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Towards Online Monitoring of Lubricant Antioxidant Depletion as Key Metric to Predict Oil Condition

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A B S T R A C T

Implementing condition-based maintenance of turbine lubricant oils is desirable to maximize machinery operation and minimize waste. Previous research indicates that relative antioxidant level is a good predictor of turbine oil condition, allowing for maintenance to consist of antioxidant replenishment. This present work investigates how antioxidants in a typical turbine oil deplete under accelerating aging conditions, and how these species can be monitored in terms of common antioxidant measurement methods based on commonly employed infrared absorbance and electrochemical methods. Common turbine lubricants typically comprise both amine and phenol antioxidants that interact in a synergistic manner, whereby the phenol antioxidant sacrificially regenerates the aminic antioxidant. The impact of this synergy on the respective observed degradation rates of the antioxidants is evaluated in terms of a simple framework, and rate equations for each species are then derived in the steady-state approximation limit. This work further evaluates the possibility of using online fluorescence sensing to track antioxidant depletion, which has fewer barriers to online implementation than current laboratory technologies. Online sensor implementation offers near real-time monitoring in contrast to the low temporal resolution of traditional offline sample-based laboratory methods, allowing operators to adopt agile lubrication management strategies.

1. INTRODUCTION

Lubricant oil has a myriad of functions, which include functions such as reduction of friction and wear between metal surfaces, heat transfer [1, 2]. Lubricant oil is a chemical mixture that consists predominantly of one or more base oils (80-90%) and chemical additives (10-20%) [3]. Despite their lower weight fraction, additives impart desirable properties to the formulation to meet target specifications and serve to prolong the useful life of the base oils. Monitoring lubricant oil to ensure that its lubricity and macroscopic physicochemical properties remain in-spec and contaminant-free is an important aspect of equipment maintenance. Doing this can prevent secondary, often costly, machinery damage and maintain equipment performance. For example, machinery corrosion can occur if oil is left unmonitored and there is an accumulation of acidic species and/or water within the oil. Industry recommended practices for oil condition monitoring are contingent on routine oil sampling followed by external laboratory analysis typically on a monthly or quarterly basis. A battery of laboratory standard test procedures has been developed, as there is no single analytical technique that can measure every relevant physicochemical property of the lubricant and screen for contaminants [4]. The main drawback of traditional oil sampling and laboratory analysis is that oil is not actively monitored in the interval between subsequent tests. In recent years, several companies have developed online sensors to provide operators with near-real time measurements of lubricant condition and contamination to enable condition and predictive-based maintenance strategies [5, 6].

Auto-oxidation in lubricant oils is the set of chemical reactions between components in the lubricant oil and oxygen species [7-9]. Typically, small molecule lubricant additives will chemically transform faster than the base oil under auto-oxidative conditions to form tribofilms on metal surfaces or oxidized byproducts [2, 9]. Auto-oxidation rates increase with temperature [10-13]. Oxidation occurs in practically all machinery usage since 21% of the earth's atmosphere is composed of oxygen, and because it has historically been uneconomic or impractical to operate machinery in all but certain niche applications under inert atmosphere [14]. Oxidation of the lubricant base oil results in changes to lubricant viscosity, which in turn affects lubricant film thickness. Insufficient film thickness can result in undesirable metal-on-metal contact during machinery operation. Lubricant manufacturers have long understood this and have mitigated the impact of auto-oxidation by adding antioxidant molecules into the formulation. The role of the antioxidant molecules is to react preferably with oxygen radical species before they can oxidize the lubricant base oil [3, 9]. By monitoring antioxidant level and its depletion rate, the remaining useful lifetime of the lubricant mixture can be estimated.

This work investigates how aminic and phenolic antioxidant additives in a typical ISO46 turbine oil deplete using the established laboratory techniques of Fourier Transform Infrared Spectroscopy (FTIR) and linear sweep voltammetry (LSV). First, several oxidized turbine oil samples were obtained by artificial lab degradation, whereby fresh lubricant was heated at an elevated temperature over the course of a few days. An in-service lubricant sample was also obtained and measured for comparison. Oxidation-induced changes were observed in both FTIR and LSV data. It was further observed that the phenolic antioxidant depleted significantly faster than the aminic antioxidant, consistent with previous literature findings. The role of phenol-amine antioxidant synergy was then investigated, and a simple kinetics model was developed and solved to yield rate equations for both phenol and aminic components within the steady state approximation. Here we show that the model can be used to fit experimental observations and provide qualitative intuition. The aim of this model is to provide industrial lubrication researchers and engineers with a practical mechanistic framework that explains the antioxidant depletion trends observed in ubiquitous amine-phenol lubricant formulations and can be further tailored or expanded. This work goes further in explaining the phenomenon of amine-phenol synergy which is typically only given cursory treatment in lubrication textbooks. Subsequently, this work evaluates the possibility of using online fluorescence to track antioxidant depletion. The data reveal that a fluorescence-based condition indicator can be used to develop a monotonic relation with phenol and aminic antioxidant level depletion obtained from LSV.

