The Decline and Recovery of Thermal Oxidative Stability of Ultra-Low Sulfur Diesel Blends

Abigail Schoor Cohen

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THE DECLINE AND RECOVERY OF THERMAL OXIDATIVE STABILITY OF ULTRA-LOW SULFUR DIESEL BLENDS

A Dissertation

Bayer School of Natural and Environmental Sciences

Duquesne University

In partial fulfillment of the requirements for

the degree of Masters of Science

By

Abigail Schoor Cohen

December 2017
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Abigail Schoor Cohen

2017
THE DECLINE AND RECOVERY OF THERMAL OXIDATIVE STABILITY OF
ULTRA-LOW SULFUR DIESEL BLENDS

By
Abigail Schoor Cohen

Approved August 30, 2017

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ABSTRACT

THE DECLINE AND RECOVERY OF THERMAL OXIDATIVE STABILITY OF
ULTRA-LOW SULFUR DIESEL BLENDS

By
Abigail Schoor Cohen

December 2017

Dissertation supervised by Professor Bruce D. Beaver

The oxidative stability of ultra-low sulfur diesel (ULSD) has generally been expected to continuously decline over time. However, recent studies have suggested that it may fluctuate.\textsuperscript{1-2} In this study, the oxidative stability of stored commercially purchased ULSD was monitored with a methanol extraction method.\textsuperscript{3} In this methodology, proposed by Hardy and Wechter, fuel blends are extracted with methanol before and after thermal stressing.\textsuperscript{4} The methanol-soluble layer contains the oxygenated and oxidizable components of the fuel (SMORS) and the change in this mass upon stressing thus represents the oxidative stability of the fuel. Over the course of 145 days of storage under various conditions; this mass difference – called the SMORS mass was observed to recover, decline and recover again.
In a concurrently run study – phenol was generated within two simplified ULSD blends consisting of 25% cumene in heptane after 38 days of lab storage. The amount of phenol peaked between days 62 and 76. Within the same time frame, the oxidative stability of the similarly stored ULSD peaked. This suggests that phenol was also generated within the ULSD and that this *in situ* generated phenol served to increase the oxidative stability. Infrared spectra of deposits formed during stress runs suggests the formation of quinones. This in turn suggests that the subsequent loss of oxidative stability is due to the conversion of the generated phenols to quinones – which would then undergo coupling reactions, eventually yielding high molecular weight deposits.³
DEDICATION

This document is dedicated to the memory of my grandmother, Jean Cohen as well as my cousin, Alan Kosher and dear friend, Glenn Wombold. Z’”l
ACKNOWLEDGEMENT

I would like to thank the following for their assistance/support in completing the research for this document: Bruce Beaver, Stephanie Wetzel, Michael Van Stipdonk, Mitch Fedak, Lance Crosby, Ian Welsh, Ben Mogesa, Sara Dille and Sergey Chepyshev.

Additional thanks go out to my parents, siblings and other relatives and friends – especially Caitlin Hargest and Chris Johnson as well as the staff of the many Squirrel Hill coffee shops.
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<tr>
<td>AMDIS</td>
<td>Automated Mass Spectral Deconvolution and Identification System</td>
</tr>
<tr>
<td>AMS</td>
<td>α-methyl Styrene</td>
</tr>
<tr>
<td>AOCS</td>
<td>American Oil Chemists’ Society</td>
</tr>
<tr>
<td>BHA</td>
<td>Butylated hydroxy anisole</td>
</tr>
<tr>
<td>BHT</td>
<td>Butylated hydroxy toluene</td>
</tr>
<tr>
<td>CA</td>
<td>Cumyl alcohol</td>
</tr>
<tr>
<td>CHP</td>
<td>Cumene hydroperoxide</td>
</tr>
<tr>
<td>FAME</td>
<td>Fatty-acid methyl ester</td>
</tr>
<tr>
<td>HAT</td>
<td>Hydrogen Atom Transfer</td>
</tr>
<tr>
<td>HDPE</td>
<td>High-density polyethylene</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>SMORS</td>
<td>Soluble macromolecular oxidatively-reactive species</td>
</tr>
<tr>
<td>SPLET</td>
<td>Single Proton Loss – Electron Transfer</td>
</tr>
<tr>
<td>TPP</td>
<td>Triphenylphosphine</td>
</tr>
<tr>
<td>TPPO</td>
<td>Triphenylphosphine oxide</td>
</tr>
<tr>
<td>ULSD</td>
<td>Ultra-low sulfur diesel</td>
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Chapter 1: Introduction

Ultra-low sulfur diesel (ULSD) and its kin are used to power a variety of vehicles – including airplanes, trains, tractor-trailers and other such commercial vehicles as well approximately one-third of all automobiles in the United Kingdom. ULSD consists of a mixture of saturated alkanes and aromatics – the removal of sulfur by hydrogenation also serves to eliminate both heterocycles and unsaturated alkanes.

One of the primary components of automotive diesel engines is the common rail (Figure 1). In the common rail, diesel is pumped from the fuel tank (A) through the filter (B) and then through the high-pressure pump and into the common rail (C) where it reached pressures around 1900 atm before being dispensed into the fuel injectors (D). Excess fuel from both the fuel injectors and the common rail is flowed back into the fuel tank (E).

![Figure 1: Schematic of diesel flow in the common rail. Dark arrows indicate diesel at low pressure, light arrows indicate high pressure.]

A. ULSD Oxidation

Engine operational conditions have been shown to lead to ULSD oxidation. During the thermal oxidation of diesel, organic hydroperoxides decay to yield an alkoxyl radical and a hydroxyl radical (Figure 2; 1). These promiscuous radicals then abstract hydrogens
from any nearby hydrocarbon, yielding an alcohol, water and two alkyl radicals. These alkyl radicals can either abstract another hydrogen, extending the chain or they can react with dissolved oxygen, yielding a peroxyl radical (Figure 2; 2). This peroxyl radical will then selectively abstract a benzylic or phenolic hydrogen, resulting in another organic hydroperoxide and a benzylic radical, propagating the radical chain (Figure 2; 3 and 4).

