was compared during simulated frying to high-18:1 sunflower oil (87.4% 18:1), soybean oil, sunflower oil, and corn

oil. The oil was heated to 185°C and moistened cotton balls were fried. The total frying time for the oil was 24 h. Peanut oil performed better than corn, soybean, and sunflower oils but worse than high-18:1 sunflower oil. The lack of 18:3 and the lower level of 18:2 in peanut oil (34.6% 18:2) compared to corn oil (58.6% 18:2), sunflower oil (71.6% 18:2), and soybean oil (54.6% 18:2) was the probable reason for this increased resistance to degradation during simulated frying (47).

Antioxidants and autoxidation inhibitors in frying oils

Antioxidants are compounds that are used in small concentrations to retard oxidative reactions in fats and oils (17). Antioxidants can be classified in two categories: chain-breaking antioxidants and other types. Chain-breaking antioxidants are compounds that interfere with either the propagation or the initiation of the autoxidation reactions. Examples of these types of compounds are tocopherols, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG), and tert-butylhydroquinone (TBHQ) (17). These compounds act as electron acceptors, stabilizing free radicals in forms that are no longer reactive.

Other types of antioxidants include metal chelators, hydroperoxide destroyers, ultraviolet light deactivators (not used in food applications), and synergists. Metal chelators inhibit the redox effect of transition metal ions, such as iron and copper. Some examples are ethylenediamine tetraacetic acid (EDTA), citric acid, and phosphoric acid. Hydroperoxide destroyers prevent oxidation by degrading hydroperoxides in either alcohols or non-radical products. Tocopherols can act as

both chain breaking antioxidants and hydroperoxide destroyers. Synergists are compounds that can reinforce the effect of other antioxidants. An example of synergism is the use of citric acid to increase the antioxidant effect of tocopherols. The effect of the two compounds used together is greater than the additive action of the two separate compounds alone (17). Some of the most important antioxidants used during frying will be described and discussed.

Synthetic antioxidants: BHA, BHT and TBHQ

The three most-used synthetic antioxidants are BHA, BHT, and TBHQ. BHA and BHT have not demonstrated protecting effects during frying (7, 48). During intermittent frying of French fries with palm olein, BHA and BHT did not show protective effects. The high temperature and the presence of steam from the food facilitated the evaporation of the antioxidants from the oil (48). The use of TBHQ alone did not improve the frying life of hydrogenated soybean oil (49) and cottonseed oil (50). However, the carryover of the TBHQ into the fried product increased the sensory properties of bread cubes during storage (49, 50).

Plant sterols and terpenic compounds

Some compounds of terpenic origin exhibit a protective effect during oxidation at elevated temperature. A methanolic oat extract rich in sterols was evaluated in soybean and cottonseed oils during frying of bread cubes. The oils treated with oat

extract showed fewer high-mw polar compounds after 10 h of frying than the untreated control oils and fewer than TBHQ and polydimethylsiloxane (PDMS)-treated oils. The protective effect was also observed during storage of the bread cubes at 60°C for 12 days, the peroxide values of the oils treated with oat extract were smaller than the rest of the treatments (50).

Linalyl oleate was evaluated at 180°C in soybean oil. It slowed oil degradation and its effect was comparable to that of PDMS, although the concentration necessary was much greater (1000 vs. 10 ppm) (9). Oleates of geraniol, perillyl alcohol, menthol, farnesol, and cholesterol also showed protective effects in soybean oil at frying temperature (51).

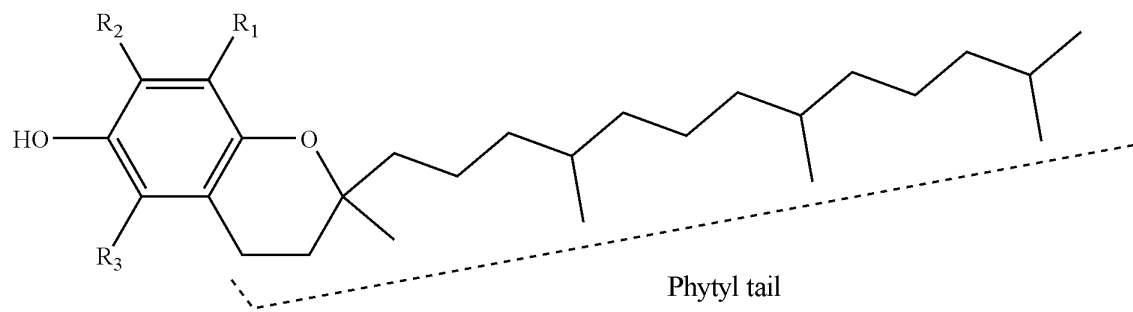
Tocopherols and tocotrienols in soybeans and soybean oil

Tocopherol and Tocotrienol Structures

Tocopherols, also known as tocots, are compounds derived from 2-methyl-2-(4,8,12-trimethyltridecyl)chroman-6-ol, and tocotrienols are compounds derived from 2-methyl-2-(4,8,12-trimethyltrideca-3,7,11-trienyl)chroman-6-ol (52). Tocopherols and tocotrienols differ in that the terpenic side chain of the tocopherols is saturated, whereas the side chain of the tocotrienols contains three double bonds. The α -, β -, γ -, and δ -tocopherol analogs differ in the number and position of methyl substituents they contain (Fig. 2).

Presence and Contents of Tocopherols

Tocopherols exhibit antioxidant properties and contribute significantly to the oxidative



α -tocopherol	$R_1 = -CH_3$	$R_2 = -CH_3$	$R_3 = -CH_3$
β -tocopherol	$R_1 = -CH_3$	$R_2 = -H$	$R_3 = -CH_3$
γ -tocopherol	$R_1 = -CH_3$	$R_2 = -CH_3$	$R_3 = -H$
δ -tocopherol	$R_1 = -CH_3$	$R_2 = -H$	$R_3 = -H$

Fig. 2. Structures of tocopherols and different analogs present in soybean oil

stability of oils (53). Typical tocopherol concentrations for crude soybean oils, representing 14 lines of soybeans exhibiting conventional fatty acid compositions grown in the Midwest, are reported in Table 2 (54). Others have reported ratios of approximately 1:13:5 for α -, γ -, and δ -tocopherols in soybean oils (55, 56). In general, tocotrienols were not detected in soybeans (57).

Typical refining, bleaching, and deodorization of soybean oil decrease the total tocopherol concentration in the refined oil to 800-1100 ppm. In one study, however, the relative proportions of the tocopherol analogs were similar before and after processing (56). Chemical refining promoted greater tocopherol loss than physical refining and the loss of α -tocopherol was greater than that of the other analogs (58). The greater the temperature and the longer the deodorization and physical refining times the greater the tocopherol loss (59).

Antioxidant and Vitamin Properties of Tocopherols

Tocopherols, located in the plastids and thylakoid membranes of plants, protect the cell against highly oxidizing oxygen molecules produced during photosynthesis (60). The tocopherol analogs vary in their antioxidant activities, and the relative effectiveness varies with the conditions. For example, α -tocopherol had the highest relative *in vivo* antioxidant activity, followed in order by β -, γ -, and δ -analogs, whereas under *in vitro* conditions the results were variable (61).

The *in vivo* vitamin E activity, as measured by Leth and Sondergaard (62) (rat resorption-gestation test), paralleled the *in vivo* antioxidant activity (28). When each one of the four

Table 2. Tocopherol Concentrations (ppm) in Crude Soybean Oil from Soybeans Grown in the Midwest (21)

	Mean ^a	Range
α -Tocopherol	96	44-158
β -Tocopherol	11	2-29
γ -Tocopherol	1048	926-1559
δ -Tocopherol	372	254-477
Total	1527	1363-2195

^a $n = 14$ lines of soybeans.

analogs was tested separately in solution under 760 torr of oxygen at 30°C, the order did not differ from that obtained from *in vivo* conditions (63). When tested in *in vitro* systems of 18:2 and 18:2-methyl esters at 37 and 47°C, γ -tocopherol was more stable than α -tocopherol (64). Tocopherol stability and antioxidant activity were tested in corn oil heated at 70°C and aerated at 100 mL/min. The order of the antioxidant activity was γ -> δ -> β -> α -tocopherol (65). When tested in menhaden oil at 37 and 50°C, both γ - and δ -analogs had greater antioxidant capacity than α -tocopherol (66). In general, when tested in oils, fats, and lipoproteins, the order of the antioxidant activity was in the opposite direction from that obtained with *in vivo* studies, with the antioxidant activity being: δ -> γ -> β - and > α -tocopherol analogs (61). Temperature, light, and presence and concentrations of other pro- and anti-oxidants all impact the antioxidant effectiveness of the tocopherol analogs (67).

Effects of Tocopherol Levels on Soybean Oil Stability

Optimal tocopherol concentrations to maximize oxidative stability in soybean oil were 100, 250, and 500 ppm for α -, γ -, and δ -tocopherol, respectively, when tested individually in the dark at 55°C (67). Similarly, at temperatures ranging from 40 to 60°C in the dark, optimal concentrations for α - and γ -tocopherols were ~100 and ~300 ppm, respectively; however, δ -tocopherol did not exhibit an optimum concentration under these conditions (55). Tocopherol concentrations are critical, because the compounds can act as pro-oxidants when in excess in the presence of other oxidation-promoting compounds, such as peroxides or metals (61). Indeed, at greater than optimal concentrations, individual

tocopherols and tocopherol mixtures were pro-oxidant, a behavior enhanced by increasing oil temperature from 40 to 60°C (55).

Warner (68) tested tocopherol-stripped soybean and sunflower oils, to which pure tocopherols had been replaced in proportions typically found in these oils. At 60°C in darkness, soybean and sunflower oils with typical soybean tocopherol composition (low α - and high γ - and δ -) had better oxidative stabilities than did those with typical sunflower tocopherol composition (high α - and low γ - and δ -). In contrast, when tested in light conditions at 30°C, oils with high α -tocopherol (sunflower composition) were more stable than oils with high γ - and δ - (soybean composition) (68), likely a result of the higher capacity of the α -analog to prevent singlet oxygen oxidation (17, 68). In another study, mid-oleic sunflower oil was stripped of the tocopherols and different combinations of α -, γ -, and δ -tocopherols were added and used to fry tortilla chips. Both γ - and δ -tocopherols were responsible for decreasing the contents of total polar compounds in the oil as well as decreasing the content of hexanal in the stored chips. Also the percentage of retention of the tocopherols in the oil after 6 h frying was $\delta > \gamma > \alpha$ (69).

Polydimethylsiloxane

Polydimethylsiloxane (PDMS) is a silicon-based polymer and has been extensively used by the food industry as an anti-foaming agent because of its low surface tension properties (6). PDMS at very low concentrations also has protective effects on frying oils (6-9). Many studies have tried to explain the cause of this protective effect of PDMS in frying oils, however, the mechanism is not entirely clear.

Freeman et al (7) studied the effect of PDMS concentration in frying oil (sunflower oil). There was no protective effect of PDMS in the percentage of unoxidized triglycerides at concentrations below 0.05-0.06 $\mu\text{g PDMS}/\text{cm}^2$. In this study, the monomer area on the surface of the oil was 20 to 25 \AA^2 (7, 70), and represented the minimum effective concentration necessary to form a monolayer of PDMS if all the PDMS was assumed to be on the surface.

The effect of PDMS seems to be dependent on its insolubility in the frying oil. When fat-soluble silicone polymer modified with fatty acids was evaluated vs. PDMS, there was no protective effect in the oil treated with the fat-soluble polymer. Also, the protective effect of PDMS improved with increasing viscosity. In general, only PDMS types with a viscosity > 20 cs were effective (10).

PDMS has been proposed to alter convective currents in the surface of the oil. Kusaka et al (11) studied the disappearance of a drop of Sudan-III-colored soybean oil when adding it to oil with and without PDMS. The color disappeared faster in the oil without PDMS. Later, Ohta and collaborators (12) observed a $\sim 20^\circ\text{C}$ decrease on the surface of oil treated with PDMS compared to the temperature in the interior of the bulk oil. They attributed this temperature decrease to the inhibition of surface convective currents by PDMS. Indeed, in other work, the presence of PDMS changed the infrared absorbance spectrum in tung oil (13). To further understand the role of the convection currents on the effect of PDMS, high-linoleate sunflower and high-oleate sunflower oils were heated in an oven and on a hotplate. For both oils, the addition of PDMS decreased the formation of polar compounds when the oil was heated on the hotplate. However, there were no differences between PDMS- treated and non-treated oil when heated in an oven (71).

The effect of PDMS addition to a frying oil was also evaluated during continuous and discontinuous frying. The protective effect was stronger during discontinuous frying; the formation of polar compounds was lesser when PDMS was added (72, 73). Similarly, the contents of tocopherols were higher in PDMS-treated oil than in untreated oil during discontinuous frying (72).

The role of PDMS in preventing oil deterioration during frying is not totally understood. The effect of PDMS on the convective currents of an oil surface may be part of its protective mechanism. Freeman et al (7) suggested that PDMS might also accumulate on the surface of the oil and form a physical barrier that prevents the entrance of oxygen into the oil, thus decreasing oxidation.

According to the World Health Organization, the acceptable daily intake of PDMS is up to 1.5 mg/kg of body weight (74) and the maximum allowed in foods by the FDA is 10 ppm (75). The amount of PDMS absorbed in fried potato chips increased exponentially with increasing PDMS contents in the frying oil (7). PDMS is used in frying oils in concentrations of ~5 ppm in the oil. If 300 g potato chips were fried in 1 L of oil treated with 5 ppm PDMS, the actual PDMS concentration in the food would be 2 ppm (7). For a 60-kg person it would be necessary to consume 45 kg of potato chips to meet the daily maximum of 1.5 mg/kg of body weight.

PDMS is thought to degrade by depolymerization and cross-linking at high temperatures. In the presence of air, thermal gravimetric analysis of PDMS indicated that thermal loss started at 290°C (76, 77). Two mechanisms were proposed for the thermal degradation of PDMS. The first mechanism led to depolymerization through the scission of the Si-O

bond and the formation of cyclic compounds. The second mechanism proceeded through the formation of free radicals from the homolytic scission of the Si-CH₃ bonds (77) and led to cross linking and loss of flexibility of the polymer chains. Indeed, the use of free radical-forming peroxides, such as benzoyl peroxide, was previously proposed as a curing method for silicone rubber, via a cross linking mechanism (78).

Oxygen solubility in oil

In general, the solubility of oxygen in oils increases with increased temperatures, between 0 and 100°C (79-81). Oxygen solubility in soybean oil at 20°C was measured at 1 atmosphere (atm) air and was 0.055 mg/g (82). In the case of olive oil, the solubility of oxygen was 0.035 mg/g when measured at 25°C and 1 atm air (81).

Oxygen pressure over frying oils is an important factor in determining the extent of oil oxidation at frying temperatures (83). A decrease in 0.05 atm in the atmospheric pressure over oil heated at 180°C decreased the formation of polar compounds by ~50%. Also, when frying was done under a stream of nitrogen, the quality of the oil after 5 h of frying was better than when the frying was done in air atmosphere (83).

4-Hydroxy-2-(E)-nonenal

During oxidation of polyunsaturated fatty acids, many compounds are formed: aldehydes, ketones, acids, and hydrocarbons are some of those. The compounds formed are characteristic of the fatty acid from which they are produced (14). One of the

characteristic products of linoleate (18:2) degradation is 4-hydroxy-2-(E)-nonenal (HNE). This hydroxyaldehyde has been the subject of much research because of its toxicity and physiological functions (84).

4-Hydroxynonenal has three functional groups, which are responsible for its great reactivity. The carbon-carbon double bond conjugated with a carbonyl group induces a partly positive charge on carbon 3, which is further accentuated by the influence of the hydroxy group on carbon 4. As a result, HNE is susceptible to nucleophilic attacks by electronegative groups, such as thiol or amino groups, primarily on carbon 3 and secondarily on carbon 1 (85).

