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Assessing the kinetics of antioxidant consumption in unstable biodiesel made from canola and soybean oils

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ABSTRACT

Biodiesel is a renewable fuel processed by the transesterification of the fatty acid groups on the triglycerides found in vegetable oil, used cooking oil, or animal fats. Unlike ethanol-based fuels, which often can take the place of important food supplies, biodiesel precursors can come from waste products. Biodiesel can be used on its own, but is more commonly used as a blend with petroleum-based diesel in order to reduce fossil fuel consumption and greenhouse gas emissions. However, biodiesel is prone to eventual degradation to unsaturated aldehydes, short-chain carboxylic acids and networked polymers. In order to minimize these effects, antioxidants have been added to both prevent oxygen from interacting with the biodiesel and to inhibit the free-radical degradation of the ester tails. Most reports have indicated that the consumption kinetics of various antioxidants in biodiesel follows a first order reaction. We have found that in the case when there is an excess of a strong antioxidant added to a fairly oxidative-unstable biodiesel that zero-order (sometimes referred to as pseudo-zero order) kinetics is observed. We propose that in certain cases, a pseudo-zero order kinetics may be more reflective of actual antioxidant concentrations over time.

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KEYWORDS: biodiesel, methyl esters of free fatty acids, oxidation stability, antioxidants, kinetics

ABBREVIATIONS

IP, Induction period; RIP, Rancimat induction period; BHA, butylated hydroxyanisole; TBHQ, tert-butylhydroquinone; BHT, butylated hydroxytoluene; PY, pyrogallo; PG, propylgallate; MSTFA, N-methyl-N-trimethylsilyltrifluoracetamide.

1. INTRODUCTION

Biodiesel is a fuel composed of fatty acid alkyl esters derived from plant or animal fats. It can be used interchangeably with petrodiesel in any diesel engine and in diesel fired heating systems, or it can be dissolved in mixtures of petrodiesel [1]. In the United States, biodiesel represents a growing share of the national energy strategy, with production hitting approximately 1.7 billion gallons in 2014. Since the biodiesel feedstock can come from used cooking oil or waste product, its production need not divert crops from food production. Biodiesel in its use requires no modification of existing infrastructure, and demand for it is expected to grow as governments mandate higher percentage blends. It has been reported by the U.S. Environmental Protection Agency that the use of biodiesel reduces greenhouse gas emissions by 57 to 86 percent.

Compared to petrodiesel, however, biodiesel is relatively unstable, and over a period of a few months most degrade to the point of being unusable [1]. Generally there are various final degradation

by-products such as aldehydes, carboxylic acids such as formic, acetic, and propionic acid and long, polymerized chains [1, 2, 3, 4]. The acid by-products may corrode engine components over time, and the long chain polymers increase the viscosity of the fuel, clogging fuel lines and injectors in addition to impeding combustion. In order to combat this effect, scientists have investigated the factors affecting biodiesel stability, in addition to finding ways to improve its processing and storage conditions [2, 3, 5, 6, 7]. Processing includes choice of feedstock, the processing method used, and the amount and type of antioxidant added. Storage conditions involve temperature, the presence of oxygen, water, exposure to metals, and the possibility of microbial contamination.

However, the composition of the feedstock and oxygen exposure cannot always be controlled environmentally, so chemical methods of preservation have been explored. These chemical methods are typically the addition of antioxidants, and many of the antioxidants used to stabilize biodiesel are the same antioxidants used to stabilize perishable consumer goods [8]. Each antioxidant, while performing what is essentially the same function, utilizes a slightly different mechanism, and so is more or less effective in stabilizing biodiesel depending on the composition of the biodiesel and the storage conditions. This manuscript reports further studies that investigates the kinetics (consumption rates) of some of the most common antioxidants and a few, commercially-available antioxidants when added to oxidatively-unstable biodiesel.

1.1. Biodiesel composition and its effects on stability

Biodiesel is composed of fatty acid methyl (and sometimes ethyl) esters obtained from the transesterification of triglycerides derived from animal or plant sources [1]. Given the variety of the sources, these fatty esters display a great deal of variation in their composition, especially in terms of saturation. Common feed stocks, such as camelina, canola, coconut, jatropha, palm, soybean and sunflower exhibit variation in the degree to which their constituent fatty acids are saturated. The variation in unsaturation is one of the first factors which can influence the stability of the resulting biodiesel (Refer to Table A-2, page 462 of [1]). Typically, feed stocks high in poly-unsaturated fatty acids produce the least stable biodiesel [2, 3]. Feed stocks especially rich in functionalities similar to the *cis*, *cis*-9,12 double bonds found in linoleic acid are especially susceptible to oxidative degradation due to the enhanced stability of their radical intermediates. The fatty acid chains found in used cooking oils, which have already been continuously heated and re-heated in open air, may have begun to degrade [1, 2, 3, 9].

The processing of biodiesel proceeds by converting the fatty acid groups of a triglyceride to fatty acid methyl esters by transesterification with methanol. This typically proceeds with the use of alkaline catalyst, such as sodium or potassium hydroxide (or their methylates). Some use strong acids for an acid-catalyzed esterification reaction, but this often requires specialized reaction vessels which need to withstand the process. Investigations have been conducted on the use of metal hydroxides, metal-supported acid and alkaline catalysts, and organometallics, but metal leeching often occurs, which can inhibit the stability of the biodiesel product [2].