1) \[ R\text{-}OOH \xrightarrow{\Delta} R\text{-}O' + HO' \]
2) Radicals \[ R'O-O' \xrightarrow{\text{reaction}} R'\text{-}O' \]
3) \[ R'O-O' \text{ reacts with } \text{other organic compounds (R'H)}, \text{yielding alkyl radicals}. \text{These radicals then react with dissolved oxygen; yielding peroxyl radicals}. \]
4) \[ \text{Benzyl radicals react with dissolved oxygen – generating a benzylic peroxyl radical.} \]

The product benzylic peroxyl radical will then abstract a hydrogen of its own; yielding a benzyl peroxide. This product may either decay as discussed previously or, in the presence of acid, can be converted into phenols (Figure 3). During this conversion, the organic peroxide (I) is protonated, yielding II, which then undergoes a phenyl migration, yielding a carbocation (III) and water. This carbocation is then attacked by water; yielding IV which undergoes a proton transfer, resulting in V ultimately collapsing into a phenol (VI) and a ketone. (Figure 3).
The primary problem with diesel oxidation is that it eventually leads to the formation of solids, which can lead to fuel system blockages. Figure 4 illustrates the process whereby the phenols and peroxy radicals formed during oxidation can transform into high molecular weight compounds and eventually into engine deposits.

A peroxy radical, such as might be formed during oxidation abstracts a hydrogen from a phenol (1) (Figure 4). The resulting phenoxide radical isomerizes (2) and reacts with dissolved oxygen, eventually yielding 3, a peroxydienone, which decays, yielding...
water and a quinone (4). The resultant quinone may in turn participate as the electrophile in an electrophilic aromatic substitution reaction with a nucleophilic species such as a phenol, an aromatic or a hydroquinone. This reaction yields a hydroquinone (5) which is then oxidized to quinone by reaction with additional peroxyl radicals. The product quinone can then react with another nucleophile, continuing the process. Eventually, compounds of sufficient molecular weight are produced such that they are no longer soluble and precipitate out of solution and accumulate either in the fuel filter or in the fuel injector, leading to blockages. Various additives have been created to counteract this, including radical scavengers such as butylated hydroxytoluene and anisole (BHT and BHA) and various dispersants to prevent/minimize deposit build up.

B. Measuring Oxidative Stability

Given the economic stakes, it is unsurprising that tests exist to predict and monitor the oxidative stability of a ULSD blend and that governments would set limits on these values. The current established method is known as the RANCIMAT (Figure 5).

![Figure 5: Schematic of a RANCIMAT device.](image)
In this method, air is flowed into the sample, which is heated to 110 °C. Volatile oxidation products, primarily formic acid, are collected in the measuring vessel. Continuous measuring of the conductivity of this vessel allows for the induction point, the point at which oxidation starts occurring rapidly, as depicted in Figure 6. European standards mandate a 20 hour minimum induction point for pure ULSD.\(^\text{10}\) There is no similar minimum in the U.S; however biodiesel blends between 6-20% have a mandated minimum induction point of 6 hrs.\(^\text{11}\)

![Figure 6: Induction points of various fuel samples.\(^\text{12}\) The bars indicate the American and European minimums.](image)

However, just because a fuel passes the RANCIMAT does not guarantee that the fuel will not cause problems. Field Sample (FS)2 met the European RANCIMAT standards, yet were reported as causing problems. Indeed, FS2 was found to be more stable than the non-problematic FS1.\(^\text{12}\)

This suggests that the indirect method used by the RANCIMAT (monitoring the formation of volatile acids) is inadequate in predicting the oxidative stability of ULSD. A
more direct method does exist – the SMORS method as developed by Hardy and Wechter.\(^{13}\) This method, which is also utilized by this group, involves the extraction and subsequent isolation of polar components from the ULSD with methanol.\(^{14}\) Among these components are the phenols, peroxides, quinones and hydroquinones discussed in Figure 2 through 4.\(^{4,13}\) However, this method is labor and chemical intensive – leading to a search for a faster, automated method. It was decided to focus on peroxides, given their importance to the overall progress of oxidation. The official American Oil Chemists Society (AOCS) method, iodometric titration suffers from the same drawbacks as the SMORS method.\(^{15}\) However, work by West et al. suggested using the reaction of triphenylphosphine (TPP) with peroxides.\(^{16}\) TPP reacts with peroxide, yielding triphenylphosphine oxide (TPPO); this reaction can be monitored with \(^{31}\)P NMR.\(^{17}\)

C. FAME

It should also be noted that Field Sample 3 from Figure 6 was also reported as containing 20% FAME.\(^{12}\) FAME refers to fatty acid methyl esters, that is to say, biodiesel. Biodiesel is commonly derived from food stock – soybeans and is used as an additive to petroleum derived diesel – primarily to minimize dependence on imported petroleum and reduce greenhouse gas emissions. The most commonly used blend is 20% biodiesel (B20); which is also the highest percentage that most diesel engines can tolerate without modification.\(^{11}\) At present, no governing bodies mandate the use of B20 – the current EU/UK standard is 6% while in Pennsylvania it is 2% but scheduled to increase with in-state production of biodiesel (Title 73 Pennsylvania Statutes, Chapter 18H, Sections 1650.3). Research has shown that the addition of FAME reduces the oxidative stability – primarily through the oxidation of the easily oxidized unsaturated fatty acid
chains. This is relevant as nearly all of the commercial fuels used by this group were purchased in Pennsylvania and thus contain 2% FAME at minimum.

D. Objectives

The goals of this research were twofold. Firstly, to assess the hypothesis that increased agitation, through vehicular transport, will lead to decreased oxidative stability via the formation of peroxides and phenols. This was done via the storage of commercial ULSD in vehicles and the in-lab storage of a cumene/heptane blend. Secondly, to develop a method to monitor the peroxide content of the fuel using $^{31}$P NMR.