The carbon-carbon double bond can react with thiol groups (from cysteine or glutathione) and through the Michael addition reaction mechanism, be reduced to yield 4-hydroxynonanal, or even be oxidized to form epoxides (85). The carbonyl group can also react with alcohols and thiols to form hemiacetals or hemithioacetals and continue further to yield acetals or thioacetals. If the double bond has undergone a reaction that converts it to a free rotating bond (reduction or Michael addition), an internal hemiacetal can be formed by the reaction of the aldehyde group and the hydroxy group in position 4. Another important reaction is the formation of a Schiff base from the reaction of the carbonyl group with a primary amine. This reaction is very common during cross linking of proteins by HNE. The carbonyl group can also oxidize or reduce to yield an acid or an alcohol, respectively. Finally, the hydroxy group can undergo oxidation to yield a ketone (85).

4-Hydroxynonenal is highly reactive towards proteins, lipids (especially phospholipids),

co-factors, vitamins, and nucleic acids, both by Michael addition and Schiff-base formation (86). At least 39 human diseases have been linked to the presence of HNE, including AIDS, atherosclerosis, chronic hepatitis B and C, diabetes mellitus, multiple sclerosis, Alzheimer's disease, and acute myocardial infarction (86). Deoxyribonucleic acid (DNA) background lesions caused by reaction with HNE were found in healthy rat and human colon and liver tissues (87). Toxicity has been established for cell cultures at the following levels and severity: $> 100 \mu\text{M}$ HNE produces a rapid cytotoxic effect leading ultimately to cell death; 1 to 20 μM HNE can inhibit protein synthesis; and $<0.1 \mu\text{M}$ HNE are probably normal basal HNE tissue concentrations (88, 89).

There is no data in the literature reporting dietary HNE absorption, however several studies show that fatty acid oxidation secondary products are absorbed (90-92), especially α,β -unsaturated aldehydes (91). When rats were fed α,β -unsaturated aldehydes (*trans*-2-nonenal and *trans*-2-pentenal), the aldehydes were absorbed, metabolized through addition of glutathione, and their metabolites excreted in the urine (91). When rats were fed thermally oxidized safflower oil (0.30 ml/day) during gestation the percentage of embryo malformations increased three times. Feeding unheated safflower oil also increased the percentage of embryo malformations, probably because of the presence of detectable lipid oxidation products in the oil, although the impact was less than that from the thermally oxidized safflower oil. The administration of α -tocopherol as a supplement helped reduce the incidence of the highly oxidized safflower oil in the percentage of embryo malformations (92). The HNE content in different Korean foods was evaluated and the daily intake of HNE calculated based on the Korean 2001 National Health and Nutrition Survey. The mean calculated intake was 16.1 $\mu\text{g}/\text{day}$ (93).

4-Hydroxynonenal formation in heat-abused soybean oil also has been studied. When soybean oil was heated at 185°C in a round bottom flask with constant air bubbling, the HNE concentration increased rapidly in the beginning followed by a decrease after reaching a maximum concentration. The maximum HNE concentration (0.27 $\mu\text{mol/g}$ oil) occurred after 6 h of heating (4). In another study, where pure methyl linoleate was heated at 185°C, the maximum HNE concentration occurred after 3 h of heating (0.54 $\mu\text{mol/g}$ FAME) and then it decreased (61). Another study reported the presence of 0.021 μmol HNE/g oil after heating soybean oil in an open beaker for 8 h with constant air bubbling (5). 4-Hydroxynonenal accumulation was studied during continuous and discontinuous heating. There were no differences in the concentration of HNE among the treatments (95).

Analytical procedures for fat degradation determination

The work accomplished in this dissertation required the use of many different analytical procedures. In many instances, there were several choices of techniques to use. An overview of these procedures is discussed.

Linoleate degradation

The degradation of 18:2 in an oil can be monitored by transesterification of the triacylglycerides into fatty acid methyl esters (FAME) (96). The FAME composition is analyzed by gas chromatography with flame ionization detection (97). When the fatty acids present in the oil are larger than twelve carbons the percentage area for each peak FAME is very close to the mass percentage of the FAME in the mixture (97). Palmitic

acid is not degraded during frying conditions, thus it is usual to report the disappearance of unsaturated fatty acids as the ratio of the percentage area of the fatty acid relative to that of 16:0 (9, 48, 50).

Tocopherol disappearance

High-performance liquid-chromatography is the most commonly used method to determine the concentration of tocopherols in oils. In general, spectrophotometric detection is used at 292 nm (UV) (97). Fluorescence detection can also be used with excitation at 290 nm and emission at 325 nm (98, 99). The use of fluorescence detection improves sensitivity and specificity by discriminating among co-eluting components (98).

Oxygen concentration

Several methods have been proposed for determining the oxygen concentration in oils. A complicated method based on volume displacement is described by Battino et al (81). Because of the requirements of temperature uniformity this method is impractical for use under frying conditions. Another method uses gas chromatography with thermal conductivity detection (100). The oil is injected in a glass chamber containing glass wool, and a stream of helium desorbs the gases dissolved in the oil at 150°C. This chamber is connected to the chromatographic column where they are separated and measured in the detector. The disadvantage of this approach is that during desorption of the gases at 150°C, oxygen reacts very quickly with polyunsaturated fatty acids and the actual concentration of oxygen may be underestimated. A method using mass spectrometry was described by Snedden et al (101). In this method, the oil is contained in a thermostatically

controlled syringe and exposed to a volume of oxygen. After equilibration, the headspace in the syringe is injected into a mass spectrometer and the oxygen concentration measured. Temperatures and conditions used during frying make this approach impractical to use. Parenti et al (102) used a portable polarographic oxygen analyzer to determine oxygen concentrations in olive oil. This principle was adapted for use under frying conditions as explained later in this dissertation.

4-Hydroxy-2-(E)-nonenal determination

The high reactivity of HNE makes it difficult to measure in oxidized oils. Several methods have been described to determine HNE concentration in oils. All of them require derivatization of HNE to improve extraction and increase stability of the compound during the analysis. Seppanen and Csallani (4) determined HNE by HPLC. They derivatized the aldehydes in the oil to dinitrophenyl hydrazones (DNPH). The DNPH derivatives were separated by thin-layer chromatography and the high polarity band was extracted and analyzed by HPLC with detection at 378 nm. The elution was done using a 50:50 mix of water:methanol as the starting solvent, followed by a linear gradient to 100% methanol in 40 min (4).

Another method utilizes gas-chromatography mass-spectrometry (GC-MS) to determine the concentration of HNE in oils (88). This method requires addition of an internal standard (deuterated HNE) to the oil (103). To remove HNE, the oil is extracted with water, followed by derivatization of the carbonyl groups with pentafluorobenzyl hydroxylamine to form pentafluorobenzyl (PFB) oximes. The PFB oxyimes are extracted with pentane and the hydroxy group is treated with *N,O* -Bis (trimethylsilyl)

trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS) to form a trimethyl silyl derivative (TMS). The derivatized extract is diluted with methylene chloride and analyzed by GC-MS using a non-polar DB-5 capillary column. If positive-electron-impact MS is used, the derivatized HNE yields three characteristic mass-to-charge fragments (m/z): 226, 242, and 352. The m/z fragments of the deuterated internal standard would depend on the number of deuterium atoms in the molecule and their position. In general, $m/z=352$ is common to both HNE and the internal standard, thus it is only used for identification. The rest of the m/z are used for quantification (104). Other researchers have proposed the inclusion of a purification step by solid-phase extraction using a C-18 silica cartridge before the PFB derivatization (93). This step can help to clean the extract, however, it is impractical when a large number of analyses are required.

Justification for work and objectives:

The effect of PDMS on fatty acid degradation during frying is poorly understood. Soybean oil, and particularly the 18:2 and 18:3, is very susceptible to oxidation at elevated temperatures, thus it is an appropriate substrate in which to evaluate the protective effect of PDMS and to facilitate the study of the kinetics of oil degradation at frying temperatures. Also, evaluation of the disappearance of tocopherols in an oil can contribute to understanding the protective mechanism of PDMS. Finally, understanding the exchange of oxygen between oil and the atmosphere in the presence of PDMS during frying is crucial. Thus, the effect of PDMS on the concentration of oxygen in the oil as well as on the formation of oxygenated degradation products, such as HNE, needs to be

evaluated. The objectives of the work in this dissertation were to:

1. Determine the effect of PDMS concentrations on the kinetic parameters of the disappearance of 18:2 and tocopherols at frying temperature.
2. Determine the effect of PDMS presence on the oxygen concentration of soybean oil at various temperatures.
3. Determine the effects of PDMS concentration on the kinetic parameters of the formation and disappearance of HNE, an oxygenated product of 18:2 oxidation.

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**CHAPTER 2. INFLUENCE OF POLYDIMETHYLSILOXANE ON THE
DEGRADATION OF SOYBEAN OIL AT FRYING TEMPERATURE**

A paper to be submitted to the Journal of the American Oil Chemists' Society

Jose A. Gerde, Earl G. Hammond and Pamela J. White*

Department of Food Science and Human Nutrition, Iowa State University, Ames, Iowa
50011

* To whom correspondence should be addressed at E262 Lagomarcino Hall, Iowa State University, Ames, IA 50011-1060. Phone: 515-294-5380, Fax: 515-294-7802, Email: pjwhite@iastate.edu

Abstract

Soybean oils treated with 5, 10, 25, 50, and 100 ppb polydimethylsiloxane (PDMS) and a control soybean oil (no PDMS) were heated at 180°C for 48 h. The decomposition of linoleate (18:2) and tocopherols was monitored. The degradation of 18:2 and both γ - and δ -tocopherols followed pseudo first-order kinetics. For 25 ppb PDMS (the concentration necessary to form a PDMS monolayer on the air-oil interface) and greater concentrations, 18:2 degradation decreased in rate, with a subsequent increase in slope during 48 h of heating. The same trend occurred for the degradation of both γ - and δ -tocopherols, but

the change in rates of degradation was observed also in the 10 ppb PDMS treatment. For treatments with PDMS concentrations similar to that needed to provide a monolayer concentration, the rates of degradation after the change were similar to the rate of degradation of the control oil, and in general, the changes occurred later at higher PDMS concentrations. The occurrence of these changes in rates of degradation was likely related to the time at which tocopherols were no longer effective in preventing oil degradation and when the PDMS was sufficiently degraded to lose its protective effect.

Keywords: polydimethylsiloxane, tocopherol, soybean oil, frying, kinetics

Introduction

Oils subjected to frying temperatures undergo a variety of degradation reactions, most of which are oxidative. Oils with a fatty acid composition rich in polyunsaturated fatty acids are greatly affected by these oxidative reactions. Polydimethylsiloxane (PDMS), a silicon-based polymer, is widely used by the food industry as an anti-foaming agent. The use of PDMS in very low concentrations in frying oils has a protective effect on the oil (1).

Extensive research has been done on the mechanism by which PDMS protects oil against degradation during frying (1, 2). Likely, PDMS viscosity impacts the effectiveness. Low viscosity PDMS (less than 5 centistokes) did not have a protective effect, whereas PDMS with viscosities between 20 and 100 cs were protective (1, 2). The protective effect also has been associated with the ability of PDMS to affect the oil-air interface of a frying oil.

The minimal effective PDMS concentration is estimated to be 0.05-0.06 $\mu\text{g}/\text{cm}^2$ of the

air-oil surface area (3).

Two mechanisms to explain the PDMS protective action on frying oils have been proposed. The first deals with inhibition of convective currents on the surface of the oil, with a consequent reduction of oxidation. The second proposed mechanism suggests the accumulation of PDMS on the air-oil interface acts as a barrier to oxygen diffusion, thus inhibiting free radical propagation, or by acting as a relatively inert surface to oxidation (3).

The impact of PDMS on the rate of degradation of linoleate (18:2) in soybean oil at 180°C was reported (4). The initial rate of 18:2 degradation in oil treated with PDMS was lower than for pure soybean oil (control). After 12 h at 180°C degrees the rate of 18:2 degradation in the PDMS-treated oil became the same as that for the control.

Tocopherols are antioxidant compounds naturally present in vegetable oils. Tocopherol retention in frying oils is important to the storage life of the fried products. Tocopherols are carried over to the fried product and protect it from oxidation during storage (5).

Soybean oil is particularly rich in γ - and δ -tocopherols, with γ -tocopherol having stronger antipolymerization properties in frying oils than α -tocopherol (5, 6). Thus, tocopherol degradation is an important factor to be considered when evaluating oil protective agents.

The effect of the concentration of PDMS on the degradation rate of 18:2 and tocopherols has not been studied. Thus, the objective of this study was to determine the impact of PDMS concentration on the degradation rate of 18:2 and of tocopherols in soybean oil held at frying temperature (180°C), and to understand the protective mechanism of PDMS on frying oils.

Experimental Procedures

Oil heating and sampling: Refined, bleached, and deodorized soybean oil with citric acid added (Golden Chef) was obtained from Archer Daniels Midland Company (Decatur, IL). The oils (200 g) were heated in a 100 x 50 mm crystallizing dish (Pyrex, Corning Inc., Corning, NY) for 48 h at 180°C. The initial surface-to-volume ratio was 0.36 cm⁻¹. The PDMS was food-grade Dow Corning 200, 350 cs (Dow Corning Co., Midland, MI).

Treatments: Treatments containing selected concentrations of PDMS were prepared. A stock solution containing 100 ppm of PDMS in hexanes was prepared, appropriate amounts were added to the crystallizing dishes and the solvent evaporated before adding the oil. All the treatments were heated simultaneously, in two separate replicates of each treatment (blocking factor). Oil aliquots (2 ml) were removed every 2 h for further analysis and stored in glass vials at -22°C. The oil removed was not replenished.

Previous research showed that the minimum efficient concentration of PDMS on the surface of oil heated at 180°C was 0.05-0.06 µg/cm² (3). Considering a PDMS monomer surface area of 20-25 Å² (7) and assuming that at 180°C practically all PDMS is at the oil-air interface, the concentration necessary to have a theoretical PDMS monolayer in the system was calculated (Eq. 7). This calculated monolayer concentration was ~25 ppb in the oil. Oil treatments included two PDMS concentrations greater than the monolayer concentration (100 and 50 ppb) and two less than (10 and 5 ppb), the monolayer concentration (25 ppb PDMS), and a control (no PDMS).

$$PDMS_{concentration} = \frac{Area_{container} \times mw_{monomer}}{Area_{monomer} \times N_A \times mass_{oil}} \quad (\text{Eq. 7})$$

where $m_{w_{\text{monomer}}}$ is 74.1 g/mol, the area of the container is 7850 mm², the area of the monomer is 20 Å², m_{oil} is 200 g, N_A is Avogadro's number, and the result is converted to ppb by multiplying by a suitable factor (1E23).

Fatty acid composition: Oil aliquots were converted to fatty acid methyl esters (FAME) (8). The FAME were injected in a Hewlett-Packard 5890 Series II chromatograph with a flame ionization detector and split/splitless injector. A 15 m x 0.25 mm x 0.2 µm film SP-2330 silica capillary column (Supelco, Bellefonte, PA) was used. The chromatographic parameters were: injector temperature, 230°C, detector temperature, 230°C, oven temperature program, 150 to 180°C at 5°C/min with no holding time. The carrier gas (He) was set at 5.4 mL/min, the auxiliary gas (He) at 19.4 mL/min, H₂ at 13.9 mL/min, and air at 426 mL/min. The split ratio was 24:1. The FAME composition was expressed as uncorrected relative area percentages of the detector output. Oil degradation throughout the heating time was evaluated by assessing the disappearance of methyl linoleate (18:2) by using methyl palmitate (16:0) as a naturally present internal standard (4). The linoleate-to-palmitate ratios (18:2/16:0) were calculated and the natural logarithm of the 18:2/16:0 ratios were plotted vs. time (Eq. 1). The slopes of the linear regressions were estimated and used as a measure of the rate of the 18:2 disappearance.

$$\ln(18:2/16:0) = \ln(18:2_0/16:0_0) - k_1 t \quad (\text{Eq.1})$$

where 18:2₀/16:0₀ is the linoleate to palmitate relative concentration in the fresh oil (time 0), k_1 is the rate constant, and t is the time in hours.