1.2. Measuring oxidative stability

Various methods have been used to determine the stability of biodiesel. Generally, the Rancimat test is the most widely accepted of the accelerated oxidation processes to characterize the oxidative stability of biodiesel. This Rancimat test has been formulated as test method EN 14112 and accepted by the European Committee for Standardization (CEN) and then by the American Society for Testing Materials (ASTM) [1, 2, 6, 10]. The Rancimat test involves heating 3.00 g samples of biodiesel to 110 °C, and sparging each sample with dry air at approximately 10 liters per hour. The sparged air is bubbled through a sample of deionized water (DI) water, where the volatile organic acids produced by the degradation of the fatty acid methyl esters become dissolved. The conductivity of the DI water is measured continually via a dual conductivity system, and once an inflection point is reached, the Rancimat instrument stops and reports the automated answer. The time taken to reach the induction point is known as the Induction Period (IP) or Rancimat Induction Period (RIP) [2, 3, 6]. The Rancimat instrument can run eight samples simultaneously, with an average relative deviation of 1-2%. In the United States, the samples must have a minimum IP of three hours, while in Europe the minimum IP required is six hours.

1.3. Oxidative degradation of biodiesel

As biodiesel sits at ambient storage conditions, it can undergo a variety of degradation processes. In the presence of oxygen, which acts as a radical initiator, the fatty alkyl chains are subject to oxidation via lipid peroxyl radical intermediates. The process begins with a radical initiator removing a proton from the alkyl chain of the fatty acid methyl ester. Propagation consists of the newly generated radical attacking oxygen, generating a peroxyl radical. Abstraction of a proton from another fatty acid methyl ester tail produces an alkyl hydroperoxide and regenerates the alkyl radical. The generated hydroperoxide can undergo homolytic bond cleavage, ultimately resulting in aldehydes. Both the aldehydes and the alkyl radical fragments can be further oxidized to form carboxylic acids, including formic, acetic, and propionic acid. In fact, it is these smaller, more volatile compounds that are carried by the sparging air into the DI water, which increase the conductivity during the Rancimat EN 14112 oxidative stability test.

As was mentioned earlier, unsaturated fatty acid methyl esters are more unstable than saturated fatty acid methyl esters. This is due to their ability to stabilize radicals, and is especially true of polyunsaturated fatty acid methyl esters with bis-allylic positions [2, 3]. As such, feed stocks high in ω-3 or ω-6 fatty acids, such as linoleic acid, will show higher instability than saturated feed stocks. Pantoja *et al*. illustrated this in a study comparing the degree of saturation of biodiesel feed stocks to oxidation stability [5]. Interestingly, feed stocks rich in poly- and mono-unsaturated fats have been shown to form dimers if processed at high temperatures of 300 °C via a Diels-Alder reaction. Dimers increase the viscosity of the biodiesel, and are one of the few known cases of thermal biodiesel degradation, which is relatively unexplored [2, 3]. Storage conditions play a large role in biodiesel stability. Exposure to heat and water, both of which decrease the stability of biodiesel, can be avoided by storage in a cool, dry place. Water can readily hydrolyze the fatty acid methyl esters back to fatty acids and methanol. Metal storage containers are not ideal, as metal contamination is known to decrease biodiesel stability. Among other things, metals serve as radical initiators and as catalysts, continuously generating the hydroperoxide radicals that lead directly to the degradation of the fatty acid methyl esters [7].

1.4. Antioxidant-enhanced oxidative stability

Precautions with regards to biodiesel manufacturing and storage conditions can be taken to enhance biodiesel stability. Very often, however, processing and storage modifications are not enough to guarantee a biodiesel with sufficient stability. Researchers have added antioxidants to samples of biodiesel in order to enhance oxidative stability [1, 2, 3]. Antioxidants work primarily by inhibiting the further propagation of the radical species that promote the degradation of the biodiesel. Although some act to decompose hydroperoxides, the most commonly used antioxidants are phenols and amines that interrupt the propagation stage of the fatty acid methyl ester oxidative degradation mechanism [2, 3, 7, 8]. They are known as ‘chain-breakers’. Common antioxidants are shown below in Fig. 1.

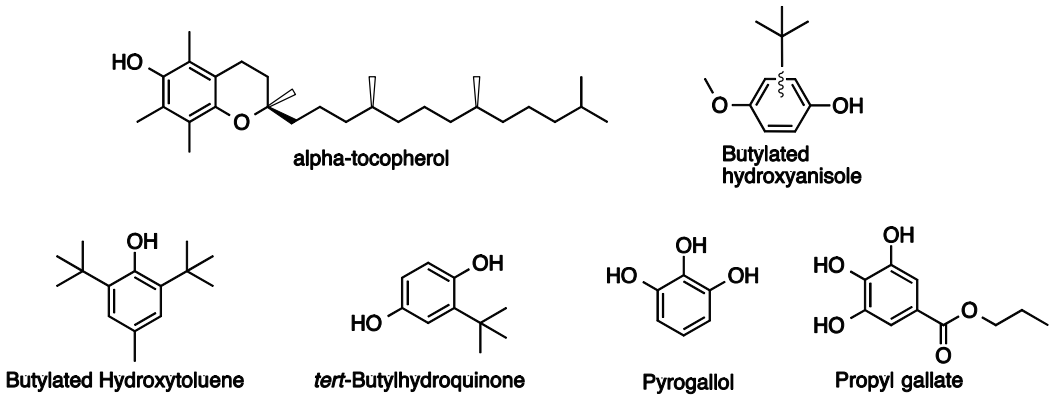

Fig. 1. Structures and common names of common antioxidants.