Toward this end, two long-term monitoring experiments were set-up. Firstly, the car storage experiment, run in Fall 2014 and again in Summer 2016, involved the storage of commercial ULSD within the trunks of vehicles. Oxidative stability was monitored via $^{31}$P NMR as well as thermal stressing/methanol extraction. Deposits were generated through thermal overstress, and analyzed via IR for the presence of oxygenation. The second experiment, utilizing a cumene/heptane blend, was run concurrently with the second run of the car storage experiment. The cumene/heptane blend was intended to represent a greatly simplified ULSD blend. Like the commercial ULSD, this simplified blend was subjected to agitation – through a gyrorotatory shaker. Being a two-component system, it was possible to use GC/MS to directly monitor the conversion of cumene to phenol (Figure 2 Figure 3).
Chapter 2: Methods

A. SMORS Extraction

This method, performed before and after thermal stressing was used for monitoring the oxidative stability of the car-stored ULSD. Twenty milliliters of the analyte fuel (public gas station) were extracted with 20 ml of methanol (extra-dry; ACROS Organics, Morris Plains, NJ). The (upper) methanol layer is drained into a pre-weighed roundbottom flask and evaporated off using a 60 °C rotovap – with the remaining residue representing the SMORS solution. Evaporation lasted approximately 15 minutes – until no further bubbling was observed within the flask. Emulsions are broken up via centrifugation, with the upper layers being then pipetted into the aforementioned roundbottom flask. After evaporation, the flasks were dried and permitted to cool prior to weighing – with the SMORS solution mass being the mass of the residue; obtained by subtracting the initial roundbottom mass from that of the roundbottom and the residue. All extractions were done in triplicate, allowing for the 95% confidence interval to be calculated.

B. Thermal Stress Run

70-75 ml of the analyte fuel (sufficient for triplicate SMORS extractions) are heated to 130 °C in a sand bath while 20% oxygen is bubbled through it at a rate of 0.3 L/min for 4 hours, after which the fuel was permitted to cool for 12 hours (Figure 7).
Figure 7: Set-up for a stress-run

1. Thermal Over-stress

Over-stress runs utilized the same three-neck flask assemblage as normal stress runs; except the flask is submerged more deeply within the bath, allowing for faster heating – resulting in sustained heating at 150 °C for the final hour of the 4 hour run. This was done with the intention of obtaining tarry deposits for IR analysis.

2. Cumene

75 ml of cumene (98% pure; ACROS) with varying additives (1000 ppm - ) were stressed using the same set-up. However, rather than continuously bubbling 20% oxygen through the flask at a set rate; the cumene was instead pre-charged by bubbling 80% oxygen at 0.3 L/min for 45 minutes prior to heating. 2 ml samples were pulled at thirty minute intervals for GC/MS analysis.

C. Deposits and Multiple Layers

1. Tarry Deposits

Tarry deposits generated over the course of a stress run were drained of remaining fuel, rinsed with 1-2 ml of methanol and allowed to dry.

2. Breezewood Lower Layer
ULSD purchased in Breezewood, PA was stressed per normal protocol. Upon cooling, two layers were observed in the three-neck flask – an amber colored upper layer and an orange lower layer. The upper layer was used for SMORS extraction while the lower layer – approximately 10 ml in volume was extracted with an equal volume of methanol and evaporated as per the SMORS protocol.

3. Washington, DC Deposit

A tan emulsion was observed during the extraction of stressed ULSD purchased in Washington, DC. Centrifugation of the emulsion yielded a friable deposit which was isolated and permitted to dry prior to analysis with SEM/EDS and IR.

D. Storage Experiments

1. Bubbling

For both runs of this experiment, freshly purchased ULSD was distributed amongst 12 125-ml erlenmyer flasks (50 ml/flask) and assigned to one of four gas treatments (ambient air, 20% oxygen, 80% oxygen and nitrogen. Initial peroxide ratios and SMORS masses were taken from the bulk fuel. During the 2015 run, flasks were bubbled with or exposed to their assigned gas for 10 minutes, once a week. This duration was upped to 20 minutes, twice a week for the 2016 run; with flowmeters allowing for 0.3 L/min flow-rate. NMR measurements were performed on alternating weeks.

2. Car

ULSD was purchased in gallon amounts and stored in HDPE (high-density polyethylene) containers. 260 ml from each container (carboy hereafter) were removed for the acquisition of SMORS as well as for the bubbling experiment. The carboys were secured to secondary containment using straps so as to prevent tipping and placed in the
enclosed or shaded trunk of a vehicle. The vehicle owners made every effort to not alter their driving habits in response to this study. Three sample vials were pulled on a biweekly basis; as with the bubbling experiment. On days 55 and 90 of this study, 150 ml were pulled for SMORS extraction and thermal stressing. An additional 75 ml was pulled from the short-distance carboy for an over-stress.

3. Shaking

A 25% cumene in heptane (99% anhydrous, Sigma-Aldrich; St. Louis, MO) blend was prepared and distributed between two clean and dry carboys (1 L/carboy). One carboy, designated ‘shaken’ was shaken using a gyrorotatory shaker – 1 hr. at 200 rpm followed by 15 min at 50 rpm with the lid off followed by an additional hour at 200 rpm. During the 15-minute breathing interval, the lid was removed from the ‘still’ container. Both containers were stored in a cabinet when not in use.

E. $^{31}$P NMR

1. Reaction vials

A 36 mMol solution of triphenylphosphine oxide (TPPO)(99%; Aldrich; St. Louis, MO) in acetone was prepared and distributed among 4-mI screwcap vials (200 µl/vial). The acetone was driven off via gentle heating. Before usage, 250 ml of 0.38 M solution of triphenylphosphine (TPP) (recrystallized from hot ethanol; 99% from ACROS) in dichloromethane were added; followed by 2 ml of the target fuel. After 15 seconds of vortexing, 200 µl were transferred to an NMR tube containing 300 µl of deuterated chloroform
2. NMR Analysis

NMR experiments were done using a 400 MHz Bruker equipped with a 5 mm PABBO BB-1H/D Z-GRD probe and a nuclear Overhauser effect suppressing pulse program. 64 total scans, 15 second relaxation time.