Fluorescence spectroscopy can be therefore used as a non-destructive proxy for antioxidant concentration. Therefore, a future viable strategy to track relative antioxidant levels online in turbine machinery oil may consist of a fluorescence based online sensor benchmarked to conventional offline measurements. Together, the integration of kinetic modelling with high temporal resolution fluorescence-based sensing represents a step towards predictive and in-situ lubricant health prognosis.

2. BACKGROUND

2.1 Turbine Lubricant Management

Although frequent scheduled draining and replacing of lubricant is a viable maintenance strategy that can be considered in certain machinery applications, there are financial and environmental costs associated with this practice [15, 16]. Cost savings can be realized in terms of preventative treatment and remediation of the lubricant oil that does not require a full drain. This is especially relevant in the context of gas turbine systems where the oil reservoirs can be significant in size, typically several thousands of liters. Full oil changes require equipment downtime, operator time and costs associated with waste disposal. Oil changes can also be a source of operator error in terms of inadvertently introducing external contaminants and/or adding incorrect oil. Therefore, machinery uptime may be optimized by operating with in-spec oil and only planning maintenance interventions when measurement reveals that the lubricant oil is no longer in-spec. This evaluation process is more commonly referred to as machinery condition-based maintenance [17]. An objective is therefore to develop good predictors and models of oil condition to ensure that condition-based maintenance is feasible.

A recent study by Ahmed *et al.* looked at lubricant oil lab analysis data of numerous turbine oil samples and found that the main predictors of turbine machinery health were acid number (AN) and solids (correlated to varnish potential) [18]. These are indeed good metrics associated with oil quality but are lagging indicators of oil degradation as these tests will typically yield high quantities only after significant oxidation of the lubricant oil has occurred. The root cause of both AN and varnish formation in turbine oils is auto-oxidation [9]. AN is a quantity that is derived from the concentration of acidic species in lubricant (organic acids formed by oxidation), whereas varnish is linked to formation of oxidized lubricant mixture components that tend to adhere to machinery surfaces or clog filters. Varnish can be soluble or insoluble forms., but the latter is typically what is tracked (in terms of ASTM D7843) using membrane patch colorimetry (MPC) [16, 19, 20].

High antioxidant levels are therefore a good indication of in-spec oil, as antioxidant depletion precedes lubricant degradation. While varnish and acids can still form prior to antioxidants reaching condemning limits (e.g. 25% of initial), their rate of formation is largely subdued until there has been significant antioxidant depletion [16, 21]. By keeping antioxidants high and trending their relative levels, varnish and acid formation rates can be effectively mitigated. To maintain elevated antioxidant levels, antioxidants can also be replenished either through bleed and feed or direct additive replenishment approaches [21]. Each approach has merits and drawbacks that should be evaluated in terms of the given application. Regardless of the approach employed, antioxidant levels should ideally be measured routinely to compute the required quantity of antioxidant required for replenishment, and to confirm that the replenishment operation was completed successfully.

2.2 Oxidation and Antioxidant Review

The fundamentals of oxidation and antioxidant additives in lubricant oils are extensively covered in textbooks and several review articles [3, 7-9]. For brevity, this section will then only provide a concise summary of the pertinent details.

The process of auto-oxidation creates peroxy radicals (ROO•) within the lubricant mixture. Primary antioxidant additives in lubricant oils are typically molecular compounds that react preferably with peroxy radicals. There are two major classes of primary antioxidants used industrially: amines, which possess a secondary amino (N-H) functional group, and phenolics, which possess a hydroxyl (O-H) functional group. General structures of phenolic and aminic antioxidants commonly used in turbine oils are given below as Fig. 1.