α-Tocopherol is a naturally occurring antioxidant found in plants that is also present in trace amounts in biodiesel because biodiesel feed stocks can be derived from natural sources. Tocopherols often perform relatively poorly in comparison to other antioxidants, with most rarely exceeding RIPs = 2, and very often closer to 1 [2, 3]. The remaining antioxidants are considered synthetic antioxidants, and their behavior varies depending on their concentration, the parent feedstock, and the biodiesel's composition. Butylated hydroxyanisole (BHA, 2-*tert*-butyl-4-hydroxyanisole and 3-*tert*-butyl-4-hydroxyanisole) is used as a mixture of the isomers of singly-substituted t-butylated anisole. BHA has been found to be most effective in biodiesels derived from castor oil [7]. Butylated hydroxytoluene (BHT, 2,5-di-*tert*-butyl-4-methylphenol) is a preservative very commonly found in foods as well as in biodiesels. It has been found effective in jatropha and palm derived biodiesels, but in both cases TBHQ is more effective at stabilizing the biodiesel than BHT is [2, 3, 7, 11]. *Tert*-butylhydroquinone (TBHQ, 2-*tert*-butyl-1,4-dihydroxybenzene) is an antioxidant that finds use in a variety of areas, including cosmetics, food, and even dietary supplements, and has been found most effective in soybean, jatropha, palm oil, and sunflower oil derived biodiesels [2, 3]. Pyrogallol (PY, 1,2,3-trihydroxybenzene) is used as a preservative in cosmetics and as an antioxidant in biodiesel. It has been found most effective in canola (rapeseed) oil, used frying oil and tallow derived biodiesels [12]. Propylgallate (PG, Propyl-3,4,5-trihydroxybenzene) has been used as a preservative in foods and has been found most effective as an antioxidant in biodiesels derived from used palm oil [2, 3, 13]. The reviews by Pullen and Saeed [2] and Jain and Sharma [3] have concluded that of the more common synthetic antioxidants, efficacy follows the order TBHQ > PY > PG.

The concentrations at which antioxidants are used play a large role in their efficacy. As would be expected, increasing antioxidant concentration increases the stability of the biodiesel. Interestingly, certain antioxidants are more effective at lower concentrations relative to other antioxidants, and some are more effective at higher concentrations. It has been found that BHT is relatively effective at lower concentrations, whereas TBHQ is effective at higher concentrations [2, 3, 11]. Typically, antioxidants are added at 500-2000, or even up to 5000 ppm by weight, depending on how long the biodiesel must be stored [1]. Generally speaking antioxidants are effective because of their ability to act as radical scavengers, interrupting the propagation of the hydroperoxide generating mechanism. Phenolic antioxidants in particular stabilize radicals by resonance, and the presence of electron donating substituents at the ortho and para positions enhances the stability of the radical product [2, 3].

1.5. Kinetics of antioxidants in biodiesel

Kinetic parameters for the use of antioxidants to stabilize biodiesels are typically determined by using a first-order rate model first reported by Xin *et al.* [14] and later used by Chen and Luo [15]; in each case these researchers used the Rancimat instrument to assay the biodiesel's oxidative stability. Assuming first-order kinetics, the change in antioxidant concentration over time can be modeled by equation 1.

$$\frac{d[C]}{dt} = -k[C] \tag{1}$$

Rearranging (1) and preparing to integrate requires selecting the proper bounds of integration. The bounds of concentration will proceed from C_o, the initial concentration, until C_{cr}, the critical antioxidant concentration at which the antioxidant no longer has any effect. The time it takes to proceed from C_o to C_{cr} can therefore be represented as $t = IP - IP_{orig}$, where IP is the induction period of a sample with antioxidant, and IP_{orig} is the induction period of a sample without antioxidant. This assumption has been used in nearly all publications that utilize this method to obtain the kinetic parameters of antioxidants in biodiesel [3, 14, 15]. This yields the following.

$$-\int_{C_o}^{C_{cr}} \frac{1}{[C]}\, d[C] = \int_0^{IP-IP_{orig}} k\, dt$$

Integrating and rearranging yields equation 2.

$$\ln C_o = k(IP - IP_{orig}) + \ln C_{cr} \tag{2}$$

Thus, by plotting $\ln C_o$ vs. $IP - IP_{orig}$, the rate constant, k, and the critical concentration, $C_{cr,}$ can be obtained. This should result in a linear equation whose correlation coefficient (R^2) values represent how well or how poorly the antioxidant tested fit the proposed first-order rate model.