F. GC/MS

Once a week, samples would be pulled from the cumene/heptane carboys and analyzed via neat injection using a Varian 3900/Saturn 2000 equipped with a Varian CP-8400 autosampler and a 30 m VF-35ms column. Oven conditions were as follows:

<table>
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<th>Flow rate</th>
<th>1.0 ml/min</th>
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<tr>
<td>Injection</td>
<td>220 °C</td>
</tr>
<tr>
<td>Start</td>
<td>80 °C</td>
</tr>
<tr>
<td>Ramp</td>
<td>10.0 °C/min</td>
</tr>
<tr>
<td>End</td>
<td>200 min</td>
</tr>
<tr>
<td>Hold</td>
<td>1 min</td>
</tr>
</tbody>
</table>

A 3.5 minute solvent delay was sufficient for both heptane and cumene to elute without ionization. Relative amounts were calculated by dividing the measured peak area by the peak area of first detection.
Chapter 3: Results

A. Car Storage Experiment

The initial objective of this experiment was to assess the impact of ambient/low temperature agitation – such as might be experienced during transport. The experimental setup was inspired by that of Lacey et al. wherein B10 diesel was stored in the fuel tanks of intermittently idled vehicles and monitored via the RANCIMAT. In the absence of diesel-powered vehicle and a RANCIMAT device; thermal stressing and $^{31}$P NMR were used to monitor the oxidative stability of fuel stored in the trunk of vehicles with differing usage habits. One car, designated ‘short’ travelled an average of 10 mi/day whereas the other – designated ‘long’ travelled 100 mi/day. The first run of this experiment commenced August 2014 and ran through November.

![Figure 8: Peroxide formation in car-stored ULSD. Single sample.](image)

The results of the peroxide monitoring do suggest that the long-distance experienced increased peroxide formation trend between days 30 to 70 followed by a severe decline (Figure 8). However, as only a single sample was analyzed; the results are inconclusive. The thermal stress results (Figure 9) are more conclusive.
After 87 days of in-car storage; both fuels were subjected to thermal stressing and SMORS extraction. The pre-stress SMORS masses for both fuels remained unchanged – both with respect to each other and to the initial values. However, the fuels differed significantly upon thermal stressing; with the long-distance ULSD forming 0.5 g more SMORS than the short distance ULSD. No initial post stress values were obtained; however other experiments with other newly-purchased fuels suggests an initial post-stress SMORS mass of ~2 g.

Given the apparent success of the Autumn 2014 run; this experiment was revisited in the Summer of 2016 – this time including an in-lab control (designated ‘still’) and triplicate sampling.

Despite these alterations, the results of the $^{31}$P NMR remained inconclusive – with no demonstrable significance at the 95% confidence interval (not shown). The thermal stress studies were of considerable interest – none of the fuels oxidized on day 55 – suggesting an increase in thermal stability. The post-stress SMORS masses gradually returned to day 0 levels afterwards (Figure 10, Table 1).
Though the day 0 post-stress results suggest otherwise, only one ULSD blend was used for this experiment – purchased in June of 2016 and divided into 3 carboys at the pump. The 0.8 g range of post-stress SMORS solution masses can be ascribed to the limitations of the current thermal stress rig – that is; the sand bath. Additionally, the combination of heat and bubbling was observed to volatilize components, such as cumene, below their boiling point. Aggregating all three runs yields an average of 2.4483 g ± 0.27 g; suggesting that any differences beyond 0.27 are due to the genuine differences in the ULSD itself, rather than experimental error (Table 1).

B. The Day 55 Anomaly or Expanded Sampling
The results of the day 55 thermal stressing represented the first time, in the history of this research group, that a ULSD has failed to oxidize. This prompted a revisit to the initial purchase site (a gas station in Fox Chapel, PA – 10 mi from Pittsburgh. Other sites sampled included gas stations in Breezewood, PA (130 mi) and Washington, D.C. (245 mi). The SMORS values for these fuels (purchased in September 2016) were compared to the average values obtained from fuels purchased between 2011 to 2015 from Fox Chapel, Butler, PA (33 mi), Somerset, PA (70 mi) and Harrisburg (200 mi) (Figure 11).

![Graph showing SMORS content of lab stored diesel fuel before and after stressing (130 C, 4 hr, 0.3 L/min) with 95% CI.](image_url)

*Figure 11: SMORS of newly purchased ULSD before and after stressing (130 C, 4 hr, 0.3 L/min); 95% CI.*

None of the three September 2016 fuels, oxidized in what could be a normal fashion – relative toward previous observations. The Fox Chapel fuel barely achieved significant oxidation; despite there being no observable difference between the 2016 blend and the two previous years (Figure 12).
The ULSD from Breezewood, PA formed a milky emulsion upon extraction – requiring the use of a centrifuge; which accounts for the larger 95% confidence interval. The IR spectrum of this fuel suggests the presence of more FAME than that from Fox Chapel – as indicated by the carbonyl stretch at 1748 wavenumbers (Figure 13).
The Breezewood ULSD was also notable in that it formed 2 layers upon oxidation – the expected amber colored layer compromising the bulk of the 70 milliliters of ULSD and a more viscous orange layer, with a volume of 10 ml. This 10 ml portion was extracted with an equal amount of methanol in an attempt to concentrate the orange coloring. The resultant viscous orange liquid was analyzed via IR.

Like the ULSD used in the car stress study, the thermal stability of the Breezewood ULSD changed over time. Shortly after purchase, this fuel was stressed and, as shown in Figure 11, failed to oxidize. When it was revisited six weeks later, it was found to have oxidized in an approximately normal fashion. Similarly, the observed orange layer was reduced considerably.