If there was a point of change in the rate of degradation, the kinetic model was split into two pseudo first-order kinetics (before and after the change; Eq. 2 & 3):

$$\text{Ln}(18:2/16:0) = \text{Ln}(18:2_0/16:0_0) - k_1 t \quad t \leq T \quad (\text{Eq. 2})$$

$$\text{Ln}(18:2/16:0) = \text{Ln}(18:2_0/16:0_0) - k_1 T - k_2 (t - T) \quad t > T \quad (\text{Eq. 3})$$

where k_2 is the rate of reaction after the change in the rate of degradation, and T is the time at which the change in the rate of degradation occurs.

Tocopherol content: Accurately weighed oil amounts were diluted with hexane to obtain 0.1 g/mL solutions, and analyzed by HPLC by using a Beckman Coulter System Gold (Beckman Coulter Inc., Fullerton, CA) equipped with a 25 cm x 4.6 mm 5 μ 60Å LiChrosorb Silica column (ES Industries Chromega Columns, West Berlin, NJ) with UV detection at 292 nm. The column was eluted with isopropanol:hexane (5:95 v/v) and the flow was set at 0.7 ml/min. The concentrations of the various tocopherols were expressed in ppm and external standards were used for quantification. In a manner similar to the calculations used for 18:2 degradation, the natural logarithm of γ - and δ -tocopherol concentrations were plotted vs. time and the slopes of the linear regressions calculated and used as an estimate of the rate of disappearance of the tocopherol types (Eq. 4).

$$\text{Ln}(\text{tocopherol}) = \text{Ln}(\text{tocopherol}_0) - k_1 t \quad (\text{Eq. 4})$$

where tocopherol_0 is the ln of the γ or δ -tocopherol concentration in the fresh oil (time 0), k_1 is the rate constant, and t is the time in hours.

If there was a change in the rate of degradation, the kinetic model was again split into two pseudo first-order plots, that is before and after the change in the rate of degradation (Eq. 5 and 6).

$$\text{Ln}(\text{tocopherol}) = \text{Ln}(\text{tocopherol}_0) - k_1 t \quad t \leq T \quad (\text{Eq. 5})$$

$$\ln(\text{tocopherol}) = \ln(\text{tocopherol}_0) - k_1 T + k_2 (t - T) \quad t > T \quad (\text{Eq. 6})$$

where k_2 is the rate constant after the change in rate of degradation and T is the time at which the change occurred.

Kinetics model parameters estimation: The parameters were estimated using GraphPad Prism software version 4.03 for Windows (GraphPad Software, San Diego, CA) and all the regression curves fitted had an $R^2 \geq 0.9$ unless otherwise indicated.

Statistical analysis: The slopes were analyzed by using analysis of variance (ANOVA) with the PROC GLM of SAS 9.1 software (SAS Institute Inc., Cary, NC). Comparisons were assessed by contrasts using Tukey's adjustment for multiple comparisons. The level of significance was set at $\alpha=0.05$ unless otherwise indicated.

Results and Discussion

Linoleate disappearance

The degradation during frying of 18:2, the major fatty acid in conventional soybean oil, was previously documented and a first-order kinetics was fitted as the most appropriate (4). During continuous heating of soybean oil in the presence of PDMS, the rate of the reaction accelerated at a certain time (the point at which the slope of the plot changed), and thereafter, the 18:2 degraded at the same rate as 18:2 in pure soybean oil (4).

In the current study, the rate of degradation changed at a specific time, after which, the rate of 18:2 disappearance accelerated for PDMS concentrations equal to or greater than the calculated PDMS monolayer concentration (25 ppb). Figure 1 illustrates the

disappearance of 18:2 and shows plots for each PDMS concentration. For 100 ppb of PDMS, the rate after T was lower than that of the slope of the control oil. The rates after T for the calculated monolayer concentration (25 ppb PDMS) and for 50 ppb PDMS were not different from the rate of the control oil. For concentrations of PDMS below the monolayer concentration no change in rate was found. For a PDMS concentration of 5 or 10 ppb, the rate of 18:2 degradation was not different from that of the control (pure soybean oil) (Table 1). In a previous paper (4) rates after the point of change were similar to those of their control oils even though the PDMS concentrations were much greater (5 and 10 ppm), but the approximate surface to volume ratio also was greater (0.92 cm^{-1} compared to 0.36 cm^{-1} in the present experiments). In a typical commercial deep-fat fryer (Star Twin Pot deep-fat fryers, model 530TA, Star Manufacturing International Inc. St. Louis, MO) the surface-to-volume ratio is much less, $\sim 0.1 \text{ cm}^{-1}$.

Tocopherol degradation

The γ - and δ -tocopherols were monitored during oil heating. Interfering compounds eluted at the same retention time as α -tocopherol; thus, it could not be measured accurately. Because the α -tocopherol is present in small concentrations in soybean oil (9) and is not the most potent antioxidant in soybean oil (10), the omission is likely not important to the findings in the current study. The γ - and δ -tocopherols were determined until concentrations became so low that co-eluting oxidation compounds interfered with their quantification.

Changes in the rates of γ - tocopherol degradation were found for PDMS concentrations of

10 ppb and above (Fig. 2). In the samples treated with 50 and 100 ppb of PDMS, the rate after T was not as great as that of the control. For 25 ppb, the calculated PDMS monolayer concentration, and 10 ppb, the degradation rate of γ -tocopherol after T was not different from that of the control. For 5 ppb of PDMS no change in rate was found. The rate changes tended to occur later as the PDMS concentration increased.

The δ -tocopherol degradation occurred at a slower rate than γ as shown in Tables 2 and 3. This pattern agrees with Barrera-Arellanos et al. (11) and confirms the greater resistance of δ -tocopherol compared with γ -tocopherol to high-temperature oxidation.

Similar to γ -tocopherol, degradation of δ - tocopherol at PDMS concentrations >10 ppm followed pseudo first-order kinetics until a time where the reaction accelerated (Fig. 3). The rate of δ -tocopherol disappearance after T was not different from that of the control oil. In treatments with 5 ppb PDMS no change of rate was observed, and the rate of the reaction was not different from that of the control oil. In the oil treated with 25 ppb PDMS, T was similar to that of γ - tocopherol; however, at PDMS concentrations greater than the monolayer concentration, the time at which the degradation of δ -tocopherol accelerated, was later than for γ -tocopherol.

At the monolayer concentration of PDMS (25 ppb), the 18:2 and γ - and δ - tocopherol degradation plots all had similar T, and the rates of oxidation of all three substrates increased to match the rate of the control soybean oil. These changes in the rates of oxidation suggest that, at this time, the PDMS had become ineffective, probably because of degradation at high temperatures (12).

The relationship between the rates of degradation of 18:2 and tocopherols before any

change in rate (k_1) and the initial concentrations of PDMS also was studied. For the 18:2 degradation, a plateau was observed at concentrations of up to 10 ppb PDMS. At greater concentrations, the rate of disappearances of 18:2 decreased exponentially. For both γ - and δ -tocopherols, the rates of degradation decreased exponentially with increasing PDMS concentrations, although no plateau was observed. For both tocopherol types, the influence of the concentration of PDMS on the rates of degradation was similar (Fig. 4). The addition of 100 ppb PDMS in the oil decreased the rate of degradation of both tocopherols and 18:2 by about ~83-87%, compared to the untreated oil. However, because of the exponential type of decay, the use of PDMS concentrations greater than 100 ppb (in this system) likely would have a minor additional impact on the reduction of the degradation rates. The absence of a plateau in the tocopherol degradation could be related to the greater reactivity of tocopherols compared to 18:2 and the greater variability of the tocopherol degradation rates at very low PDMS concentrations (Fig. 4). Although color and viscosity were not measured in a systematic fashion, in all cases, the oils clearly became progressively darker with time as observed by the authors, with the darkening being faster at lower PDMS concentrations. Oil viscosity showed a similar trend. There was a progressive thickening with time, and this thickening was more obvious at low PDMS concentrations.

Conclusions

The protective effect of PDMS in high-temperature oil systems was demonstrated by the decrease in the rate of disappearance of 18:2, and δ -, and γ -tocopherols. The PDMS effect

was evident at concentrations equal to or greater than the calculated monolayer concentration (25 ppb PDMS), suggesting that PDMS accumulated in the surface of the oil where it possibly acted as a barrier to oxygen transfer into the oil.

At greater PDMS concentrations, such as 50 and 100 ppb, the change in rate of tocopherol disappearance occurred later than in the treatment with 25 ppb, and the 18:2 oxidation rate after the change of rate was slower than in that of the control oil. This difference in rates suggests that the tocopherols controlled the occurrence of the changes in rate, and the slower rate of 18:2 oxidation was caused by the PDMS still being at an effective concentration.

In general, the loss of γ -tocopherol was faster than that of the δ -tocopherol. This difference in the rate of degradation suggests that γ -tocopherol was more susceptible to oxidation than δ -tocopherol, and spared the oxidation of the δ -until the γ -tocopherol reached a concentration where it no longer controlled the rate.

These results indicate that the slope of the logarithm of the disappearance of 18:2 and the times of changes of slopes may be good measures of the effectiveness and duration of antioxidants and other oxidation inhibitors in frying oils.

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Table 1 The time of change in rates (T) and rates of ln(18:2/16:0) vs. time in soybean oil with various amounts of PDMS heated to 180°C

Treatment (ppb PDMS)	Mean T (h)	Mean rate before change (k ₁)	Mean rate after change (k ₂)
0 Control	-	0.0139 ^w	0.0139 ^w
5	-	0.0141 ^w	0.0141 ^w
10	-	0.0141 ^w	0.0141 ^w
25	13 ^w	0.0080 ^{a, x}	0.0135 ^{b, w}
50	21 ^w	0.0046 ^{a, y}	0.0121 ^{b, w}
100	17 ^w	0.0023 ^{a, z}	0.0049 ^{b, x}

^{a-b} Different superscripts in the same row indicate significant differences at p<0.05

^{w-z} Different superscripts in the same column indicate significant differences at p<0.05

Table 2 The time of change in rates (T) and rates of $\ln(\gamma\text{-tocopherol})$ vs. time in soybean oil with various amounts of PDMS at 180°C

Treatment (ppb PDMS)	Mean T (h)	Mean rate before change (k_1)	Mean rate after change (k_2)
0 Control	-	0.4852 ^x	0.4852 ^x
5	-	0.4003 ^x	0.4003 ^{xy}
10	7 ^x	0.2486 ^{a, y}	0.4578 ^{b, x}
25	11 ^x	0.1788 ^{a, yz}	0.3968 ^{b, xy}
50	13 ^x	0.0756 ^{a, z}	0.2380 ^{b, yz}
100	26 ^x	0.0597 ^{a, z}	0.2068 ^{b, z}

^{a-b} Different superscripts in the same row indicate significant differences at $p < 0.05$

^{x-z} Different superscripts in the same column indicate significant differences at $p < 0.05$

Table 3 The time of change in rates (T) and rates of $\ln(\delta\text{-tocopherol})$ vs. time in soybean oil with various amount of PDMS at 180°C

Treatment (ppb PDMS)	Mean T (h)	Mean rate before change (k_1)	Mean rate after change (k_2)
0 Control	-	0.1390 ^x	0.1390 ^x
5	-	0.1710 ^x	0.1710 ^x
10	5 ^x	0.0604 ^{a, xyz}	0.1211 ^{b, x}
25	10 ^x	0.0467 ^{a, yz}	0.1143 ^{b, x}
50	19 ^x	0.0287 ^{a, yz}	0.1480 ^{b, x}
100	35 ^y	0.0217 ^{a, z}	0.1444 ^{b, x}

^{a-b} Different superscripts in the same row indicate significant differences at $p < 0.05$

^{x-z} Different superscripts in the same column indicate significant differences at $p < 0.05$

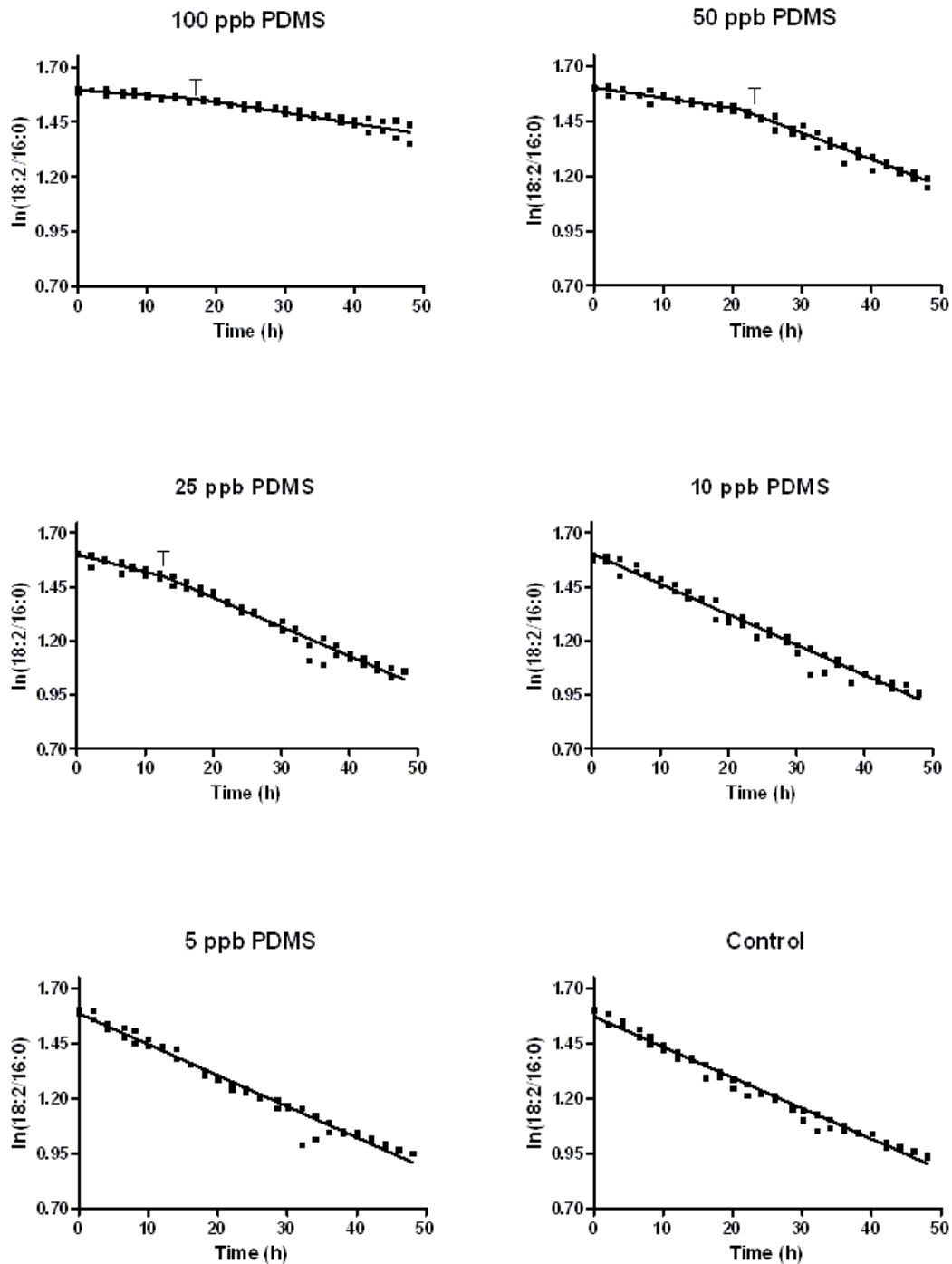


Fig. 1 Semi logarithmic plots of the 18:2/16:0 ratio vs. time of soybean oil without added PDMS (control) and of soybean oil treated with 5, 10, 25, 50, and 100 ppb PDMS and the curves generated from the mean of the parameters of the respective fitted curves