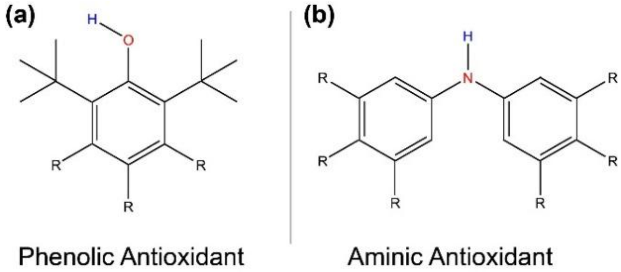

Fig. 1. Generic structures of antioxidants used in lubricants. (a) Phenolic general structure. (b) Aminic general structure

The importance of the hydrogen containing functional groups is that it provides a dissociable hydrogen atom that reduces the radical oxygen species and then leaves a corresponding aminyl or hydroxyl radical (N• or O•). Note that the O-H and N-H functional groups are attached to aromatic rings. Aromatic rings are necessary to impart stability of the N• or O• through resonance stabilization. The -R groups on the structures are ligands associated with providing solubility.

So, more generally, an antioxidant can be defined as AH, and its oxidized radical form as A•. The reaction of an antioxidant with a peroxy radical is given by equation (1):

$$AH + ROO\bullet \rightarrow A\bullet + ROOH \qquad (1)$$

Where AH is an antioxidant, ROO• is a peroxy radical species, A• is an antioxidant radical species and ROOH is a hydroperoxide.

2.3 Methods to measure antioxidants or oxidation resistance

There are various laboratory methods to measure lubricant antioxidant levels or oxidation resistance. Four commonly used approaches, Linear Sweep Voltammetry (LSV), Fourier Transform Infrared Spectroscopy (FTIR), Rotating Pressure Vessel Oxidation Test (RPVOT), and High-Performance Liquid Chromatography (HPLC) are contrasted in **Table *1.*** List of methods used to measure antioxidants and lubricant oxidation.Table 1. Clarifying descriptions and rationale for the entries in each cell of the table are provided in the respective subsections below. The cost rating refers to the typical relative laboratory cost of running a sample or setting up a new method that a commercial lab would charge to a typical machinery operator.

Table 1. List of methods used to measure antioxidants and lubricant oxidation.

Method	LSV	FTIR	RPVOT	HPLC
Raw Meas.	Current	Optical	ΔP	Optical
Meas. Antioxidant	Yes	Partial	No	Yes
Meas. Oxidation	No	Yes	Yes	Partial
Min. Sample qty	< 1 mL	< 1 mL	~60 mL	< 1 mL
Upkeep Level	Medium	Low	High	High
Consum.	Yes	No	Yes	Yes
Cost	$$	$	$$$	$$$$

2.4 Linear Sweep Voltammetry (LSV)

LSV is an industry standard method that is associated with measuring remaining antioxidants. It does this electrochemically, through the oxidation of remaining antioxidant molecules in the lubricant. The remaining antioxidant is proportional to the measured current. The main ASTM method associated with the technique is ASTM D6971. Linear Sweep voltammetry can distinguish between amine and phenol species as their oxidation potentials are significantly different. LSV is viewed in industry as a useful, but niche expensive measurement. Details such as electrolyte selection, scan rate, electrode polishing, and pulse modulation techniques also impact LSV data quality. Commercial labs typically use the settings suggested in reference to ASTM standards. Electrode cleaning and resurfacing is time consuming, and LSV requires pre-prepared or commercial proprietary electrolyte solvents as consumables (consum.). For this reason, it is not as commonly used in oil analysis as FTIR-based methods.

2.5 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a ubiquitous method of choice for oil analysis in the lubricant industry. FTIR has general sensitivity to many components within the lubricant mixture. At a qualitative level FTIR can detect presence of antioxidants. For instance, the signature of aminic antioxidants is a N-H stretching mode, whereas the presence of phenolic antioxidants is associated with presence of an O-H stretching mode. Despite this, the drawback is that quantitative FTIR can be difficult to achieve, due to spectral interferences, baseline drift and changes in vibration mode position due to matrix effects. Quantitative outcomes can sometimes be realized by employing internal standards at the cost of further method development. For this reason, FTIR is generally employed in the lubricant industry for semi-quantitative oxidation trend analysis and qualitative assessment, rather than for quantitative measurements of antioxidant levels. Trend analysis methods are described in more detail in ASTM E2412.