The ULSD from Washington, D.C. yielded a friable tan deposit and required centrifugation prior to extraction. EDS/SEM of this deposit showed that it was a mixture of metal salts – which suggests corrosion and microbial infiltration of the underground

Figure 13: ULSD purchased in Late August/Early September 2016.
storage tank (Table 2). Because of this, no further tests were performed on this ULSD.

![Figure 14: Deposits formed during thermal stressing. A) Orange layer in six-week-old Breezewood ULSD B. Friable deposit from Washington, D.C. ULSD](image)

Table 2: Elemental composition of Washington, D.C. deposit. 5 samples: 95% CI

<table>
<thead>
<tr>
<th>Element</th>
<th>WT. %</th>
</tr>
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<tbody>
<tr>
<td>C</td>
<td>39.46 ± 12</td>
</tr>
<tr>
<td>O</td>
<td>22.12 ± 5</td>
</tr>
<tr>
<td>Na</td>
<td>2.96 ± 2</td>
</tr>
<tr>
<td>Mg</td>
<td>0.74 ± 9</td>
</tr>
<tr>
<td>Al</td>
<td>7.78 ± 5</td>
</tr>
<tr>
<td>Si</td>
<td>20.59 ± 5</td>
</tr>
<tr>
<td>K</td>
<td>5.37 ± 0.5</td>
</tr>
</tbody>
</table>

C. Overstress

As deposits are not usually generated under the general thermal stress conditions (4 hrs., 130 °C, 0.3 L/min 20% oxygen), an overstress was performed on the short-distance fuel – selected due to the intensity of its yellow color relative to its peers. This run yielded a methanol and acetone insoluble tarry deposit (Figure 15).
Figure 15: IR of tarry deposit and post-stress SMORS generated during thermal overstress (4 hr., 130 - 150 °C, 0.3 L/min 20% oxygen) of the short-distance stored ULSD.

Figure 16: Comparison between the tarry overstress deposit from the Fox Chapel ULSD and the Breezewood tarry layer formed during normal thermal stress.
D. Shaking Experiment

The Car Storage experiment was conceived as a means of comparing the impact of transport agitation on ULSD storage stability; the differences in vehicle model (SUV vs sedan) and parking habits introduced additional variables into the experiment. Furthermore, ULSD itself is a complex mixture – making the identification and tracking of individual components a difficult task. Therefore, an analog system using a model compound was constructed – consisting of 25% v/v cumene in heptane. Cumene was chosen as a model aromatic because of its industrial use in phenol production, while its volume percentage was derived from various ULSD standards.\textsuperscript{21,10} One carboy filled with this model system was agitated on a gyrorotatory shaker (‘shaken’) and compared to an unshaken (‘still’) carboy. The simple, two-component system allowed for GC/MS monitoring of cumene oxidation productions over time – focusing primarily on phenol, α-methylstyrene (‘AMS’), cumyl alcohol (‘CA’) and cumene hydroperoxide (CHP) (Figure 18). AMS Oxide (AMSO) was also observed (Figure 17). In the absence of laboratory samples of these compounds, identification of the non-phenolic compounds determined via comparison to the NIST database.

Figure 17: Storage oxidation products: phenol, cumyl alcohol, α-methylstyrene and oxide.
Figure 18: Full-length chromatogram of lab-stored cumene:heptane blend. Detection of unoxidized cumene was blocked by the solvent delay.

Figure 19: Close-up view of phenol peak on day 38. Confirmed via retention time and spectrum to a lab sample of phenol.
Figure 20: Spectra of A) Phenol formed in stored Cumene/Heptane and B) Laboratory sample of Phenol
Figure 21: Formation of cumene oxidation products over time. Values relative to initial amount. Post day 50; all measurements were done in triplicate.

Figure 22: Formation of phenol in a cumene:heptane blend stored under ambient conditions.

Phenol was detected, in trace amounts, starting on day 38 (Figure 19); this identification was confirmed with laboratory sample (Figure 20). The amount of phenol increased in both containers until day 76, where it declined in the still container yet
continued increasing in the shaken (Figure 21). Contrary to expectations, it seemed that agitation served to slow the formation of cumene oxidation products; though not to a significant extent (Figure 22).

E. Cumene Thermal Stressing

In addition to ambient temperature oxidation; cumene was also subject to thermal stressing. In short, a sample of neat cumene was pre-charged with 80% oxygen and thermally stressed at 130 °C without bubbling for 4 hours over the course of two days. (Previous experiments having shown that even gentlest of agitation was sufficient to evaporate the cumene at this temperature.) As with the long-term storage experiment; GC-MS analysis was used to monitor the formation of oxidation products over time. As with the shaker experiments, cumyl alcohol, phenol, α-methylstyrene and its oxide (AMSO) were all observed. Additionally, cumene hydroperoxide, phenylglyoxalhydrate (PGH) and dicumyl were also observed (Figure 23)

![Diagram of thermal oxidation products of cumene](image)

*Figure 23: Thermal oxidation products of cumene; cumyl alcohol, cumene hydroperoxide, α-methylstyrene and oxide (AMSO, AMSO), phenylglyoxal hydrate (PGH) and dicumyl.*
Cumene hydroperoxide, cumyl alcohol, phenylglyoxal and α-methylstyrene were all detected on the outset. CHP underwent a series of declining peaks and troughs; broadening on the second day of heating. This is likely due to the consumption of dissolved oxygen. CA and PGH gradually increased over the course of both days.

Dicumyl was first detected 60 minutes into the run and was the dominant component for the final 30 minutes of the first day of heating and remained as such over the pause. AMS was present in low percentages during the first day, averaging 1.25%. This percentage increased to 4.69% by 240 minutes in; consistent with the decrease in CHP. Phenol was detected in trace amounts using the built-in AMDIS deconvolution software starting at 270 minutes in.