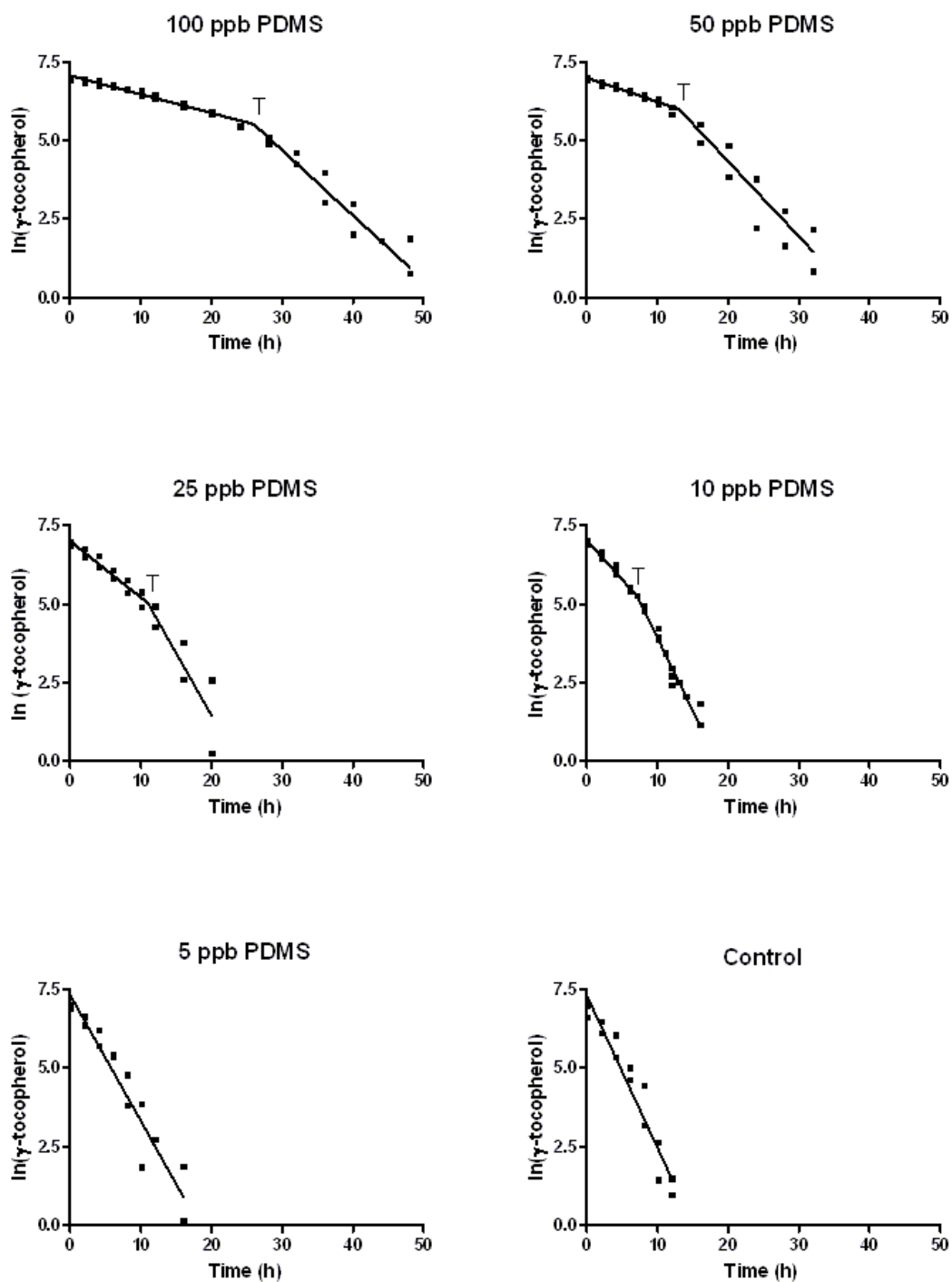


Fig. 2 Semi logarithmic plots of the [γ -tocopherol] vs. time of soybean oil without added PDMS (control) and of soybean oil treated with 5, 10, 25, 50, and 100 ppb PDMS and the curves generated from the mean of the parameters of the respective fitted curves

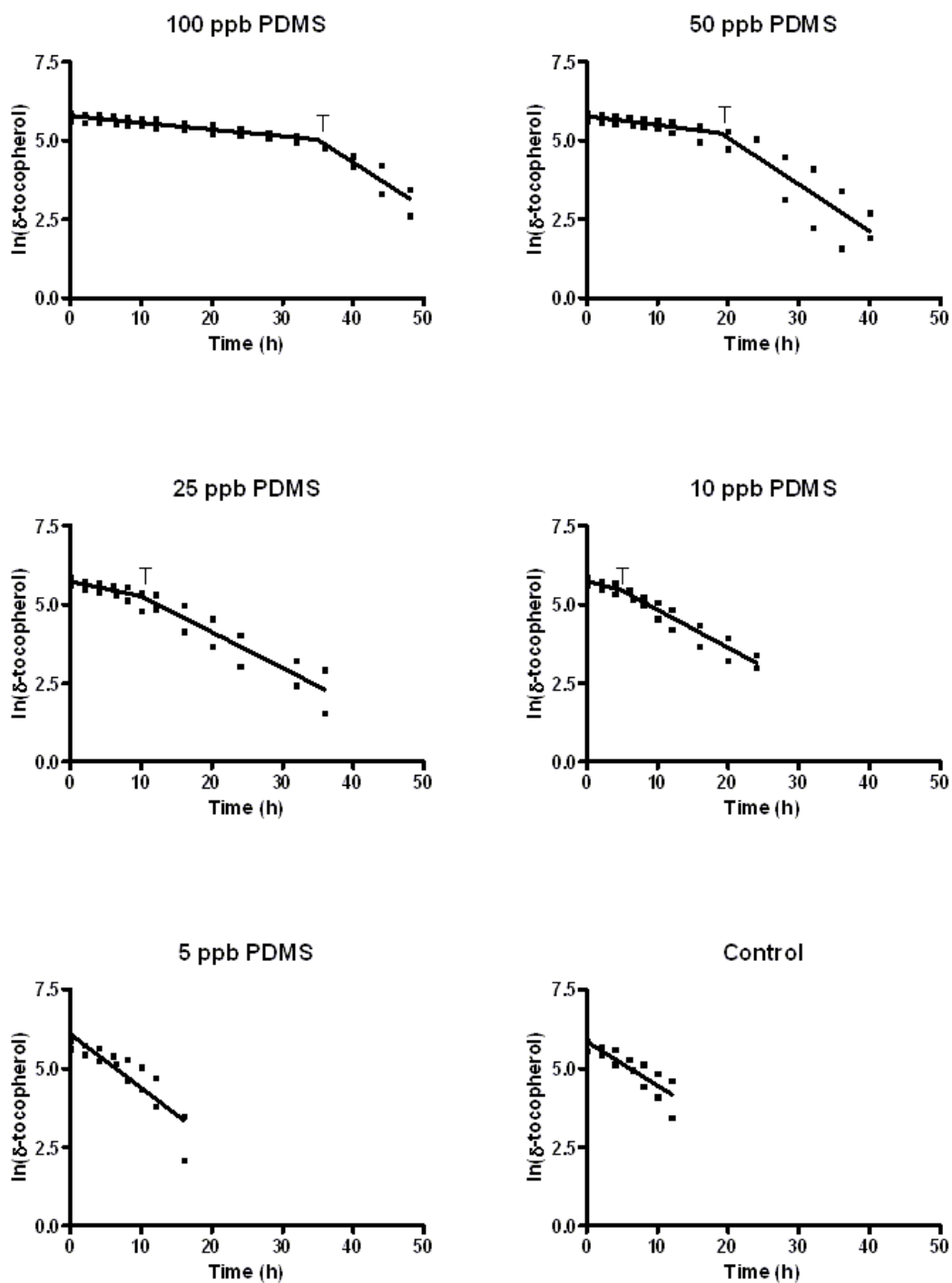


Fig. 3 Semi logarithmic plots of the [δ -tocopherol] vs. time of soybean oil without added PDMS (control) and of soybean oil treated with 5, 10, 25, 50, and 100 ppb PDMS (rep 2 of the 5 ppb PDMS treatment had $R^2=0.7$) and the curves generated from the mean of the parameters of the respective fitted curves

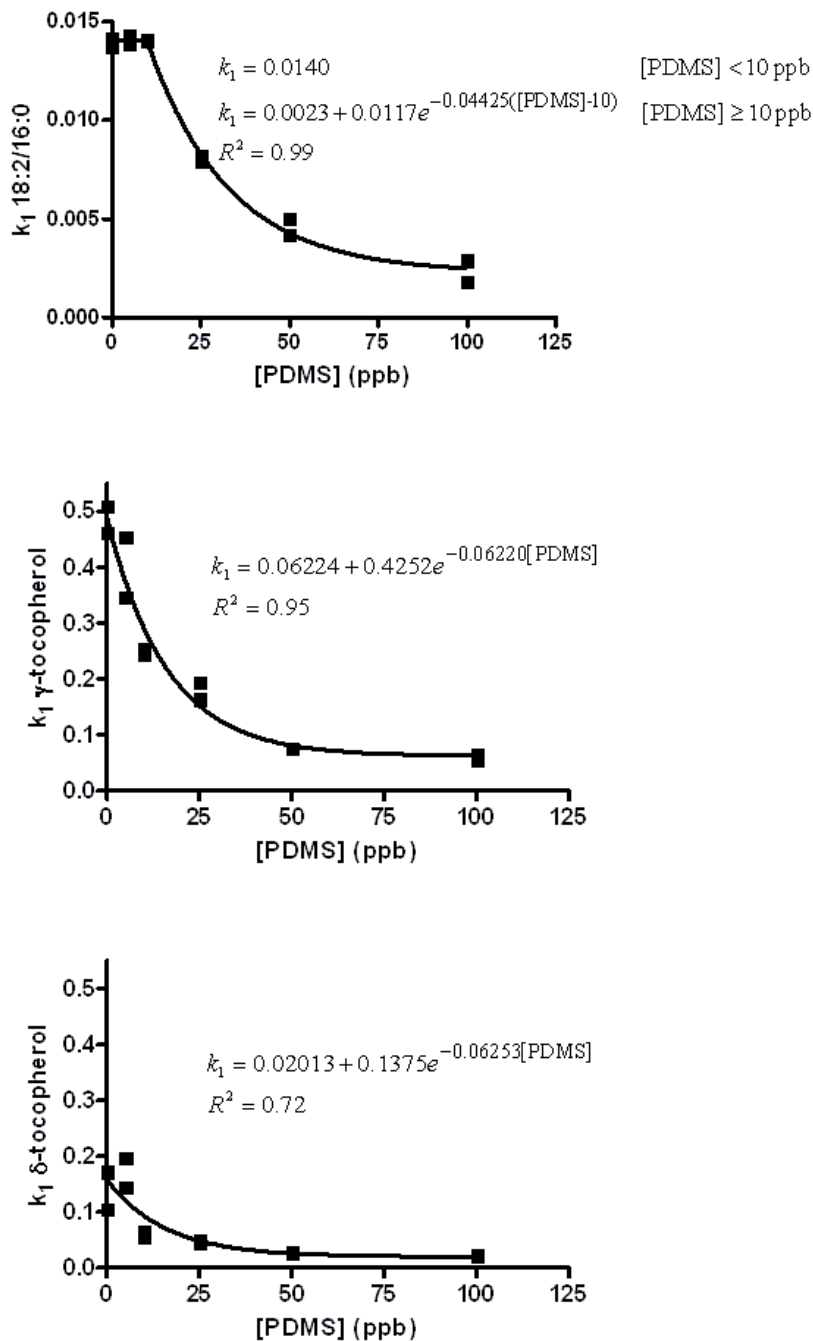


Fig. 4 Relationship between initial degradation rates (k_1) for 18:2 and γ - and δ -tocopherols vs. [PDMS] and their respective coefficients of determination

**INFLUENCE OF POLYDIMETHYLSILOXANE ON THE OXYGEN
CONCENTRATION OF OILS AT VARIOUS TEMPERATURES**

A paper to be submitted to the Journal of the American Oil Chemists' Society

Jose A. Gerde, Earl G. Hammond and Pamela J. White *

Department of Food Science and Human Nutrition, Iowa State University, Ames, Iowa
50011

*To whom correspondence should be addressed at E262 Lagomarcino Hall, Iowa State University, Ames, IA 50011-1060. Phone: 515-294-5380, Fax: 515-294-7802, Email: pjwhite@iastate.edu

Abstract

The effect of temperature on the oil oxygen concentration, tested in both soybean and olive oils with no added polydimethylsiloxane (PDMS), showed that the oxygen concentration increased with temperature to approximately 100°C. Above 100°C, the oxygen concentration abruptly decreased. This change was attributed to the balance between the rates of oxygen uptake and consumption by oil oxidation, which favored oxygen consumption over uptake at temperatures above 100°C. The addition of 100 ppb PDMS to soybean oil, enough to form a continuous layer over the surface of the oil, reduced the oxygen concentration when compared to a soybean oil control containing no added PDMS at temperatures ranging from 93 to 180°C; thus suggesting an oxygen

barrier effect of PDMS. The accumulation of PDMS at the air-oil interface in soybean oil held at 180°C was determined by comparing the oil's internal temperature and the apparent surface temperature. A decrease in the apparent surface temperature while the oil was held at a constant internal temperature was attributed to a change in the emissivity of the surface as a consequence of the accumulation of PDMS in the air-oil interface. The presence of PDMS at the air-oil interface was confirmed for 100 ppm of PDMS, a concentration greater than the concentration necessary to form a monolayer of PDMS on the oil surface.

Keywords: oxygen concentration, polydimethylsiloxane, soybean oil, oil surface temperature

Introduction

During frying, oils degrade as a consequence of oxidative reactions. The high temperature in frying (~180°C) accelerates these reactions, especially in polyunsaturated oils. A very important factor in the degradation of oils is the availability of oxygen, which allows the free radical autoxidation reaction to propagate. Oxygen solubility in oil increases with increasing temperature for temperatures <100°C (1, 2). Information on the solubility of oxygen in vegetable oils is minimal. Values previously reported include 0.055 mg/g for soybean oil at 20°C (3) and 0.035 mg/g for olive oil at 25°C (4).