2. MATERIAL AND METHODS

2.1. Material, reagents and methods

Locally bought, pure vegetable cooking oils- canola (rapeseed) and soybean oil (both sold commercially by Wesson Brand, ConAgra Foods, Inc. of Omaha, Nebraska, USA.) were used as feed stocks. The methanol was from Fischer, Inc., certified ACS Reagent grade, Assay > 99.8%, and the potassium hydroxide pellets, A.C.S. reagent grade, was purchased from J.T. Baker, Inc. The following commercial antioxidants were compared. Both 2,6-di-*tert*-butyl-4-methylphenol (BHT), CAS 128-37-0, 99% and Pyrogallol, 1,2,3-trihydroxybenzene (PY), reagent grade, CAS 87-66-1, > 98%, were from Sigma/ Aldrich. *tert*-butylhydroquinone, (TBHQ), CAS 1948-33-0, 97% was from Jansen-Chimica. The following commercial antioxidant were donated: Naugalube® 403, Lot RC-997 is N,N'-di-*sec*-butyl-p-phenylenediamine, CAS 101-96-2, from Chemtura Corp. of Middlebury, Connecticut, USA. and Ethanox® 4760 R, Lot #12, which is reported to be a mixture of various phenols and N,N'-di-*sec*-butyl-p-phenylenediamine, whose composition was described by Chen and Luo [15], was from Albemarle Corp. of Baton Rouge, Louisiana, USA. All of the above anti-oxidants were used as received.

The transesterification of the cooking oils to their corresponding unstable biodiesels was accomplished as follows: In a round bottom, 2.0 L flask, 1.0 L of the neat commercial vegetable oil was heated to 70 °C, and a drop-wise addition with mixing of about two-thirds of the methanol/potassium hydroxide was slowly added over a period of 4 hours. The methanol concentration was in a 6 molar excess to the starting, neat vegetable oil, while the potassium hydroxide was in a 1.0 weight percent amount. Thereupon the resulting mixture was allowed to cool overnight with the bottom glyceride layer settling out. The next day, the glycerin layer was removed by decanting off the bottom, and the remaining third of the methanol/KOH mixture added to the top oily layer with mixing and again with heating to 70 °C. It had been found that by removing the initial by-product, glycerine layer, and adding more of the reactant for a second transesterification step, caused the overall transesterification equilibrium to shift substantially towards the products, with conversion rates consistently greater that 99.7%. The remaining glycerin layer was decanted as before, and the top oily layer was washed several times with equal volumes of distilled water in a separatory funnel, until the water layer tested to a pH of 7 with pH paper. This repetitive washing was found to be effective at removing the excess methanol and KOH from the biodiesel produced. In order to remove the water remaining from the biodiesel and to cause its oxidation stability to be reduced, compressed air was bubbled overnight through the biodiesel in a process called 'stripping' using an effective sparging system. Oxidation stability values obtained by the Rancimat instrument showed that the biodiesel made from the soybean oil had an initial induction period, IP_{orig} of 0.8 hours, while the biodiesel made from the canola oil had an initial induction period of 2.3 hours. Table 1 reports many of the key properties of these two biodiesel studied.

Solutions of approximately 2000 ppm (µg/mL) by weight of each antioxidant were added to the soybean-based biodiesel. Then additional dilutions, as outlined on Table 2 were made from the 2000 ppm antioxidant solution by adding appropriate amounts of the unstable biodiesel. Then 3.00 ± .01 g samples at each of the various antioxidant concentrations were placed in each of the separate Rancimat tubes.

2.2. Accelerated oxidation test method

The accelerated oxidation method employed followed the established European Committee of Standardization, EN 14214 method, employing a Rancimat piece of equipment, Model 743 (Metrohm, Hesisau, Switzerland) [10]. A complete description of the Rancimat instrument has been described in [1, 2, 3, 10] and used in previous reports studying the kinetic behavior of various antioxidants added to biodiesel [14, 15]. For all of our studies the automated Rancimat Induction Period (commonly referred to as RIP) was used.

2.3. Additional instrumentation

In order to more fully assess the accuracy of the kinetic models considered, a direct measurement of BHT and PY antioxidant concentrations over time in only the more oxidatively-unstable, soybean-derived biodiesel was done using quantification via gas chromatography equipped with a flame ionization detector (GC/FID), with certain of the peak identifications verified by gas chromatography/ mass spectrometry (GC/MS). Quantitation was

Table 1. Key properties of the canola- and soybean-based biodiesels used.

Properties	Test method	Unit	Required test results	Value biodiesel (Canola-based)	Value biodiesel (Soybean-based)
Oxidation stability	EN14112	hours	> 6 Eu, > 3 U.S	2.3	0.8
Density at 15 °C	D4052	g/cm^3	0.86-0.90	0.881	0.883
Viscosity at 40 °C	D445	mm^2/s	3.5-5.0	4.443	4.139
Cloud point	D2500	°C	report	-2.7	0.8
Free glycerine	D6584	wt%	< 0.02	0.002	0.010
Total glycerine	D6584	wt%	< 0.24	0.158	0.151
Monoglyceride	D6584	wt%	report	0.147	0.133
Diglyceride	D6584	wt%	report	0.009	0.008
Triglyceride	D6584	wt%	report	0.000	0.000
Ester content (total)	EN14103	wt%	report	100 +/- 1	100 +/- 1
Ester (linolenate)	EN14103	wt%	report	20.9	55.4
Acid number	D664	mg (KOH)/g	< 0.5	0.052	0.13
Water/Sediment	D2709	cm	< 0.05	0.00	0.00

Table 2. Antioxidant concentrations used in kinetic parameter determination.