Two additional cumene stresses were performed: one with 1 ml of acid acetic acid added and the other with 1 ml FAME. As acid is required to catalyze the conversion of cumene to phenol; it was expected that the addition of acetic acid would increase the relative rate of phenol formation. Similarly, as FAME is known to reduce the oxidative stability, it was expected to enhance the formation of peroxide.
Figure 25: Impact of additives on the formation cumene oxidation products. Single run, single sample; values are relative to initial count

Phenol was detected 60 minutes sooner in the presence of either additive. However, the addition of acetic acid served to slow the formation rate while FAME increased it (Figure 25, C). However, acetic acid did serve to increase the formation rate of both AMS and phenylglyoxal hydrate (Figure 25, A and D). The neat reaction experienced a drop in the relative amount of peroxide present – indicating either slower rate of formation or an increased rate of consumption; both additives prevented this drop (Figure 25, B).
Chapter 4: Discussion

A. Increase in ULSD Stability

The car storage study was initially conceived as a means of explaining the results of a survey of commercial biodiesel blends by Tang et al. In this study, half of the fuels tested failed the then current ASTM standard for oxidative stability – a 6 hr. minimum induction period in a 110 °C RANCIMAT.\(^23\) As all of these fuels ought to have met this requirement prior to being delivered to the gas station; the loss of stability had to have been the result of something that occurred during the interval in between. At first, storage conditions in the underground tanks were thought to be the culprit – the admixture of aged and fresh fuels has been observed to exacerbate oxidative degradation.\(^24\) However, the majority of the gas stations surveyed were resupplied once a week; dispensing about 10,000 gallons/month – suggesting a too short of dwell time within the tank for significant oxidation to occur.\(^23\) Most of the fuel blends were prepared via sequential or splash blending – first the ULSD and then the additives are placed in the tanker-truck and combined by the truck’s motion. This motion also serves to aerate the fuel.\(^25-26\) Thus, transport agitation was proposed as the cause of the loss of oxidative stability; with more agitation leading to more instability.

The results of the 2014 car storage study seemed to support this; the ULSD stored in the long-distance car formed more peroxides and formed more SMORS solution after thermal stressing than the short distance car (Figure 8, Figure 9). However, the peroxide values were based on a single measurement and there was neither an in-lab, un-agitation control nor any Day 0 thermal stress results. This experiment was revisited in 2016, with multiple NMR samples, more frequent thermal stressing and an in-lab control; however,
no significant differences in peroxide content were observed between the agitated and un-agitated samples. More unusually, none of the fuels oxidized when thermally stressed on day 55, a previously unobserved phenomenon (Figure 10).

On day 90, all 3 samples showed signs of losing oxidative stability – as indicated by the increase in SMORS solution mass upon thermal stressing; especially the short distance sample. Of the two vehicle-stored samples, this sample was most exposed to external temperatures – being stored underneath a simple sunshade in an open-compartment vehicle whereas the long-distance sample was kept in a closed-compartment trunk. By day 145, the short distance sample had regained some of its thermal stability; while the other two showed signs of increasing instability (Figure 10).

A similar pattern of fluctuating oxidative stability was observed by Lacey et al. in their 2010 vehicle storage study. In this study, 10% biodiesel fuel, blended with various amounts of BHT to yield low, medium and high stability fuels was stored in the gas tanks of commercial and passenger vehicles which were periodically idled. The fuel blends in this study were subjected to weekly RANCIMAT testing (among others).²
Figure 26: Results from Lacey et al. Note the sudden drop in induction period from delivery to placement in vehicle and the rebound at week 1. This trend was observed in all vehicle stored samples across all three fuel blends.²
The researchers observed an initial recovery in the induction period of all three fuel blends; in both vehicle types. In two of the commercial vehicle blends; this recovery persisted for the entirety of the study. While the medium stability commercial vehicle blend didn’t display this persistent recovery, it does undergo a series of declines and recoveries – rather similar to the decline-peak-decline experienced by the short-distance stored ULSD (
Figure 26).
A similar study done by Christensen et al using B20 noted a similar week 1-2 decrease in induction period with concomitant increase in peroxides and acids followed by a recovery, a gradual decline and another recovery by the end of the run.\textsuperscript{1} They, as did Lacey et al. attributed the initial deviation to improper handling and consequently chose not to display these results. However, similar crashes and recoveries in oxidative stability were observed in the studies in this lab – in a commercial B2 fuel that been delivered directly from the pump to the containers used in this study (Figure 10).

We propose that the storage-generated phenols, as formed in the cumene-shaker experiment, had a homosynergistic interaction with the added BHT. In homosynergism, two antioxidants of the same type – such as two phenolic antioxidants, will interact. For example, BHT donates a hydrogen to the phenoxy radical of another antioxidant, regenerating it while leaving BHT as a stable radical(Figure 27)\textsuperscript{27}.

\[
\begin{align*}
\text{Ar-OH} + \text{RO-O}^- \quad \longrightarrow \quad \text{Ar-O}^- + \text{RO-OH} \\
\text{Ar-O}^- + \text{Ar'-OH} \quad \longrightarrow \quad \text{Ar'-O}^- + \text{Ar-OH}
\end{align*}
\]

\textit{Figure 27: Homosynergism. Phenolic antioxidant Ar-OH is regenerated by the donation of a hydrogen by Ar'-OH.}
Such relationships are not unknown in the fuel world – BHT is known to regenerate BHA.\textsuperscript{28}

However, the fuel blends studied by both Christensen and Tang contained only BHT; while no further antioxidants were added to the commercially purchased ULSD – meaning that the necessary synergistic partners had to have been formed endogenously. The formation of phenol during the concomitantly run cumene-storage demonstrates this possibility.

As BHT is a hindered phenol; its resultant phenoxy radical is quite stable and consequently, synergistic regeneration occurs only to a limited extent\textsuperscript{29}; though the presence of electron-donating substituents \textit{para} to the phenol group may increase the rate.\textsuperscript{30} Another alternative is that the BHT radicals can undergo a disproportionation reaction with \textit{para}-alkyl phenoxy radical, yielding regenerated BHT and a quinone methide (Figure 28).\textsuperscript{30-31} The generated quinone methide can than couple with other quinone methides, other phenols as well as other nucleophiles. \textsuperscript{32}
The BHT content of a fuel used in a car storage study in which the fuel was stored in the gas tank of the vehicle and subjected to periodic engine idling was monitored and found to remain fairly constant, despite fluctuations in peroxide content and induction point over the course of the study.
Figure 26). This suggests that either the BHT was being regenerated either through homosynergism or disproportionation.