Polydimethylsiloxane (PDMS), a silicon-based polymer extensively used in industrial

frying as an anti-foaming agent at very low concentrations, has a powerful protective effect on oil oxidation (5). The mechanism of protection, although extensively studied, is not well understood. The viscosity and solubility of the PDMS both affect the extent of oil oxidation. PDMS with a viscosity greater than 20 cs prevented fat oxidation better than low-viscosity PDMS, and PDMS modified with fatty acids to make it more fat-soluble was less effective than unmodified PDMS (6). The protective effect also has been associated with the accumulation of PDMS in the air-oil interface and a PDMS concentration there of 0.05-0.06 $\mu\text{g}/\text{cm}^2$ or more (7). Inhibitions of convection currents (7, 8) and oxygen transfer to the oil have been proposed as mechanisms for the beneficial effect of PDMS on frying oils (7). The influence of PDMS on the oxygen concentration in an oil previously was studied (9), however, the study did not reveal the influence of PDMS on oxygen concentration at high temperatures. These authors measured oxygen by desorbing the gases from the oil with a stream of He at 105°C followed by gas chromatography with thermal conductivity detection. PDMS accumulation on the surface of an oil has been demonstrated (10), but the impact of surface area coverage as a mechanism for its effectiveness has not been determined. The objectives of the current study were to determine the effects of temperature on the oxygen concentration in soybean and olive oils, and of 100 ppb PDMS, the amount needed to form a multilayer on the surface, on the oxygen concentration of soybean oil heated between 93 and 180°C.

Experimental Procedures

Oil heating: Refined, bleached, and deodorized soybean oil with citric acid added

(Golden Chef, Archer Daniels Midland Company, Decatur, IL) and refined commercial olive oil were obtained at a local grocery store. The oils (200 g) were heated in a 100 x 50 mm crystallizing dish (Pyrex, Corning Inc., Corning, NY) at selected temperatures and a surface to volume ratio of 0.36 cm^{-1} . A solution of 100 ppm of PDMS (Dow Corning 200, 350 cs, Dow Corning Co., Midland, MI) was prepared and appropriate amounts were applied to the crystallizing dishes and the solvent evaporated before the addition of the oil.

Oxygen concentration measurement: Figure 1 shows a diagram of the experimental apparatus. The oxygen concentration was measured using an YSI Model 53 Biological Oxygen Monitor (Yellow Springs Instrument Co. Inc., Yellow Springs, OH). The oil in the experiment flowed continuously into the measuring apparatus through a 55-cm long and 2-mm i.d. stainless-steel tube connected to the oil. Before entering the measuring chamber the oil was cooled to 20°C by passage through a thermostat-controlled water bath. The measuring chamber was connected to a peristaltic pump (Masterflex, Cole-Parmer Instrument Co., Chicago, IL) that controlled the oil flow rate at 2 mL/min. After the oil reached a selected temperature, it was equilibrated for 10 min before the oxygen concentration was measured. The oil was collected both from near the surface and the bottom of the oil container. After equilibration, the oil was pumped for 4 min before the oxygen concentration was observed. After measurements at each temperature, the oil removed was returned to the heating vessel.

To study the effect of temperature on the oxygen concentration of oils, the oxygen analyzer was calibrated at 70% of its measuring scale with air-saturated soybean oil at 20°C . Air-saturated soybean oil and olive oil at 20°C were heated to selected

temperatures, and the oxygen concentrations were measured, both on the surface and near the bottom of the vessel.

To study the effect of 100 ppb PDMS, the amount needed to form a multilayer on the oil surface, on the oxygen concentration, treatments containing 100 ppb PDMS and no PDMS were heated at various temperatures. The oxygen analyzer was calibrated at 100% with air-saturated soybean oil at 20°C. The treatments were applied to 20°C saturated soybean oil and the oils heated to the desired temperatures. The oil removed from the heating vessel during testing was returned to the vessel after each measurement to keep the ratio of PDMS/oil constant. Oil aliquots were taken from the surface of the oil and from the bottom of the oil at selected temperatures ranging from 93 to 180°C and the oxygen percentage saturation relative to pure soybean oil at 20°C measured.

Surface temperature determination: A Traceable Infrared Thermometer (Control Company, Friendswood, TX) was used to monitor the apparent surface temperature of the oils. The IR thermometer was installed 16 cm above the oil surface. The temperature inside the bulk oil was measured by using a glass thermometer tested at 100°C in boiling water and at 180°C in soybean oil vs. other glass thermometers to confirm the accuracy of the measured temperature. Soybean oils treated with 5, 10, 25, 50, and 100 ppb of PDMS and a control without PDMS were heated to an internal temperature of 180°C. After reaching 180°C the oil was stirred with the thermometer, and after 1 min, the apparent temperature of the surface of the oil was measured by using the infrared thermometer.

The minimum effective concentration of PDMS was calculated to be 0.05-0.06 $\mu\text{g}/\text{cm}^2$ by

Freeman and collaborators (7). Assuming a monomer cross-section area of 20-25 Å² (11) and assuming all the PDMS to be in the air-oil interface, the PDMS concentration necessary to form a monolayer is

$$PDMS_{concentration} = \frac{Area_{container} \times mw_{monomer}}{Area_{monomer} \times N_A \times mass_{oil}} \quad (Eq.1)$$

In the vessel used, the PDMS concentration necessary to form a monolayer was estimated to be 25 ppb.

Statistical analysis: Treatments (PDMS concentrations and oil types) were run in duplicate. Measurements were made in duplicate and averaged. Means were analyzed by ANOVA using PROC MIXED from SAS Institute Inc. (Cary, NC). Comparisons were performed by contrasts using the Tukey adjustment for multiple comparisons (12). The level of significance was set at $P \leq 0.05$ unless otherwise indicated.

Results and Discussion

Influence of temperature on the oil oxygen concentration

The oxygen concentration increased in soybean oil for temperatures <112°C in agreement with previously reported results (1, 2). Above 112°C, the oil concentration abruptly decreased, probably as a result of an increase in the reaction of oxygen and the unsaturated fatty acids in the oil (Fig. 2). For olive oil, oxygen concentration reached a maximum at 78°C. Above this temperature, the oxygen concentration slowly decreased

with increasing temperatures until the temperature reached 112°C. After this point, the oxygen concentration also fell, showing a behavior similar to that of soybean oil (Fig. 2).

The differences in apparent oxygen solubility between soybean oil and olive oil during the inclined portion of the curve may result from differences in the composition of the two oils. But for both oils, the oxygen solubility increased with increased temperature until a certain point, after which it dropped. At this point, oxygen consumption by the autoxidation reactions was probably beginning, thus decreasing the equilibrium oxygen concentration.

Influence of PDMS on the oil oxygen concentration

In general, the oxygen concentration decreased with increased temperatures in both the surface and bottom aliquots. For temperatures ranging from 93°C to ~130°C, the oxygen concentration for the oil treated with 100 ppb PDMS oil was less than that for the untreated control. The same trend continued at temperatures greater than 130°C, especially for surface aliquots; however, because of the low oxygen concentrations the differences were not significant (Fig. 3). This reduction in oxygen concentration with the addition of PDMS strongly suggests that PDMS acted as a barrier to oxygen. This reduction in the oxygen concentration is likely responsible for the protective effect of PDMS in frying oil. In a previous study, a 4% decrease in atmospheric pressure had a 50% impact in the reduction of oil deterioration, presumably because of the drop in oxygen concentration (13).

At 112°C, the oxygen concentration on the surface in the PDMS-treated oil was greater

than in the bottom of the vessel (Fig.3). For the other treatments, no differences between surface and bottom aliquots were observed.

Oil surface temperature

Table 1 shows the mean values of the core and surface temperatures for the various treatments. The apparent surface temperatures for PDMS treatments greater than the monolayer concentration were significantly lower than the temperature in the core of the oil by $\sim 10^{\circ}\text{C}$. It previously was suggested that such differences between surface and core temperatures result from convective currents being inhibited by the PDMS and resulting in a decrease in surface temperature (14). Intuitively, the presence of a 10°C difference between the surface and the bulk oil would seem very difficult to maintain. However, the output of infrared thermometers is dependent on the distance between the measured object and the thermometer, the temperature of the object, and the emissivity of the object. The emissivity of an object is dependent on the material making up the surface, surface characteristics such as smoothness or roughness, the wavelength being measured, and the actual temperature (15). In this case, the change in apparent surface temperature, as read with the infrared thermometer, may not be caused by a real change in temperature but by a change in emissivity of the surface. For the 50- and 100-ppb PDMS treatments, the amounts of PDMS were enough to form 2 or 4 layers, respectively, of the polymer on the oil, if all the PDMS were on the surface. The accumulation of PDMS on the air-oil interface may have changed the optical characteristics of the interface, which was translated as a seemingly lower surface temperature. Thus, for 100-ppb PDMS the

observed apparent surface temperature was less than for 50 ppb PDMS, possibly meaning that the amount of PDMS on the air-oil interface was greater for the 100 ppb treatment.

Internal and apparent surface temperatures in pure PDMS at 180°C also were tested. In this case, the variability of the surface temperature measurements was very high, and the mean readings tended to be higher than the internal PDMS temperature. The variability of the surface temperature began at ~130 - 150°C (data not shown), which is the temperature at which the PDMS decomposes as noted on the label of the manufacturer. These findings suggest that the change in apparent surface temperature is caused not only by the PDMS on the surface, but also by an interaction with the soybean oil along with PDMS degradation products which may accumulate on the air-oil interface.

Conclusions

For both soybean and olive oils, the oxygen concentration increased with increased temperature until a certain point where it abruptly decreased. At this point, autoxidation reactions rapidly consumed the oxygen, thus decreasing its concentration.

The PDMS accumulated in the air-oil interface as demonstrated by a change in the internal and apparent surface temperatures of the oil, a measurement likely a consequence of a change in emissivity of the oil surface. At temperatures above 93°C, PDMS-treated soybean oil had a lower oxygen concentration than a control soybean oil with no added PDMS. Thus, PDMS accumulation on the surface of the oil decreased the uptake of oxygen from the oil. This decrease in oxygen uptake could account for the protective effect of PDMS in frying oils.

Acknowledgment

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Table 1 Internal and apparent surface temperatures of oil containing selected concentrations of PDMS

PDMS concentration (ppb)	0	5	10	25	50	100
Apparent surface temp. (°C)	183 ^a	183 ^a	181 ^a	181 ^a	174 ^b	170 ^c
Internal temp. (°C)	180 ^a	180 ^a	180 ^a	180 ^a	180 ^a	180 ^a

^{a-c}Different superscripts within the table denote a significant statistical difference

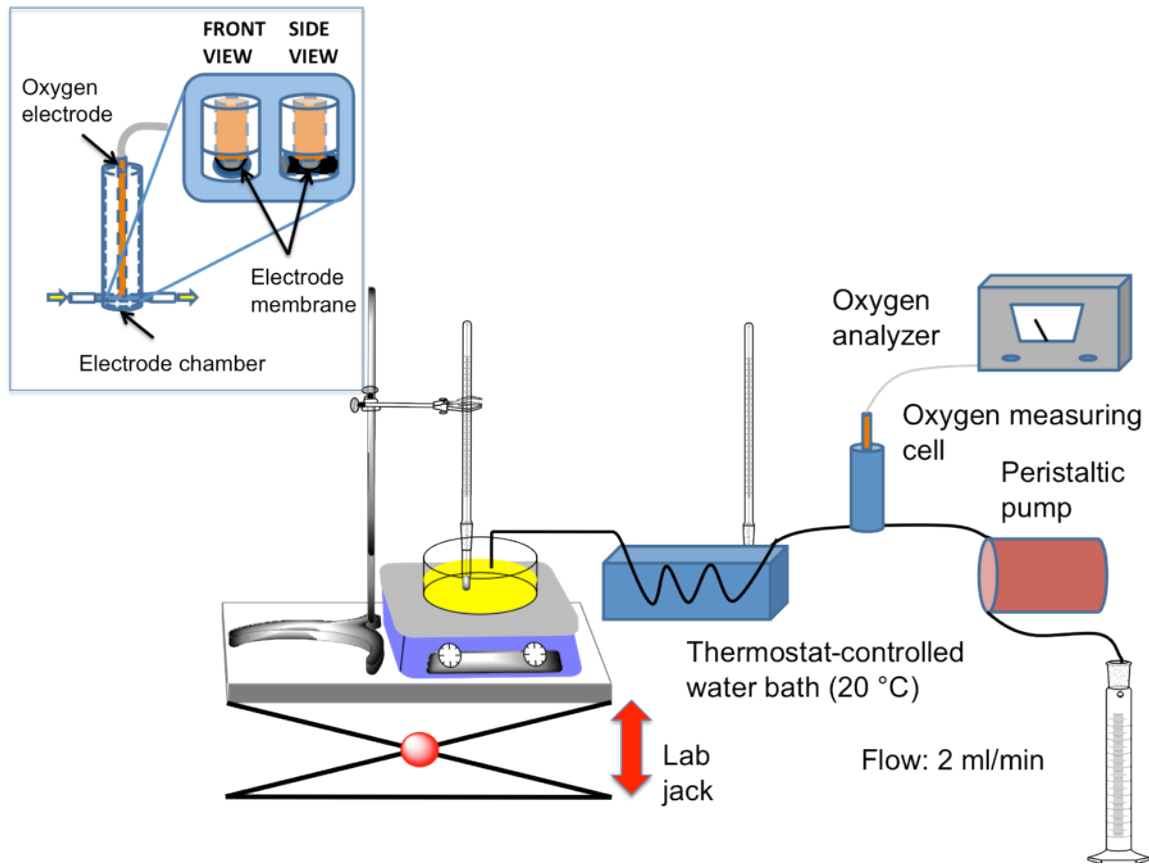


Fig. 1 Scheme of the apparatus used to measure the oxygen concentration in oil at various temperatures. The lab jack was adjusted to take oil aliquots from the surface or the bottom of the oil

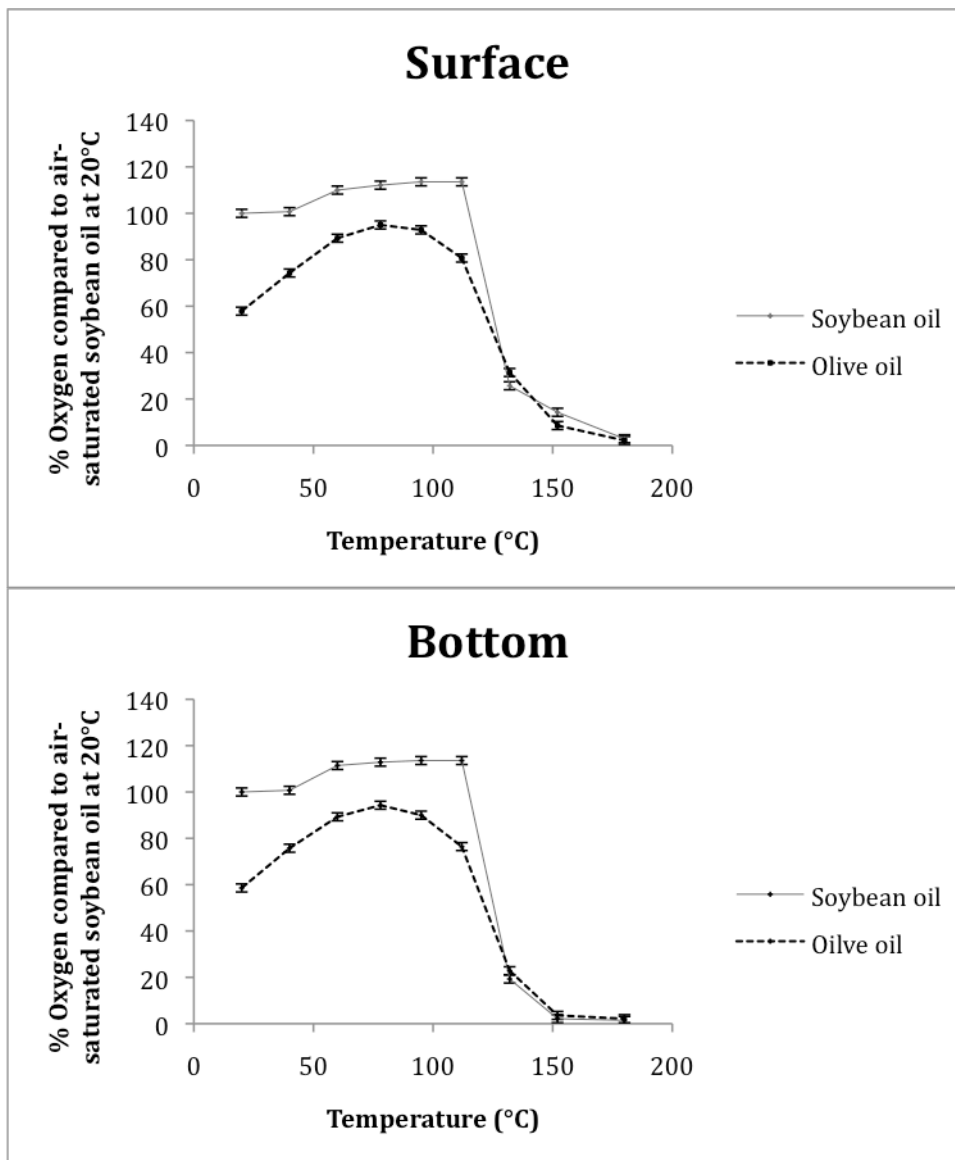


Fig. 2 Percentages of oxygen in soybean and olive oils at selected temperatures for samples collected near the top and bottom of the oil. 100% represents the solubility of the oxygen in the oils at 20°C. Bars around each data point indicate standard error of the mean for all data points