Concentration (PPM)	g 2000 PPM stock	g biodiesel
0	0.00	3.00
50	0.075	2.925
100	0.150	2.85
200	0.300	2.70
500	0.750	2.25
1000	1.50	1.50
1500	2.25	0.75
2000	3.00	0.00

achieved following ASTM D6584-12a [16]; the test method utilized by The University of Connecticut's Biofuel Testing Laboratory. This method involved using a Hewlet-Packard (Agilent) HP 6890 Series GC System equipped with a Restek MXT®-Biodiesel TG w/Integra-Gap®,14 m x 0.53 mm ID x 0.16 µm df column, with a HP 6890 Series on-column, automated injector, and an Agilent flame ionization detector (FID) with a hydrogen/air flame. Eight 3.00 ± 0.01 g samples, made by adding the correct amount of the BHT or PY antioxidants to the oxidative unstable soybean to give actual concentrations of 2000 ppm, were placed on the Metrohm 743 Rancimat, where they were heated to 110 °C and sparged at a rate of 10.5 L/h. At 0.5 h time intervals, samples were removed from the instrument, the time recorded, and the sample concentration determined by the fore-mentioned GC/FID method. A sample not subjected to Rancimat degradation was used as a t = 0 sample. n-Butanetriol was used as the internal standard. The correct identification of the GC peaks for the internal standard and antioxidant peaks were identified by subsequent gas chromatography/ mass spectrometry. The peak eluting at 6.91 minutes was determined to be the internal standard, the peak at 7.91 minutes was determined to be the BHT peak, and the peak at 9.18 minutes was determined to be the N-methyl-N-trimethylsilyltrifluoracetamide, MSTFA-derivatized BHT peak. The areas of both BHT and derivatized BHT peaks were added together and used to represent the total BHT injected. An identical method to assess the concentration of PY was done, which is not detailed here.

Sample preparation for GC injections was as follows. Known weights in the range of 100 mg for each biodiesel sample was added to a 10 mL volumetric flask. 100 µL of neat MSTFA was then added to the

volumetric flask along with 100 µL of 117.04 µg/ 100 µL of n-butanetriol (the first internal standard) in pyridine, and 904 µg/100 µL of tricaprin in pyridine, used as the later eluting internal standard. The resulting mixture was allowed to sit for approximately 20 minutes to undergo derivatization of the existing hydroxyl groups to their tri-methylsilyl derivatives, after which it was diluted with n-heptane to volume (10.00 mL). One microliter of this mixture was then injected into the GC/FID. The resulting peak areas were manually integrated using the ChemStation software and converted to their appropriate weights using the previous calibrations following equations given in Standard ASTM D6584 test method [16].

3. RESULTS

3.1. Determination of the kinetic parameters of common antioxidants in biodiesel

Appropriate concentrations of the various antioxidants dissolved in both the canola- and the soybean-based biodiesels were tested on the Metrohm Rancimat instrument following the parameters specified in EN 14112. Employing equation (2) in section 1.5, the natural logarithm of the initial concentration vs. IP – IP_{orig} was plotted, and the rate constant and critical concentration were obtained. The stability factor (F) at the 1000 ppm antioxidant level was calculated using the equation (IP – IP_{orig})/IP_{orig}. Tables 3 and 4 summarize these important parameters.

The above tables show that PY and TBHQ had the highest Stability Factors (F) at the 1000 ppm concentration level in the soybean- and canola-based biodiesels for the synthetic antioxidants tested. This is in agreement with virtually all of the reports [2, 3, 5, 6, 7, 11, 12] except for [15]. However, despite having the highest stability factor in soybean-based biodiesel, PY did not have the lowest rate constant, k. TBHQ had the lowest rate constant, and thus the longest induction period in both the soybean- and canola-based biodiesels. Overall, BHT was the least effective antioxidant in both biodiesel samples studied. Of the synthetic antioxidants tested, PY had an effect at lower concentrations than TBHQ and BHT. PY had the best fit to the first-order rate model, with the highest R^2 values in both soybean- and canola-based biodiesel, and TBHQ had the worst, with the lowest R^2 values in both biodiesels studied. The two proprietary antioxidants displayed lower

Table 3. Summary of important parameters of antioxidants in soybean-based biodiesel.

Biodiesel (Soybean-based)	F (1000 ppm)	k	C_{cr}	R^2
BHT	2.41	1.093	87.61	0.898
Naugalube 403	4.13	0.719	55.41	0.962
TBHQ	6.76	0.275	108.29	0.829
Ethanox 4760	4.00	0.661	68.51	0.926
PY	11.33	0.336	59.06	0.950

Table 4. Summary of important parameters of antioxidants in canola-based biodiesel.

Biodiesel (Canola-based)	F (1000 ppm)	k	C_{cr}	R^2
BHT	1.84	0.534	74.10	0.940
Naugalube 403	3.73	0.298	60.32	0.942
TBHQ	8.41	0.088	104.03	0.850
Ethanox 4760	6.15	0.242	25.81	0.981
PY	5.18	0.222	59.40	0.944

critical concentrations, indicative of effectiveness at low concentrations, in addition to relatively low rate constants, and relatively tight fits to the first order kinetics model. In both biodiesel samples, the Ethanox® 4760 had a lower rate constant than the Naugalube® 403.