A third alternative is based an observation by Ohkatsu and Suzuki. They observed that the synergism between 4-methoxyphenol and BHT declined as the polarity of the solvent increased(Figure 29).

This solvent-dependency of synergism is not unknown within food chemistry. Similar trends – where the rate of synergism decreases as the polarity of the solvent increases have been observed for various phenolic and catecholic antioxidants in solvents ranging from acetone to hexane, as well as various alcohol/water blends. This phenomenon is explained by food chemists as the result in a change in the mechanism of oxidation.

In non-polar solvents, oxidation is thought to proceed via the radical-based hydrogen atom transfer (HAT) whereas in more polar solvents, sequential proton-loss electron transfer (SPLET), predominates. SPLET involves ion intermediates which is stabilized by the solvent and not affected by radical scavengers (Figure 30). Depending on the structure of the antioxidant used (α-tocopherol, for example) different oxidation productions have been detected as a result of solvent variation.
1) HAT
ArOH + R* → ArO⁻ + R-H

2) SPLET
ArOH ⇌ ArO⁻ + H⁺
ArO⁻ + R* → ArO⁻ + R⁻
R⁻ + H⁺ → R-H

Figure 30: Comparison between hydrogen atom transfer and single proton loss-electron transfer mechanisms. SPLET – with is proton and carbanion intermediates is favored in polar solvents.18

The loss of synergism due to increases in solvent polarity requires a cause or a source for the polarity-increasing components (water, alcohols). As illustrated in Figure 2, the decay of an organic hydroperoxide yields a hydroxyl and alkoxyl radicals, which will eventually yield an alcohol and water. The formation of cumyl alcohol demonstrates that this occurs at ambient temperatures.39 Furthermore, the formation of the phenols themselves yields acetone (Figure 3).

Ohkatsu and Suzuki propose that the non-polarity of the solvent serves to sequester the phenoxy radicals with the phenols while preventing them from actually reacting; effectively enabling the non-hindered phenols to function as their hindered brethren. However, such an arrangement does not seem likely – given that non-polar solvents enhance the rates synergism40 and disproportionation41 between phenoxy radicals and phenols. Any sequestering would only serve to enhance the rates of both homosynergism and disproportionation. Admittedly, increased regeneration of the BHT would have the same effect as activating the non-hindered phenols.

It had been anticipated that the shaking would allow for the faster dissolution of oxygen and thus the formation of oxidation products.42 Instead, the unshaken or still container formed oxidation products (phenol, cumyl alcohol (CA), α-methylstyrene
(AMS)) at a faster rate (Figure 21, Figure 22). The non-detection of CHP in either container suggests that the open-air shaking did not serve to increase oxidation but rather served to better disperse the generated phenols, which could serve an antioxidant role.\textsuperscript{43}

The relative impact of all three proposed routes – homosynergism, disproportionation and solvent interaction; no doubt depends upon the make-up of the fuel in question. However, in all cases there is a limit to their effectiveness – once this concentration threshold is exceeded; the phenols and peroxides and will react and ULSD stability will decline.

B. Decrease in ULSD Stability

It had been expected that peroxide formation would mirror that of volatile acids – with an induction period followed by exponential growth (Figure 6); this would serve to allow the peroxide value of a fuel to serve as a predictor of future oxidative stability. Indeed, Christensen and McCormick et al. observed that the induction period of biodiesel blends correlated inversely to the peroxide value.\textsuperscript{1} However, various studies suggest a logarithmic\textsuperscript{44} or linear\textsuperscript{1} increase in the peroxide content of a fuel over the course of storage (Figure 31A).

Nor did thermal stressing generate the expected induction point. Thermal stressing of an antioxidant-free fuel analog (cumene) yielded the same logarithmic curve as with long-term storage (Figure 24). However, thermal stressing of a commercial ULSD yielded a parabolic curve (Figure 31B). A similar parabolic rise and fall is observed in the BHT containing B20 blend which had been subjected to several months of storage in an intermittently idled vehicle (Figure 31A).\textsuperscript{1} The presence of antioxidants within the ULSD served to prevent the formation of peroxides for the first 48 minutes of the stress run; but
once these had been depleted, the peroxide content increased 50-fold within the span of 40 minutes.

Figure 3.1: Formation of peroxides in fuel blends over time. A. From Christensen et al. 20% biodiesel blends with added BHT (High) or made with previously stressed biodiesel (Low). Both blends as well as neat diesel were stored in periodically idled automobile engines\(^1\). B. In-house thermal stress time course study featuring a commercial ULSD (130 °C, 20% O\(_2\)); monitored via \(^{31}\)NMR.
The rise and decline in peroxide content in the thermally stressed ULSD sample was accompanied by an increase in post-stress SMORS mass. This suggests that the peroxides were consumed in the process of forming oxidation products.

These observations likely explain the loss of thermal stability in the car storage fuels observed on days 90 and 145 (Figure 10) as well as the formation of oxygenated compounds in both the post stress SMORS (carbonyl stretch 1740 cm\(^{-1}\) and overtone at 3458 cm\(^{-1}\)) as well as conjugated carbonyls (1707 cm\(^{-1}\)) and hydroxyl groups (3373 cm\(^{-1}\)) neither of which are present in the initial fuel (Figure 15, Figure 12). These peaks, present in both the Fox Chapel over-stress deposit and the Breezewood oily layer, approximate those present in the IR spectrum of quinone (Figure 32).\(^4\) This lends credence to the proposed mechanism in Figure 4, where several peroxides are required for the conversion of a phenol to a hydroquinone and then to a quinone.\(^3\) Forming quinones and higher molecular weight compounds would thus serve to decrease the amount of peroxides.
Additionally, the formation of higher molecular weight compounds and subsequent oily/tarry layer deposition might explain the seeming stability of FS2 in Figure 6. As previously mentioned, FS2 was reported by users as causing engine troubles, yet passed the RANCIMAT test with flying colors. The deposition of higher molecular weight, oxidized compounds toward the bottom of the storage container would serve to sequester other oxygenated compounds – removing them from the bulk solution. This would give the appearance of stability when sampled.