2.6 Rotating Pressure Vessel Oxidation Test (RPVOT)

RPVOT looks at the oxidation potential of the lubricant mixture, by measuring the pressure drop (ΔP) of oxygen gas in a sealed vessel along with a lubricant sample, water and copper catalyst. Although it can provide information with respect to the oxidative stability of the lubricant, it does not further discriminate in terms of the antioxidant type or provide chemical information. Test length and catalyst preparation drive up the cost of the method. Additionally, at approximately 60 mL (50g) of oil, minimum sample quantity is significantly higher than the other techniques.

2.7 High Performance Liquid Chromatography (HPLC)

HPLC is arguably the method that is the most versatile to study many aspects of the lubricant mixture as chromatography effectively isolates specific molecular components of the lubricant mixture for analysis. For this reason, given a suitable method, antioxidants and other additives can be directly observed using HPLC. The major drawbacks are that elution conditions and column choice need to be tailored to the oil formulation, requiring added cost in method development. Furthermore, in terms of retention time either molecular standards or additional information concerning the spectral properties of the antioxidants are required to correctly identify chromatographic peaks. If the antioxidant structure is known, then Liquid Chromatography can be coupled to Mass Spectroscopy (MS) to confirm antioxidant identity. This is also not always straightforward and may also require substantial method development.

2.8 Summary and Outlook

Based on minimum sample volumes, cost and ability to discriminate and measure phenolic and aminic antioxidants, the combined use of FTIR and LSV offers a practical, balanced and generally cost-effective solution to monitor lubrication health. Due to its lower sample cost, FTIR offers the highest value proposition for operators, and therefore will generally be the most utilized method. Although true quantitative determination is better achieved with HPLC, LSV can still yield relative antioxidant levels for both aminic and phenolic antioxidants. The relative quantitative information obtained by LSV can be further supported by information obtained by semi-quantitative FTIR oxidation trending to limit false positives and negatives. Ultimately, the goal is to use LSV and FTIR as ground truth training data for online sensor development.

3. EXPERIMENTAL METHODS

3.1 FTIR

A Fourier Transform Infrared-Spectrometer (FTIR) (Agilent Cary 600) equipped with variable pathlength (DialPath®) liquid sample accessory was used. The path length was set to 200 μm. Loading liquid samples onto the DialPath® is similar in usage to FTIR ATR-based instruments and requires only a small amount (<200 μL) of neat lubricant sample to be applied over the surface of the window. FTIR measurements were obtained 4000-600 cm^{-1} with a total of 155 scans and spectral resolution of 4 cm^{-1}. A baseline under ambient conditions was taken prior to each measurement and automatically subtracted from each measurement within the instrument software.

Oxidation Number analysis was baseline corrected and computed as per ASTM E2412 using the Direct trending approach [22]. FTIR data was smoothed using Savitzky-Golay filter and then areas were integrated using the trapezoidal method. Oxidation Number values obtained by integration from 1800 cm^{-1} and 1670 cm^{-1} were divided by a factor of 2 to correct to a 100 μm optical pathlength.

3.2 LSV

Linear Sweep Voltammetry (LSV) measurements and raw data analysis were outsourced to a commercial laboratory.

Computed amine and phenol % levels along with raw amperogram vs time plots were provided by the external laboratory. Computed amine and phenol % values were used as-is without further modification from the external laboratory. LSV instrument settings and experimental details were not disclosed by the laboratory. Total area analyses were computed by baseline correcting and integrating regions under the respective areas using the trapezoidal area method.

3.3 Fluorescence

Fluorescence measurements were taken using a fiber-optic based fluorescence apparatus setup developed by Gastops Ltd. which is described in prior works [23, 24].

3.4 Lubricants received

Lubricant samples consisted of fresh and in-service commercial GT 46 oil samples provided by Saudi Aramco (Abqaiq, Saudi Arabia). The in-service sample is not necessarily from the same batch as the received fresh GT46. The samples received were stored at room temperature for the duration of the study prior to degradation.

3.5 Sample degradation

To degrade samples, a 1L heating mantle (Digital Laboratory 1000ml Heating Mantle with Magnetic Stirrer, Joanlab) set to a fixed temperature of 170°C was used in conjunction with a 3-neck borosilicate round-bottom flask and PTFE coated olive stir bar (35mm). The apparatus was installed in a chemical fume hood with proper ventilation. Approximately 500 mL of fresh GT46 oil was added to the 3-neck flask. A schematic of the setup is provided below as Fig. 2. The fresh GT46 oil appeared translucent and yellow, whereas the degraded samples gradually darkened to a brown color over time. The 170 °C temperature was found to be a good compromise between ability to degrade the GT46 oil to a condemning limit within the test period, allowing for several samples to be drawn across three working days (42 hours total time). Magnetic stirring was employed and the rate held constant throughout the degradation process to ensure adequate mixing.