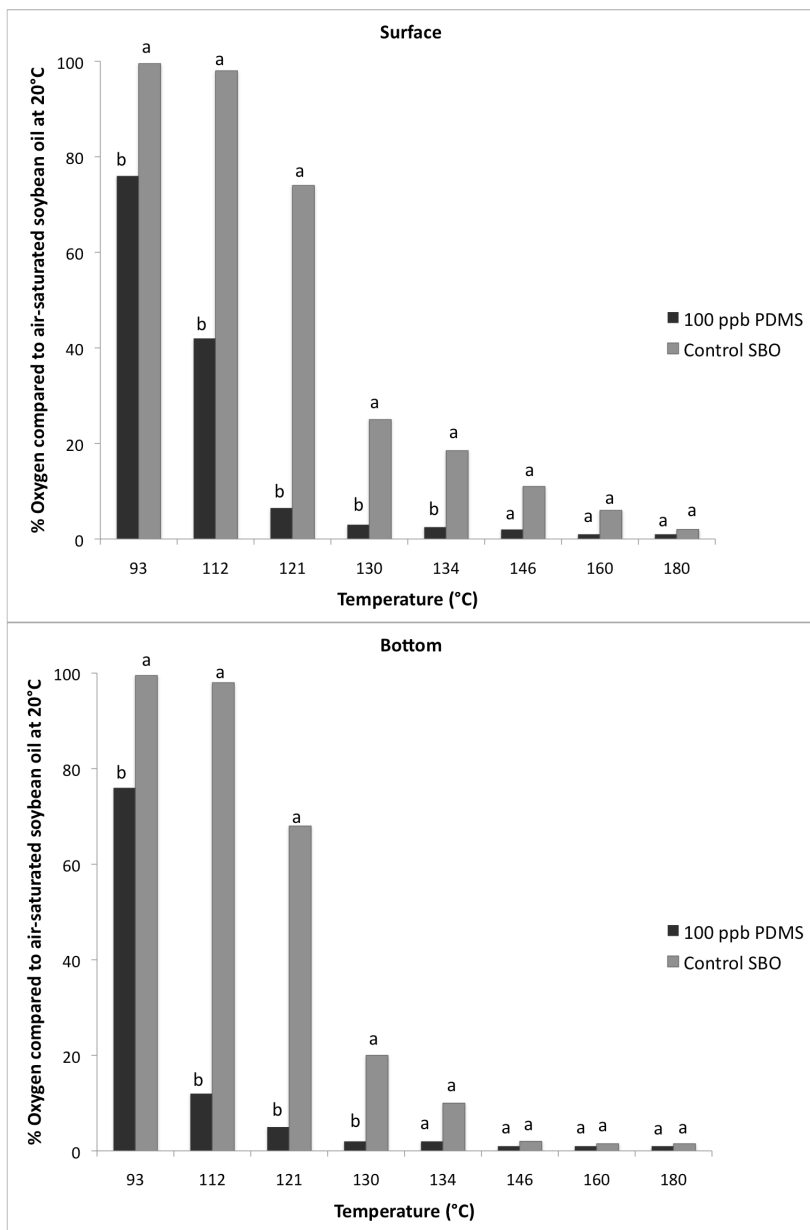


Fig. 3 Percentages oxygen saturation of soybean oil containing 100 ppb PDMS and a control soybean oil containing no added PDMS at selected temperatures collected near the top and bottom of the oil. Different letters within a temperature denote significant differences

**CHAPTER 4. INFLUENCE OF POLYDIMETHYLSILOXANE ON THE
FORMATION OF 4-HYDROXYNONENAL IN SOYBEAN OIL AT FRYING
TEMPERATURE**

A paper to be submitted to the Journal of the American Oil Chemists' Society

Jose A. Gerde, Earl G. Hammond and Pamela J. White*

Department of Food Science and Human Nutrition, Iowa State University, Ames, Iowa

50011

*To whom correspondence should be addressed at E262 Lagomarcino Hall, Iowa State University, Ames, IA 50011-1060. Phone: 515-294-5380, Fax: 515-294-7802, Email:

pjwhite@iastate.edu

Abstract

Soybean oils treated with 25 or 100 ppb polydimethylsiloxane (PDMS) and a control with no PDMS were heated at 180°C for 48 h. The decomposition of linoleate and tocopherols was monitored as well as the changes in concentration of 4-hydroxynonenal (HNE). 4-Hydroxynonenal was rapidly formed at the beginning of the heating period in the control and in the oil containing 25 ppb PDMS. After reaching a maximum (~0.033 $\mu\text{mol/g}$ oil), the HNE concentration slowly decreased because of degradation. The maximum HNE

concentration occurred earlier in the control oil (~18 h, 0.034 $\mu\text{mol/g}$ oil) than in the 25-ppb PDMS oil (28 h, 0.033 $\mu\text{mol/g}$ oil). In the 100-ppb PDMS treatment, the increase in HNE concentration was very slow during the first 32 h. After this point, likely because of both tocopherol disappearance and PDMS degradation, the HNE concentration increased faster, reaching 0.033 $\mu\text{mol/g}$ oil at 46 h. For this treatment, the HNE concentration did not begin declining within 48 h heating. Overall, PDMS had a positive effect in preventing the formation of the toxic HNE. Thus, it should be considered as a beneficial additive in frying oils, especially for discontinuous frying operations where long standby times are required.

Keywords: 4-hydroxynonenal, polydimethylsiloxane, soybean oil, frying, tocopherol

Introduction

During frying, oils are exposed to oxygen and high temperature. These harsh conditions are especially critical for frying oils such as soybean oil, which is rich in polyunsaturated esters. Polyunsaturated fatty acid oxidation products include aldehydes, ketones, alcohols and hydrocarbons. The fatty acid present in the greatest proportion in soybean oil is linoleic acid, which accounts for more than 50% of the fatty acids. One linoleic acid degradation product is 4-hydroxy-2-(E)-nonenal (HNE) (1).

The physiological role of HNE has been studied extensively, as a product of lipid peroxidation and for its effect on oxidative stress (2). 4-Hydroxynonenal can react

spontaneously with glutathione (GSH) (2), which is abundant in the cells of the gastrointestinal tract where it serves as a defense against oxidative stress. Thus, HNE production may contribute to the reduction of GSH and impair defenses against oxidative compounds (3). DNA and protein synthesis have been reported to be affected by HNE at concentrations between 1 and 50 μM (4).

Polydimethylsiloxane (PDMS) is a silicon-based polymer used by the fried-food industry as an antifoaming agent during frying. Previous studies have demonstrated a protective effect of PDMS in frying oils when used at a concentration greater than the concentration necessary to form a monolayer in the air-oil interface (5, 6). The effect of PDMS on the formation of HNE in oils rich in linoleic acid has not been evaluated. The objective of this paper was to study the influence of PDMS on the formation and degradation of HNE from linoleate as well as to understand the degradation of PDMS at frying temperature.

Experimental Procedures

Materials: The oil used was refined, bleached, and deodorized soybean oil with citric acid added (Golden Chef, Archer Daniels Midland Company, Decatur, IL). The PDMS was food-grade Dow Corning 200, 350 centistokes (Dow Corning Co., Midland, MI).

Treatments: A stock solution containing 100 ppm of PDMS in hexane was prepared, and appropriate amounts were added to 100 x 50 mm crystallizing dishes (Pyrex, Corning Inc., Corning, NY) and the solvent was evaporated. Two replicates of all treatments were prepared. Two hundred grams of soybean oil was added to each container giving an initial surface to volume ratio of 0.36 cm^{-1} . The treatments were heated simultaneously to

180°C and held for 48 h. Oil aliquots of 2.5 mL were removed every 2 h for further analysis and immediately frozen by immersion in liquid nitrogen, and stored in glass vials at -80°C. The amount of oil removed was not replenished.

Fatty acid composition: Oil aliquots were converted to fatty acid methyl esters (FAME) according to Hammond (7). The FAME were analyzed by gas chromatography using a Hewlett-Packard 5890 Series II chromatograph with a flame ionization detector and split/splitless injector. The column was 15 m with a 0.25 mm x 0.2 µm film of SP-2330 (Supelco, Bellefonte, PA). The chromatographic conditions were the same as those for Gerde et al (6): injector temperature, 230°C, detector temperature, 230°C, oven temperature program, 150 to 180°C at 5°C/min with no holding time. The carrier gas (He) was set at 5.4 ml/min, the auxiliary gas flow (He) was 19.4 mL/min. Hydrogen flow was 13.9 mL/min, and air flow 426 mL/min. The split ratio was 24:1. The disappearance of methyl linoleate (18:2) was monitored by using the amount of methyl palmitate present in the oil as an internal standard and the linoleate to palmitate ratios (18:2/16:0) were calculated and transformed to µmol 18:2/g FAME. The natural logarithm of the concentrations were computed and plotted vs. time. Linear or bilinear equations, if points of change in slope were present, were fitted to pseudo first-order kinetics for the degradation of 18:2, and the rate constants were calculated before and after the change of slopes (k_1 and k_2) (6).

Tocopherol concentration: Oil aliquots were accurately weighed and diluted with hexane to obtain 0.1 g/mL solutions. The concentrations of the various tocopherols were determined by injecting 20 µL of the solution in a Beckman Coulter System Gold HPLC (Beckman Coulter Inc., Fullerton, CA) equipped with a 25 cm x 4.6 mm 5µ 60Å

LiChrosorb Silica column (ES Industries Chromega Columns, West Berlin, NJ) with a photo diode array detector set at 292 nm. The elution solvent was isopropanol:hexane (5:95 v/v) and the flow rate was 0.7 mL/min. The tocopherol concentrations were expressed as ppm and external standards were used for quantification. Assuming the disappearance of the tocopherols followed first order kinetics, the natural logarithms of the tocopherol concentrations were calculated and plotted versus time. Linear or bilinear equations, if changes in slope were present, were fitted to a model and the rate constants were calculated before and after the changes in slope (k_1 and k_2) (6).

HNE concentration: The HNE concentration in the oil was measured as described by LaFond (8). Briefly, after adding a known amount of 4-hydroxy-9,9,9-d₃-non-2E-enal (HNE-d₃) (Cayman Chemical Co., Ann Arbor, MI), the oil aliquots were extracted twice for 20 min with 10 mL water, and the combined water extracts were treated with 1 mL of 1% O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA, Sigma-Aldrich Corp., Saint Louis, MO) solution in methanol to derivatize the aldehyde group. The PFBHA solution also contained 0.1% tert-butyl hydroxytoluene (BHT) to minimize oxidation. The reaction mixture was sonicated at room temperature for 1 h and extracted twice with 10 mL pentane. After evaporating the pentane under a gentle stream of nitrogen, the extracts were treated with 200 μ L of *N,O*-Bis (trimethylsilyl) trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS, Sigma-Aldrich Corp., Saint Louis, MO) (9:1 v/v) and heated at 90°C in sealed tubes to derivatize the alcohol group.

The reaction mixtures were then diluted to 1 mL with methylene chloride, and the samples were analyzed by gas chromatography electron impact mass spectrometry (GC-

MS). The GC-MS was an Agilent 6890 (Agilent Technologies Inc., Santa Clara, CA) connected to a Micromass GCT Time of Flight (TOF) mass spectrometer (Waters Corp., Milford, MA). The GC separation was done using a 30 m x 0.25 mm x 0.25 μ m film DB-5MS capillary column (Agilent Technologies Inc., Santa Clara, CA) with a 1-m guard column (uncoated, Agilent Technologies Inc., Santa Clara, CA). The chromatographic parameters were: injector temperature, 260°C and oven temperature program, 100°C for 1 min, 100 to 240°C at 8°C/min, and 240 to 300°C at 25°C/min with a final holding time of 3.1 min. The carrier gas (helium) flow was 1.0 ml/min. The mass spectrometer conditions were: 2 scans/sec, ionization mode, positive electron impact, function type, TOF MS, and mass range 45 to 600. The m/z (mass to charge ratio) 352, 226, and 242 fragments were used to identify the HNE peaks and the m/z 352, 229, and 245 were used to identify the HNE-d₃ peaks. Because the m/z 352 fragment is common to HNE and HNE-d₃, only the areas of the integrated peaks corresponding to the m/z 226 and 242 fragments and the m/z 229 and 245 fragments were used for HNE and HNE-d₃ quantification, respectively. The concentration of HNE and HNE-d₃ standard solutions used were monitored spectrophotometrically by evaporating the solvent of an aliquot of the standard solution, re-dissolving it in water, and reading it in the spectrophotometer at $\lambda=223$ nm. The concentration was calculated by using the molar extinction coefficient of HNE in water at $\lambda=223$ nm $\epsilon=13750$ (9, 10).

Kinetics model parameters estimation: The equation parameters were estimated by using GraphPad Prism software version 4.03 for Windows (GraphPad Software, San Diego, CA) and all the regression curves fitted had an $R^2 > 0.9$.

Statistical analysis: The estimated kinetic coefficients were analyzed using analysis of

variance (ANOVA) with the SAS 9.1 software mixed models procedure (SAS Institute Inc., Cary, NC). Comparisons were evaluated by contrasts using Tukey's modification at a level of significance of $\alpha=0.05$ unless otherwise indicated (11).

Results and Discussion

Degradation of 18:2 and tocopherols

For both the 25-ppb and 100-ppb PDMS treatments, there was an increase of slope (rate of degradation) in the plots of $\ln [18:2]$ versus time during the heating of the oil (Fig. 1) in agreement with previously reported data (6). The times of change in the rate of degradation (T) were calculated, and the rates before and after this time were compared (Table 1). The rates after T were different from the rates before T ($p<0.065$). For the control oil, no change in rate was observed. The rate after T for the 25-ppb PDMS treatment was not significantly different from that of the control oil. But for the 100 ppb PDMS treatment, the rate of 18:2 degradation after T was less than that of the control oil. The T occurred later for the 100 ppb PDMS treatment than for the 25 ppb PDMS treatment ($p=0.055$). As previously suggested, this change in slopes of 18:2 degradation may be controlled by the disappearance of tocopherols at PDMS concentrations greater than the monolayer concentration (6).

For γ -tocopherol disappearance, there was a change in rate only in the 100-ppb PDMS treatment (Fig. 2). A change in rate was not detected for the 25-ppb PDMS treatment. The rate after T in the 100-ppb PDMS treatment was not different from the rates of γ -tocopherol in the control or 25-ppb PDMS-treated oils (Table 2).