Deviation from the proposed first-order model (equation 2 of section 1.5) may be evidence of variation in the degradation kinetics of antioxidant samples. In order to illustrate those differences, one can either check for a logarithmic trend line (for first order) or a linear trend line (for pseudo-zero order) of an IP vs. C_o plot. This was done for each antioxidant with the results summarized in Tables 5 and 6. A reaction following first order kinetics should show a better fit to the logarithmic trend line, while a reaction following pseudo-zero order kinetics should show a better fit to a linear trend line.

As is summarized in Tables 5 and 6, some antioxidants exhibit a superior linear fit, indicating pseudo-zero order kinetics, while others exhibit a superior logarithmic fit, indicating potential first order kinetics. The tables above contain the R^2 values of the linear and logarithmic fits for the tested antioxidants in both biodiesel samples. PY is the only antioxidant that strongly adhered to a logarithmic fit in both soybean- and canola-based biodiesel. Although the Naugalube® 403 fit is more logarithmic than linear in soybean-based biodiesel, it is only slightly so. Similarly, the Ethanox® 4760 linear fit is only slightly stronger than its logarithmic fit. The most dramatic cases present themselves in TBHQ and BHT. TBHQ, which has a linear R^2 of nearly 1 in canola-based biodiesel, exhibits the strongest preference for a linear fit over a logarithmic one in both soybean- and canola-based biodiesels.

This raises the possibility of defining when certain antioxidants in biodiesel will either behave in a first order or a pseudo-zero order kinetic fashion. Pseudo-zero order reactions are most commonly the consequences of what might actually be a first or higher order reaction in which one of the reactants is in a great excess. That is, if [C], the antioxidant concentration, is substantially greater than [B], and B is consumed rapidly,

$$\frac{d[C]}{dt} = -k[C][B] \cong -k'[C]^0 \qquad (3)$$

$$k' = Constant \cong k([C]_{initial} - [C]_{final})$$

then d[C]/dt would not appear to change if the quantity of [C] does not appreciably change, since the fraction change in [C], being in great excess, would be negligible when compared to fraction change in [B]. If an antioxidant used in this experiment

Table 5. Linear and logarithmic best fit of antioxidants in soybean-based biodiesel.

Biodiesel (Soybean-based)	Linear R^2	Logarithmic R^2	Best fit
BHT	.988	.897	Linear
Naugalube® 403	.955	.962	Logarithmic
TBHQ	.996	.828	Linear
PY	.826	.949	Logarithmic
Ethanox® 4760	.981	.928	Linear

Table 6. Linear and logarithmic best fit of antioxidants in canola-based biodiesel.

Biodiesel (Canola-based)	Linear R^2	Logarithmic R^2	Best fit
BHT	.973	.939	Linear
Naugalube® 403	.972	.943	Linear
TBHQ	.999	.848	Linear
PY	.777	.981	Logarithmic
Ethanox® 4760	.971	.942	Linear

exhibits pseudo-zero order kinetics, it should be in great excess relative to whatever it is acting on. However, as the antioxidant is slowly degraded, its behavior will begin to deviate from zero order kinetics as its concentration decreases and the approximation no longer holds.

Another mechanism by which pseudo-zero order antioxidant activity may be observed was proposed by Machado *et al*. [17], as a result of their study of the kinetics of antioxidants in sunflower and soybean derived biodiesel. While they observed uniformly first order kinetics in their soybean-based biodiesel, zero order kinetics were observed in the sunflower-based biodiesel. They rationalized their findings by approximating the exponential C_o vs. t equation with a Maclaurin series as shown below in equation (4). Starting from a rearranged form of equation (2) and adapting the method employed by Machado *et al*. to obtain the appropriate series, a similar expression is obtained. This can be represented by a Maclaurin series. If the product $k(IP - IP_{orig})$ is sufficiently small, the series can be approximated by using the first two terms ($i = 0$, $i = 1$).

or

$$\frac{C_O}{C_{cr}} = e^{k(IP-IP_{orig})} = \sum_{i=0}^{\infty} \frac{k(IP-IP_{orig})^i}{i!} \cong 1 + k(IP - IP_{orig})$$

$$\frac{C_O}{C_{cr}} = 1 + k(IP - IP_{orig}) \quad (4)$$

The above equation should exhibit a linear relationship between initial concentration and the induction period. This approximation is applicable only when the $k(IP - IP_{orig})$ is sufficiently small. Machado *et al.* proposed that, since sunflower-based biodiesel, being the more unstable biodiesel, had a much higher concentration of fatty acid methyl esters containing bis-allylic positions than soybean-based biodiesel, it would degrade much more rapidly, and in doing so consume a larger amount of antioxidant over a shorter period of time. It was suggested that this holds true for antioxidants that are rapidly consumed, typically in biodiesel that rapidly degrades. Machado *et al.* concluded that this zero order approximation should only hold for fuels with rapid IP, in which antioxidants are rapidly consumed. That is, it should only be true with $(IP - IP_{orig})$ being small enough to overcome the high k (degradation rate constant) and allow the term $k(IP - IP_{orig})$ to be sufficiently small for the approximation to work [17].