As with the thermal stress run in Figure 31, at some point the ability of the blended and generated phenolic antioxidants within the car-stored ULSD to prevent hydroperoxide formation was exhausted. Upon thermal stressing, the generated phenols
and hydroperoxides react; yielding higher molecular weight oxidation products, such as quinones. This, in turn, leads to the higher observed increase in post-stress SMORS mass.
Chapter 5: Conclusions and Further Work

A. Oxidative formation of phenol at ambient temperatures

Commercial oxidative formation of phenol from cumene requires both high temperatures (70 - 80 °C) and acid catalysts.21 In the cumene-shaker experiment, however, trace amounts of phenol were detected within 38 days of storage at room temperature (Figure 19). Extrapolating from this model system suggests that phenols could also form within commercially available ULSD.

B. ULSD thermal stability fluctuates over time

The results of the second run of the car-stress experiment suggest that it is possible for a ULSD to recover its thermal oxidative stability (Figure 10). The formation of phenols within a similar timeframe during the concurrently run cumene-storage experiment suggests phenols may have been formed in situ generated phenols within the commercial ULSD. Furthermore, these phenols served to increase the oxidative stability of the ULSD – either directly by serving as additional antioxidants or by regenerating the added antioxidants though either homosynergism or disproportionation. The benefit of these generated phenols peaked at 55 days of storage before declining by day 90. Similarly, the relative amount of phenol detected in the cumene blends peaked between days 62-76 before declining around day 98 (Figure 22). This in turn suggests that the analogous phenols within the ULSD had similarly reacted further; yielding quinones, hydroquinones and quinone methides; which upon thermal stressing would undergo coupling reactions, increasing in mass and forming oily layers and tars. The formation of quinone-like conjugated carbonyls is tentatively confirmed by the downshifting of the
carbonyl band(s) in the IR chromatogram of one such oily layer relative to the SMORS extract.

The \textit{in situ} phenols responsible for the increase in oxidative stability are thought to be generated from organic hydroperoxides (Figure 3).\textsuperscript{3} Long-term storage studies by Christensen and Lacey have shown that high peroxide concentrations correspond to lowered oxidative stability and vice versa.\textsuperscript{1,2} Similarly, a time-trial \textsuperscript{31}P NMR thermal stress showed that the concentration of peroxides will rise and fall over the course of oxidative stressing (Figure 31). This suggests that the Day 0 SMORS formation was due to a high concentration of peroxides. Over the course of storage, these peroxides were converted to phenols – which serve a protective role. In accordance with the proposed mechanism, these phenols would then react with additional peroxides, eventually yielding hydroquinones (Figure 4). The loss of the phenols and their protective benefits would allow for the gradual accumulation of peroxides while reducing the thermal stability – this is demonstrated by the slight increase in SMORS mass observed for the still and long-distance ULSD on Day 90 of car storage. (The short-distance ULSD was exposed to more environmental heat due to the construction of the vehicle and thus declined faster). These rebound peroxides can react with the generated phenols to yield hydroquinones; which can be converted to quinones during thermal stress. This is demonstrated by the quinone-like carbonyl bands in the IR spectra of generated tars and oils (Figure 16). As the quinones undergo further coupling reactions they will increase in molecular weight and eventually precipitate from solution – leading to the formation of oily layers and tars. The removal of these oxidatively reactive species from the bulk fuel is perhaps the reason
why the short-distance ULSD seemed to regain oxidative stability on Day 145 and why
the oily layer in the post-stress week 6 Breezewood ULSD was considerably reduced.

C. Hydroperoxide concentration and predicting storage stability

One of the earlier aims of this project had been to develop a method to monitor the
hydroperoxide concentration of fuel that was more automated than and less chemical
hungry than iodometric titration. This was done with the hopes that the results from this
method could be used to predict the oxidative stability of a fuel. This failed on both
counts. Firstly, the developed $^{31}$P NMR method lacked both sensitivity and
reproducibility. Secondly, the peroxide levels in an unstressed fuel have been observed to
increase in a more linear fashion – dependent on the make-up of the fuel rather than its
physical treatment. The two low-stability B20 blends in Figure 31A have similar
peroxide concentration, despite the fact that one was subject to the engine stressing and
one was not.

D. Agitation does not decrease the oxidative stability of a fuel blend

It had been anticipated that increased sloshing and agitation of a fuel blend would
serve to decrease its thermal stability. Indeed, the results of the initial car-storage
experiment seemed to suggest as much; as the more agitated fuel formed more peroxides
during the study and produced more SMORS upon thermal stressing (Figure 8\Figure 9).
However, the results of both bubbling experiments failed to confirm this observation;
neither did a repeat of the initial car storage experiment. Additionally, the unshaken
cumene/heptane blend formed more oxidation products (Figure 21). Rather, the
construction of the vehicle seemed to a be greater factor – the short distance car featured
a sun shade rather than a solid trunk. Furthermore, the in-lab stored ULSD generated the
most SMORS on the day 145 thermal stress, despite the fact that it had not been
subjected to any environmental stress.

E. Further Work

Given that the results of the car-storage study were utterly anomalous, the logical next
step would be to repeat the experiment, eliminating the agitation component and with
increased sampling. Additionally, since the results of the cumene storage experiment
indicate the formation of phenol under the same storage conditions – one of the storage
carboys should be spiked with a para-substituted phenol; so as to gauge whether such
phenols could serve a beneficial role in oxidative stability. Similarly, the cumene storage
ought to also be repeated – using tetradecane or some other high-boiling alkane solvent
rather than heptane, so as to allow for thermal stress studies.
Works Cited


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