The degradation of δ -tocopherol showed rate changes for both the 25- and 100-ppb PDMS-treated oils (Table 2) in agreement with previously reported results (6). The T occurred later in the 100-ppb PDMS treatment than in the 25-ppb PDMS treatment. For the 25 ppb PDMS treatment treatments, the rate after T was not different from the rate of the degradation of δ -tocopherol in the control oil (Fig. 2). For the 100 ppb PDMS the rate after T was greater than in both the control and the 25-ppb PDMS-treated oils. Table 2 shows that γ -tocopherol degraded faster than δ -tocopherol, in agreement with previous reports (6, 12). Interfering compounds co-eluted with α -tocopherol, so its rate of disappearance could not be determined.

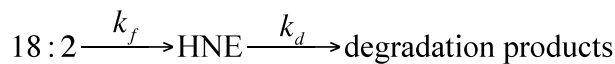
4-Hydroxynonenal formation

The concentration of HNE at selected times was measured. For the control oil, HNE concentration rapidly increased during the first 14 h of heating, then slowed, reaching a maximum concentration at ~18 h heating of 0.034 $\mu\text{mol/g}$ oil (Fig. 3). For the 25-ppb PDMS oil, the increase in HNE concentration was less steep, and the maximum, 0.033 $\mu\text{mol/g}$ oil, occurred at 28 h (Fig. 3). For both treatments, there was a slow decrease in the HNE concentration with time after reaching the maximum. In the 100-ppb PDMS treatment, the increase in HNE concentration was much slower than in the other treatments during the first 32 h heating. After 32 h the HNE concentration increased faster, and after 46 h of heating, reached levels comparable to the maxima found for the other treatments (0.033 $\mu\text{mol/g}$ oil) (Fig. 4). There was no perceptible decline in HNE concentration during the 48 h the oil was heated.

HNE is formed as a product of linoleate degradation, but it may further degrade by additional reactions. Assuming pseudo first-order kinetics for these degradations:



Where $k_{18:2}$ could be k_1 or k_2 , depending on the stage of degradation of 18:2 (6).



$$\frac{d[18:2]}{dt} = -k_{18:2}[18:2] \quad (\text{Eq. 1})$$

$$\frac{d[\text{HNE}]}{dt} = k_f[18:2] - k_d[\text{HNE}] \quad (\text{Eq. 2})$$

$$[18:2] = [18:2]_0 e^{-k_{18:2}t} \quad (\text{Eq. 3})$$

$$[\text{HNE}] = [\text{HNE}]_0 e^{-k_d t} + \frac{k_f[18:2]_0}{k_d - k_{18:2}} (e^{-k_{18:2}t} - e^{-k_d t}) \quad (\text{Eq. 4})$$

For the control oil and the 25 ppb (the monolayer concentration) treatments $[\text{HNE}]_0$ was 0, as measured in the unheated oil, with the model for those treatments described by Eq. 5.

$$[\text{HNE}] = \frac{k_f[18:2]_0}{k_d - k_{18:2}} (e^{-k_{18:2}t} - e^{-k_d t}) \quad (\text{Eq. 5})$$

Although there was a slight change in slope during heating of the 25-ppb PDMS treatment, to simplify the model, degradation of 18:2 was assumed to follow a pseudo

first-order kinetics with a constant slope $k_{18:2} = 0.0134$. Based on this assumption, the kinetic parameters of the degradation of 18:2 and the formation and degradation of HNE in the control oil and the 25 ppb PDMS oil are presented in Table 4 and the data points with the curves generated from the mean of the parameters of the respective fitted curves in Figs. 3 and 4.

In the treatment with 100-ppb PDMS, the model is more complicated so the data was fitted by dividing the plot into several intervals (Fig. 4). At the beginning of the heating period (before 4 h zone I), there was an abrupt increase in the HNE concentration. After this period, there was a linear increase in the concentration of HNE for approximately 32 h (zone II). At this point there was a transition zone (zone III), where the velocity of the reaction increased until the concentration of HNE followed kinetics comparable to that of the control oil (38-48 h, zone IV). In zone I, the rapid increase in HNE concentration probably resulted from the decomposition of peroxides formed during the temperature rise in the oil, coupled with the protective effect at higher temperatures of ample amounts of PDMS that reduced the destruction of HNE to very low levels. The initial period lasted 4 h in this study because that was the first aliquot analyzed after the system reached 180°C.

During the second stage (zone II) the concentration of HNE increased at a very low rate (Fig. 4). Because of the very low concentration of HNE and the comparatively high concentration of 18:2, the probability of oxygen or a free radical attacking HNE instead of 18:2 was very low. Thus, it was assumed that, during this period, the degradation of HNE should be very small compared to the rate of formation of HNE. To compare the rest of the parameters with the models obtained for the control and the 25-ppb PDMS

treated oils, the time (t) and the initial concentration of HNE ($[HNE]_0$) were adjusted to consider 4 h the initial point of zone II. Thus, $t = t - 4$ h and $[HNE]_0$ was the $[HNE]$ measured in the initial point of zone II (4 h after the start of heating). Likewise, the degradation of 18:2 that occurred in zone I was taken into account; therefore, the initial concentration of 18:2 ($[18:2]_0$) was the concentration of 18:2 after heating the oil for 4 h.

Zone III likely was a transition zone between zones II and IV, in which the system adjusted to a lower PDMS level similar to that of the unprotected soybean oil. Also during this period, the points of change in slope of the degradation of tocopherols and 18:2 occurred. For zone IV (Fig. 4) it was again necessary to consider the changes that occurred in the system before the starting time and to adjust the parameters appropriately: $t = t - 38$, $[HNE]_0$ and $[18:2]_0$ were the concentrations of HNE and 18:2 at $t = 38$ h, respectively. Both k_f and k_d in zone II were smaller than in zone IV. In zone II of the 100-ppb PDMS treatment both k_f and k_d were smaller than those in the control oil and the 25-ppb PDMS treatment. In zone IV, k_f for the 100-ppb PDMS treatment was not different from k_f in either the control or the 25-ppb PDMS treatment. At the same stage, the k_d of the 100-ppb PDMS treatment was less than that of the control oil, but similar to that of the 25-ppb PDMS treatment (Table 3).

The k_f , the kinetic constant for the formation reaction of HNE, is a function of $k_{18:2}$. Therefore, the ratio of $k_f/k_{18:2}$ is a measure of the proportion of HNE formed compared to other 18:2 degradation products. This ratio was greater in zone IV and in the control oil than in zone II, probably because of the effect of PDMS on the rate of oxygen uptake by the oil (6). After the PDMS degraded to a level where it could no longer maintain a low oxygen uptake (zone IV), the formation of oxygenated degradation products, such as

HNE, would have been favored, thus explaining the similarity of $k_f/k_{18:2}$ for the control oil and the 100-ppb PDMS treatment during zone IV.

The production of HNE in heat-abused oils has been previously studied (1, 13). In one study, soybean oil was heated at 185°C in a round bottom flask with constant air bubbling. The HNE increased rapidly in the beginning followed by a decrease after reaching a maximum concentration. The maximum HNE concentration (0.27 $\mu\text{mol/g}$ oil) occurred after 6 h heating (13). In another study, pure methyl linoleate was heated at 185°C, the maximum HNE concentration was measured after 3 h heating (0.54 $\mu\text{mol/g}$ FAME) and then it decreased (1). These values are considerably higher than those found in the current study, but show similar trends. Bubbling air through the oil would produce much better oxygenation, leading to higher levels of HNE in the early stages when there would be abundant amounts of linoleate. Another study reported the presence of 0.021 μmol HNE/g oil after heating soybean oil in an open beaker for 8 h with constant air bubbling (14). This value is much closer to the values obtained in the current study.

The change in the kinetic constants of the disappearance of both tocopherols and 18:2 and in the formation and degradation of HNE for the three treatments suggests that the protective effect of PDMS is lost after heating for several hours. PDMS is believed to depolymerize and degrade by a free radical mechanism when heated to high temperatures (290°C in the presence of air) (15).

Conclusions

The protective effect against oxidation by PDMS was confirmed in soybean oil. To be

effective, the concentration of PDMS seemingly must be greater than the calculated monolayer concentration, which, in our study, was about 25 ppb. In soybean oil with 100 ppb PDMS, the slopes of γ - and δ -tocopherol and 18:2 degradation decreased compared to the control, and changes in rates occurred. The PDMS concentration also influenced the formation and degradation of HNE. To facilitate the analysis of the evolution of the concentration of HNE in soybean oil with 100-ppb PDMS, the data was divided into four intervals (zones I, II, III, and IV). The times at which the changes in rates for 18:2 and tocopherol degradation occurred were very close to or within the transition zone III of the HNE curve when 100-ppb PDMS was used. As previously suggested, this change in slopes of 18:2 degradation may be controlled by the disappearance of tocopherols at PDMS concentrations greater than the monolayer concentration. However, the increase in the rate of formation of HNE in zone IV of the 100-ppb PDMS treatment may have occurred because of PDMS degradation. Thus, a consequent increase in the uptake of oxygen may be the reason for the greater $k_f/k_{18:2}$ ratio in zone IV of the 100-ppb PDMS treatment than in both the 25-ppb PDMS treatment and the control oil.

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Table 1 The time of change in rates (T) and rates of ln[linoleate] vs. time in a control soybean oil with no PDMS added and in soybean oil with 25 or 100 ppb PDMS heated at 180°C

Treatment (ppb PDMS)	Mean T (h)	Mean rate ($k_{18:2}$)	
		before change (k_1)	after change (k_2)
0 Control	-	0.0154 ^x	0.0154 ^x
25	17 ^y	0.0108 ^{a, y}	0.0146 ^{b, x}
100	29 ^x	0.0031 ^{a, z}	0.0064 ^{b, y}

^{a-b}Different superscripts in the same row of columns 3 and 4 indicate significant differences at $p \leq 0.065$

^{x-z}Different superscripts in the same column indicate significant differences at $p \leq 0.055$

Table 2 The time of change in rates (T) and rates of $\ln[\gamma\text{-tocopherol}]$ vs. time and $\ln[\delta\text{-tocopherol}]$ vs. time in a control soybean oil with no PDMS added and in soybean oil with 25 or 100 ppb PDMS heated at 180°C

	Treatment (ppb PDMS)	Mean T (h)	Mean rate before change (k_1)	Mean rate after change (k_2)
γ -Tocopherol	0 Control	-	0.3559 ^x	0.3559 ^x
	25	-	0.2279 ^{xy}	0.2279 ^x
	100	32	0.0590 ^{a, y}	0.3724 ^{b, x}
δ -Tocopherol	0 Control	-	0.1424 ^x	0.1424 ^y
	25	13 ^y	0.0835 ^{a, y}	0.1536 ^{b, y}
	100	37 ^x	0.0287 ^{a, z}	0.1963 ^{b, x}

^{a-b}Different superscripts in the same row of columns 3 and 4 indicate significant differences at $p \leq 0.05$

^{x-z}Different superscripts in the same column indicate significant differences at $p \leq 0.05$ within each tocopherol type

Table 3 Mean kinetic parameters of the formation of HNE in soybean oil with no PDMS added and in soybean oil with 25 or 100 ppb PDMS held at 180°C

	100 ppb PDMS		25 ppb PDMS	Control
	Zone II (t=t-4 h)	Zone IV (t=t-38 h)		
[18:2] ₀ (*)	1771 µmol/g	1531 µmol/g	1807 µmol/g	1807 µmol/g
k _{18:2} (*)	0.0031	0.0064	0.0134(**)	0.0154
k _f	1.598E-7 ^c	2.310E-6 ^{ab}	1.720E-6 ^b	3.262E-6 ^a
k _d	0.0082 ^c	0.0529 ^b	0.0656 ^b	0.1295 ^a
k _f /k _{18:2}	5.19E-5 ^c	3.524E-4 ^a	1.230E-4 ^{bc}	2.121E-4 ^{ab}

(*)[18:2]₀ and k_{18:2} were obtained from the curves representing degradation of 18:2 vs. time and fixed during the fitting of the other parameters

(**)18:2 degradation in 25 ppb PDMS was considered to be linear to simplify the calculations

^{a, c}Different superscripts in the same row indicate significant differences at p≤0.05

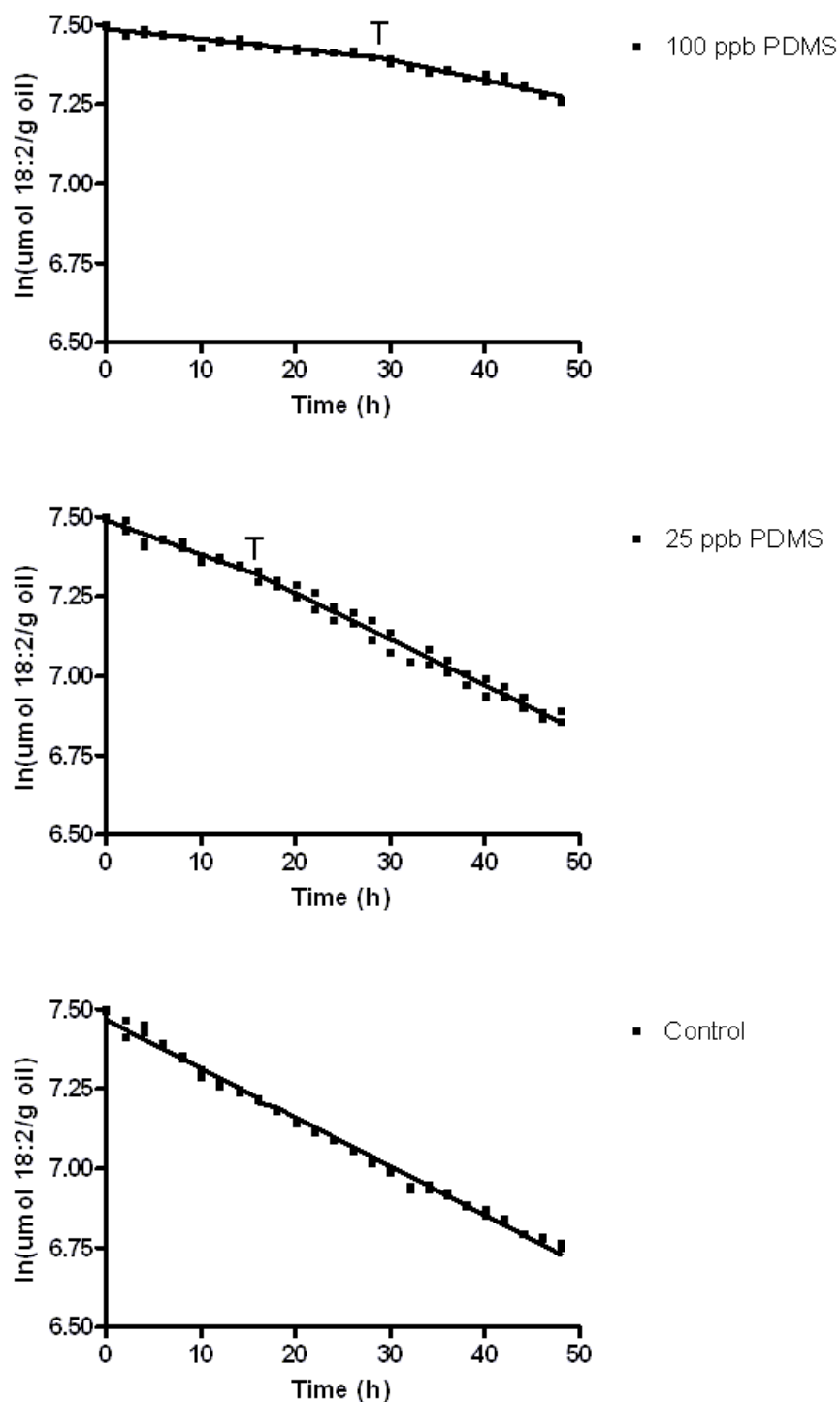


Fig. 1 Decrease of the natural logarithm of the [linoleate] in two replications of control soybean oil containing no polydimethylsiloxane (PDMS) and in soybean oil treated with 25-ppb or 100-ppb PDMS during heating at 180°C and the curves generated from the mean of the parameters of the respective fitted curves