Evidence from our experiments, however, indicates that there are other conditions by which pseudo-zero order kinetics may be observed. The kinetics of TBHQ, despite having the lowest degradation rate parameter, k and greatest stability factor (both reported in Tables 3 and 4), fits most tightly to a linear relationship between concentration and IP. If k is sufficiently small (that is, the antioxidant is consumed very slowly), the term $k(IP - IP_{orig})$ may remain sufficiently small for the above approximation to hold. In the following section, analytical experiments were undertaken to assess the accuracy of the first order and the pseudo-zero order kinetic modeling on BHT and PY in soybean-based biodiesel.

3.2. Assessment of model accuracy by direct quantification of BHT and PY with GC/FID

As was indicated by the previous experiment, it has been observed that certain antioxidants deviate from the proposed first order degradation of antioxidants in biodiesel. In order to more fully assess the model's accuracy, a direct measurement of BHT and PY concentrations was done by using quantification in the more oxidatively-unstable, soybean-based biodiesel via gas chromatography/ flame ionization detection (GC/FID). BHT was chosen because of its short IP and apparent zero order behavior in soybean-based biodiesel. PY was chosen because of its high IP and how tightly it fitted to the proposed first order model (refer to Tables 3 and 5).

Recall equation 2 from section 1.5

$$lnC_o = k(IP - IP_{orig}) + lnC_{cr} \quad (2)$$

Raising e to the power of both sides of the equation and rearranging, yields (5), where $t = (IP - IP_{orig})$.

$$C = C_o e^{-kt} \quad (5)$$

If, however, the antioxidant degradation is more accurately modeled for a time by zero order kinetics, the following equation applies.

$$C = C_o - kt \quad (6)$$

The parameter k in equation (6) is obtained by simply graphing C_o vs. $IP\text{-}IP_{orig}$ from the data and

taking the slope of the best fit line. By graphing the experimentally determined concentration vs. time, and the predicted concentration vs. time curves for both the zero and first order kinetic models (shown below in Figs. 2 and 3), the differences in accuracy in the models can be seen directly.

The first order rate constants used to predict the first order concentration curves were obtained by taking Co and IP-IP_{orig} for BHT and PY in soybean-based biodiesel from Table 3, graphing ln(Co) vs. IP-IP_{orig}, and taking the slopes of the resulting curves. The pseudo-zero order rate constants used to predict the pseudo-zero order concentration curves were obtained by plotting Co vs. IP-IP_{orig} (obtained as before from Table 3) and taking the slope of that line. Once obtained, the first and pseudo-zero order rate constants were used in equations (5) and (6) to generate the predicted concentrations over time of BHT and PY, which are shown in Tables 7 and 8, and the results plotted in Figs. 2 and 3. The percent errors shown were calculated by comparing the predicted BHT and PY concentrations to the concentrations of BHT and PY determined by GC/FID.

4. DISCUSSION

Using the kinetic parameters obtained from the data (for zero order- k = -617.38 ppm/h, for first order- k = 1.0933 h^{-1}), referring to Fig. 2, it is striking how tightly the actual concentration profile of BHT fits the zero order kinetics for t = 0 h until t = 3 h. In fact, there are two points, t = 1.5 h and t = 2.0 h, when the zero order model predicted almost exactly the

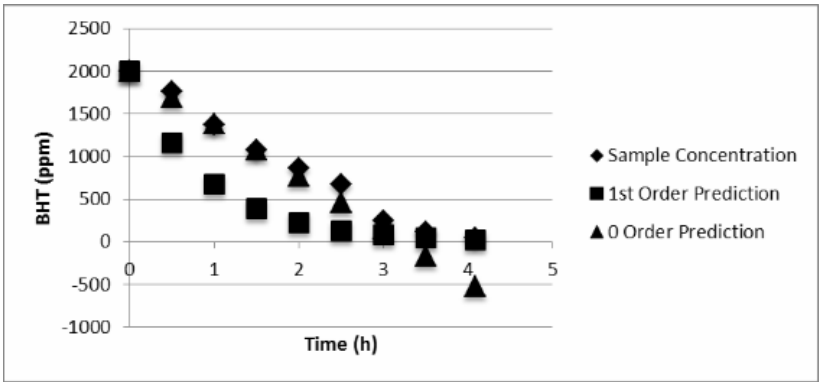

Fig. 2. BHT concentration vs. time of sample, and 1st and 0 order predictions.

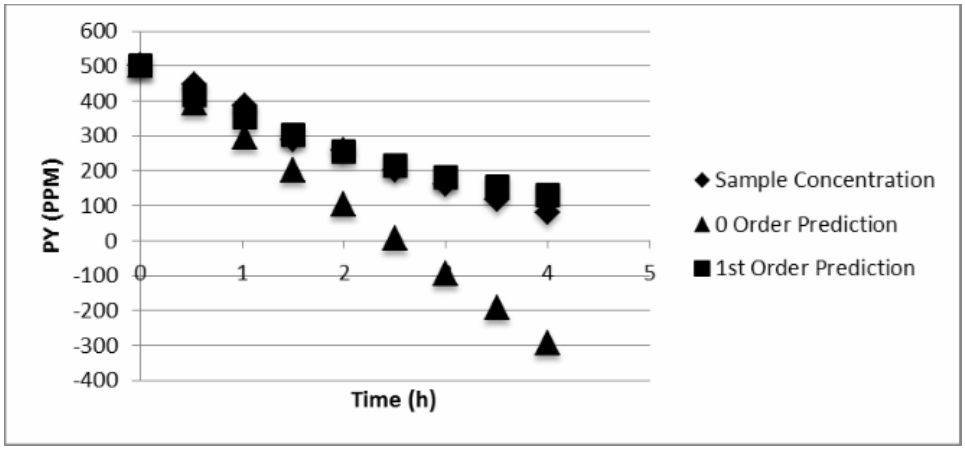

Fig. 3. PY concentration vs. time of sample, and 1st and 0 order predictions.