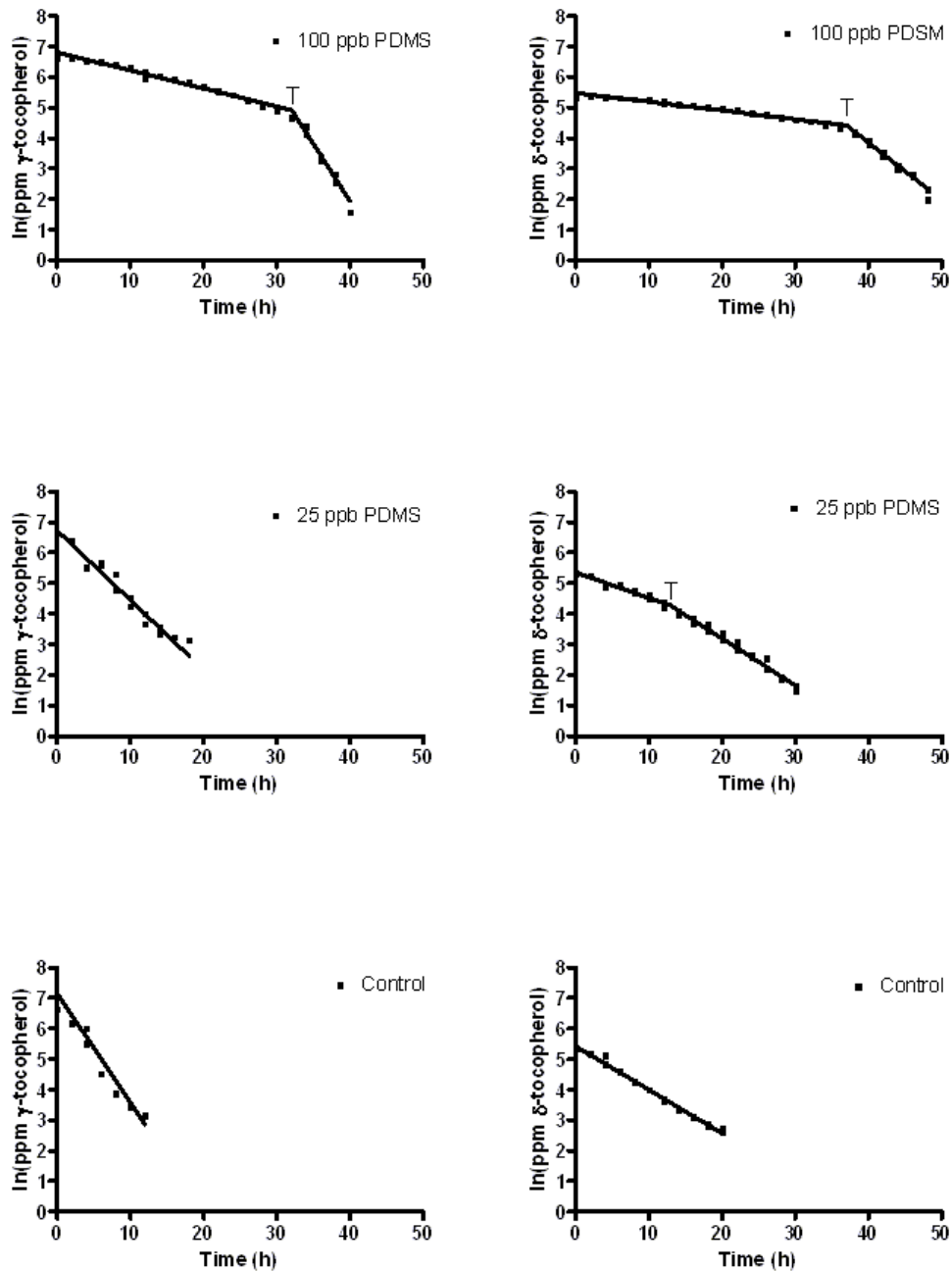


Fig. 2 Decrease of the natural logarithm of the $[\gamma\text{-tocopherol}]$ and $[\delta\text{-tocopherol}]$ in two replications of control soybean oil containing no polydimethylsiloxane (PDMS) and in soybean oil treated with 25-ppb or 100-ppb PDMS during heating at 180°C and the curves generated from the mean of the parameters of the respective fitted curves

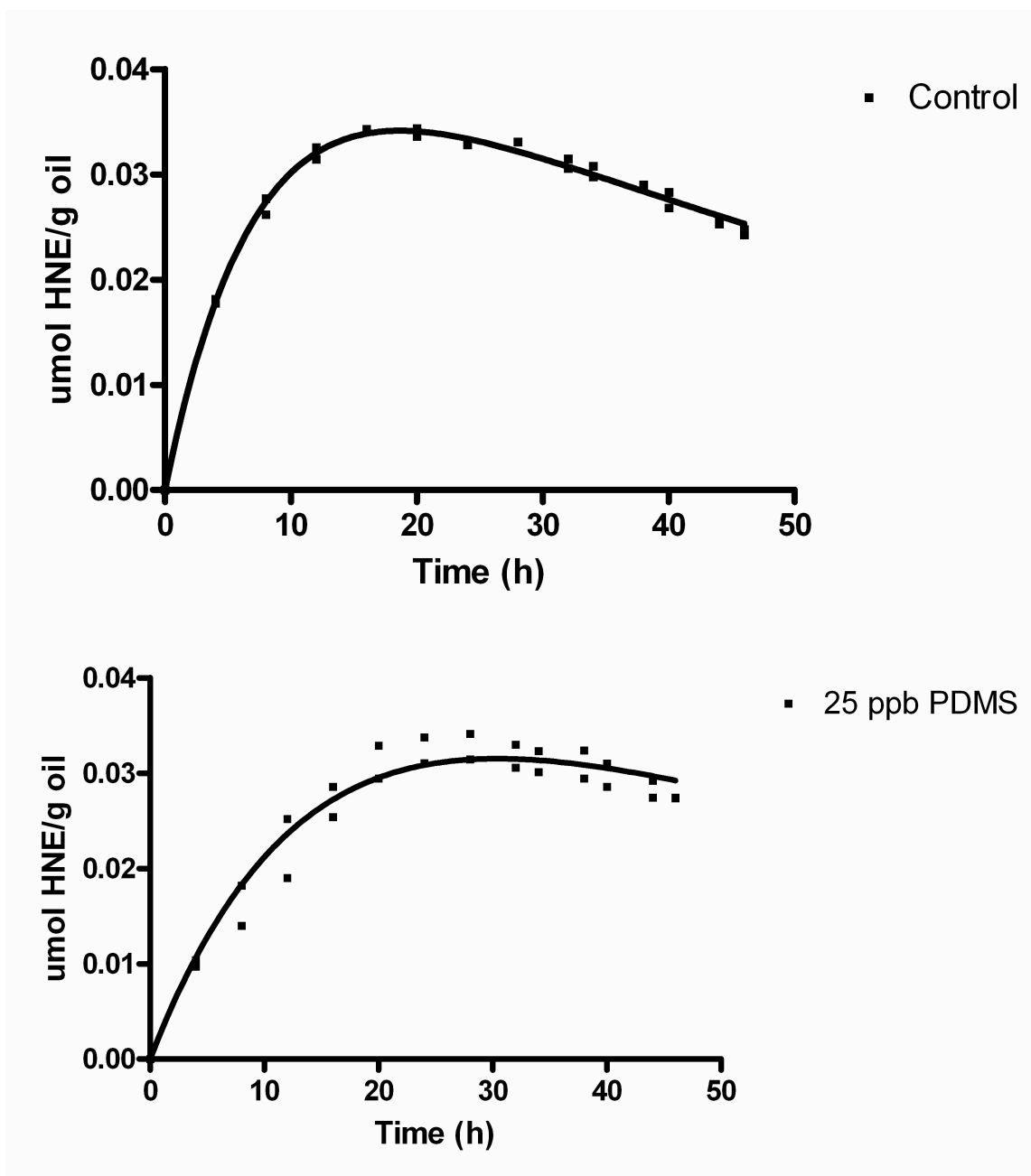


Fig. 3 Change in HNE concentration ($\mu\text{mol/g}$) in two replications of control soybean oil with no PDMS added and soybean oil with 25-ppb PDMS heated at 180°C and the curve generated from the mean of the parameters from the respective fitted curves

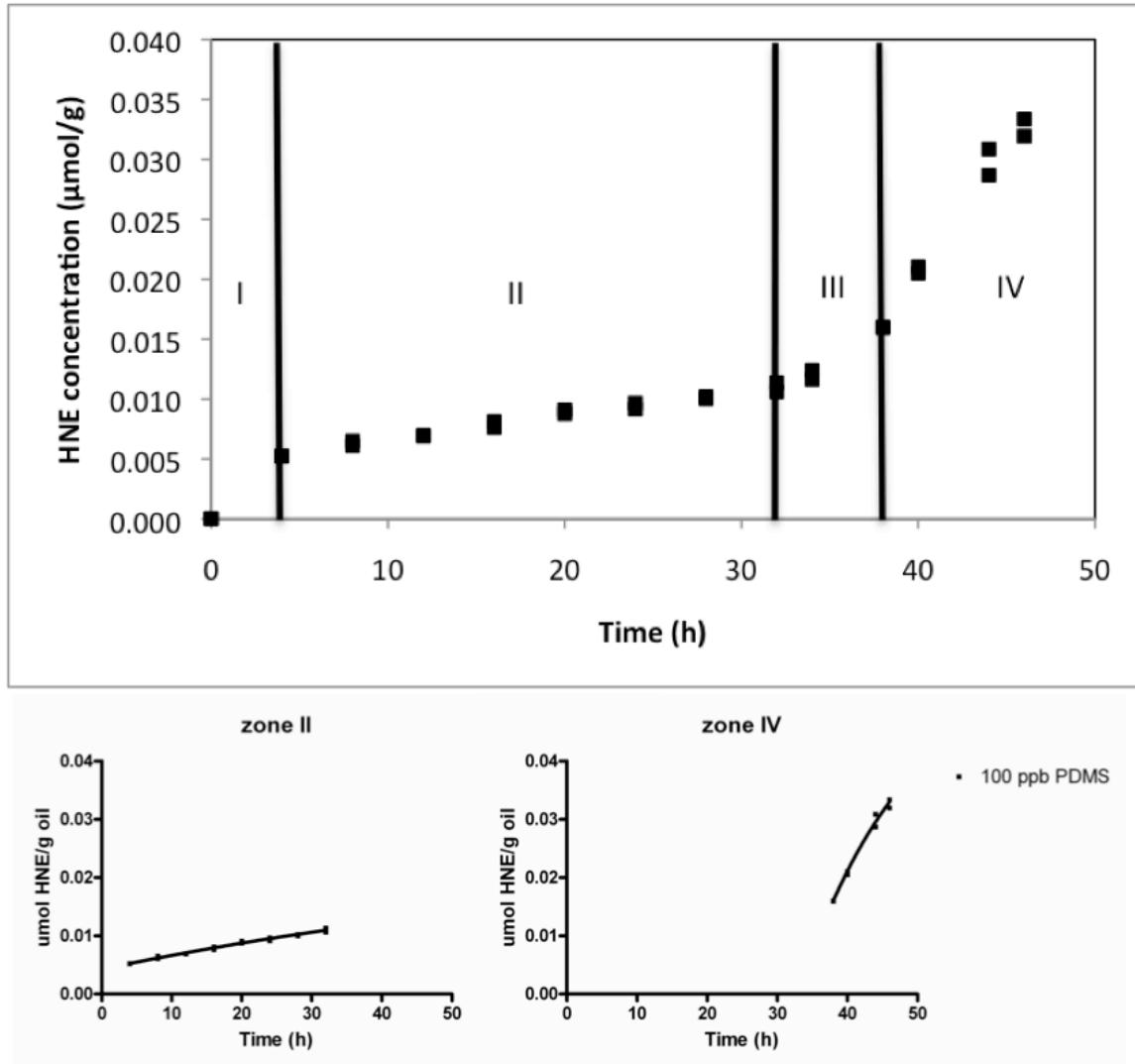


Fig. 4 Change in HNE concentration ($\mu\text{mol/g}$) in two replications of soybean oil treated with 100-ppb PDMS heated at 180°C . The chart was divided into four zones, designating the different stages of HNE concentration evolution to simplify curve fitting. Details of zones II and IV data points with their corresponding fitted curves are presented

CHAPTER 5. GENERAL CONCLUSIONS

The protective effects of PDMS in high-temperature oil systems were demonstrated by the decrease in the rates of disappearance of 18:2, and δ -, and γ -tocopherol. The effects of PDMS were evident at concentrations equal to or greater than the calculated monolayer concentration (25 ppb PDMS), suggesting that PDMS accumulated at the surface of the oil where it could act as a barrier to oxygen transfer into the oil.

At the monolayer concentration of PDMS (25 ppb), 18:2 and γ - and δ - tocopherol degradations all had similar times of change in rate (T), with the rates of oxidation of all three substrates increasing to match the rate of the control soybean oil after this point. These changes in the rates of oxidation suggest that at this time the PDMS had become ineffective, probably because of degradation at high temperatures. At greater PDMS concentrations, such as 50 and 100 ppb, the T for tocopherol disappearances occurred later, and the 18:2 oxidation rate after T was slower than that of the control oil. This difference in rates suggests that the tocopherols control the occurrence of T and the slower rate of 18:2 oxidation is caused by the PDMS still being at an effective concentration.

In general, the loss of γ -tocopherol was faster than that of the δ -tocopherol, probably because the first was sparing the last. This difference in rate of degradation suggests that γ -tocopherol was more susceptible to oxidation than δ -tocopherol, and spared the oxidation of δ - until γ -tocopherol reached a concentration where it no longer controlled the rate.

The PDMS accumulates at the air-oil interface as demonstrated by a difference in the internal and apparent surface temperatures of the oil, likely as a consequence of a change in emissivity of the oil surface. At temperatures above 93°C, PDMS-treated soybean oil had lower oxygen concentrations than untreated soybean oil. Thus, PDMS accumulation on the surface of the oil decreased the uptake of oxygen from the oil. This decrease in oxygen uptake could account for the protective effect of PDMS in frying oils.

The PDMS concentration also influenced the formation and degradation of HNE. At a PDMS concentration greater than that of the monolayer concentration (100-ppb PDMS) the concentration of HNE increased very slowly. After a transition zone, the change in HNE concentration occurred at rates similar to those in the unprotected oil. The times at which the changes in rate for 18:2 and tocopherol degradation occurred were within this transition zone of the HNE curve when 100 ppb PDMS was used. As previously suggested, this change in slope of 18:2 degradation may be controlled by the disappearance of tocopherols at PDMS concentrations greater than the monolayer concentration. However, the increase in the rate of formation of HNE in the final stage of the 100-ppb PDMS treatment may have occurred because of PDMS degradation. Thus, a consequential increase in the uptake of oxygen may be the reason for the greater ratio of formation of HNE in the 100-ppb PDMS treatment than in both the 25-ppb PDMS treatment and the control oil.

The use of PDMS prevented the rapid formation of toxic HNE and decreased the degradation of tocopherols and polyunsaturated fatty acids in a non-agitated

system. Thus, it is advisable to use PDMS in oils for discontinuous frying operations, such as those in fast food restaurants, to maintain the safety and nutritional quality of foods, especially during standby times when no agitation is produced and to prevent the formation of foam in the fryer.