Table 7. Predicted BHT concentrations and prediction % error.

Sample	1st Order predicted PPM	1st Order % error	0 Order predicted PPM	0 Order % error
1	1999.686	0.000	1999.686	0.000
2	1157.764	34.320	1690.771	4.083
3	670.314	51.056	1381.856	0.898
4	388.094	63.812	1072.941	0.046
5	224.696	73.941	764.026	11.392
6	130.093	80.780	455.111	32.760
7	75.320	69.211	146.196	40.239
8	43.608	60.698	-162.719	246.651
9	22.883	44.051	-527.238	1389.112

Table 8. Predicted PY concentrations and prediction % error.

Sample	1st Order predicted PPM	1st Order % error	0 Order predicted PPM	0 Order % error
1	499.926	0.000	499.926	0.000
2	418.486	6.447	394.991	11.700
3	354.452	8.148	296.986	23.040
4	302.236	4.880	202.941	29.577
5	255.561	0.946	103.946	59.711
6	216.093	7.678	4.951	97.533
7	182.721	13.255	-94.044	158.291
8	154.502	31.283	-193.039	264.028
9	130.642	64.756	-292.034	468.292

actual BHT concentration. As predicted by the approximations made to derive a pseudo-zero order kinetics, equation (3), pseudo-zero order kinetics for BHT broke down at low concentrations. At $t > 3.5$ h, the zero order model predicted negative concentration. This is obviously unrealistic, and quite clearly illustrated the time at which the approximations needed for pseudo-zero order kinetics no longer hold. Instead, the first order model become a more accurate model for the concentration of BHT at approximately $t = 3$ h. Pseudo-zero order behavior was observed until the concentration of BHT reached a certain level, at which time a first order behavior begins to emerge.

When this method was applied to the PY, (refer to Fig. 3) the first order kinetics seen in section 3.2 for PY in soybean-based biodiesel provided a better prediction of PY concentration over time than did a pseudo-zero kinetics. One can conclude that the first order kinetics has better predictive power for PY than the pseudo-zero order kinetics. The question remains as to how it might be explained that certain antioxidants exhibit first order behavior, while others exhibit pseudo-zero order behavior. It has been shown by Machado *et al.* [17] that rapidly degraded antioxidants exhibit zero order behavior. However, TBHQ, the slowest-degrading antioxidant tested, exhibited pseudo-zero order behavior in this

experiment. PY, which degraded somewhat slowly, exhibited first order behavior, while the two commercial antioxidants were neither completely first order nor completely zero order in their behavior. In section 3.2, two potential explanations for zero order behavior were given. The first assumes that the antioxidant is in much higher concentration than the reactive species with which it reacts. The second, as adapted from the Machado's paper, what appears as zero order behavior is really a special case of first order behavior, produced when ($IP - IP_{orig}$) is sufficiently small. It is claimed that since the biodiesel was so unstable, the observed ($IP - IP_{orig}$) values were sufficiently small for that approximation to work.

However, the soybean-based biodiesel tested here had a lower IP_{orig} (0.8 hours) in comparison to Machado's reported value of 1.54 hours for his group's sunflower oil biodiesel, leading to a larger ($IP - IP_{orig}$) value. It is possible that if the term $k(IP - IP_{orig})$ is kept sufficiently small via a sufficiently small rate constant k, then Maclaurin Series approximation will hold. This agrees with the 'excess concentration' model, since, if the antioxidant is in tremendous excess, then the degradation rate constant would appear to be low for that antioxidant.

If that is the case, it might demonstrate that the variability in effectiveness between antioxidants is due in part to their interacting with different reactive products of the degradation process. In this case, TBHQ seems to be interfering with a reactive species present at low concentration, while BHT, the least effective antioxidant present, may be reacting with a species present in higher concentration. Perhaps a low concentration intermediate is reacting with TBHQ as the radical initiator, while BHT is reacting with a product produced further down the degradation pathway. Due to the variability in biodiesel composition, the species that play the role of radical initiator may vary between biodiesels, explaining the variation in effectiveness of antioxidants between biodiesel samples.

5. CONCLUSION

Taken together, direct quantitation of antioxidants over time show that certain antioxidants are better modeled as following pseudo-zero order kinetics. It was shown via direct quantification of BHT in soybean-based biodiesel that the rate constant obtained by a pseudo-zero order kinetics was more accurate at predicting BHT concentration from the EN 14112 Rancimat test than the rate constant obtained by a first order kinetics at the concentrations at which BHT was an effective antioxidant. While it has been shown that for most biodiesel when reacted with most antioxidants, first order kinetics are observed, our experiments show that in the case of a strong antioxidant in excess concentration added to a fairly oxidatively-unstable biodiesel, pseudo-zero order kinetics may be a better fit to the experimental data.

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CONFLICT OF INTEREST STATEMENT

The authors confirm that the research in this manuscript has no conflicts of interest.

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