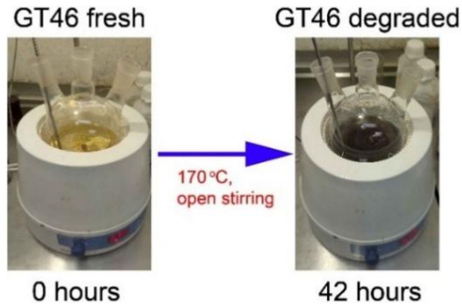

Fig. 2. GT46 sample degradation schematic showing photos of fresh and degraded states of GT46 sample in heating mantle.

The procedure outlined above is generally applicable to many lubricant types. The temperature of 170 °C also balances the time required to oxidize the lubricant sample and the corresponding risk of boiling and/or burning samples at higher temperatures. It should be noted that while this work did not explicitly evaluate the variance of sample degradation, we expect that this will be the major contributor to experimental uncertainty. Future work will aim to quantify this variance and compare it to replicate measurement uncertainties of the FTIR, fluorescence and LSV methods. It should be noted that our experience has been that measurement uncertainty is generally not provided in commercial laboratory reports, and so this work may preclude outsourcing samples for analysis.

3.6 Sample drawing

Samples consisted of GT 46 samples drawn from the round bottom flask at 3, 18, 24 and 42 hours. At various intervals 20 mL samples were drawn from the heating mantle using a disposable lab glass pipette and bulb into a 50 mL glass beaker over the course of approximately 1 minute. Caution: The oil is quite hot, despite the low thermal conductivity of the glass pipette, so ensure that proper heat-resistant PPE is used. The oil collected in the glass beaker was left in the fume hood to cool down to room temperature. 20 mL of fresh unheated sample was also set aside and used as a reference (0 hours). 20 mL of unheated in-service GT46 sample was also included in the dataset for comparison.

The 20 mL quantity of each sample was chosen to have sufficient sample for the measurements. The breakdown is: approximately one drop (~200 μL) was required for FTIR analysis using measurement accessory and pathlength specified above; approximately 10-15 mL of sample was needed for non-destructive fluorescence measurements using a similar fluorescence apparatus setup described in prior work [23]. A minimum of 4 mL per sample was required to send for external LSV analysis as specified by the external laboratory.

3.7 Software

Custom code using Python 3, NumPy, Matplotlib, Sklearn and SciPy libraries were used to process data, prepare plots, compute kinetic models and fit models to data, and calculations in the manuscript. Differential equations were solved numerically with the SciPy library, using RK45 or Radau methods.

4. RESULTS AND DISCUSSION

FTIR was first employed as a screening tool as samples were collected at the degradation times specified above. FTIR was first used to qualitatively determine the presence of phenolic and aminic antioxidant features in GT 46, and how these spectral features are impacted by degradation time. Fig. 3 shows the FTIR spectra of the GT46 lubricant at various degradation times in addition to an in-service sample of GT46 in the spectral regions of 3700 cm^{-1} – 3550 cm^{-1} and 3500 cm^{-1} – 3300 cm^{-1} respectively. These regions correspond to where phenolic and aminic antioxidant features are generally present. The FTIR results suggest that both phenolic and aminic antioxidants are present with peaks within the GT46 lubricant.

Panel (a) shows the O-H stretch mode highlighted in blue, with a central peak frequency of 3645 cm^{-1}. From the initial time to 42 hours the central peak frequency is observed to red-shift by approximately 6 cm^{-1}. The red-shifting associated with phenol decay is consistent with previous observations [25]. Panel (b) shows the aminic antioxidant stretch shown in blue with a central peak frequency of 3436 cm^{-1}. In contrast to the phenolic peak, the aminic peak does not show prominent spectral shifts over time. For comparison, FTIR peak frequencies obtained from the literature of a sterically hindered phenol (2,6-Di-tert-butylphenol) and diphenyl amine (Benzenamine, N-phenyl-) are plotted in (a) and (b) as vertical dashed lines. The O-H stretching frequency for 2,6-Di-tert-butylphenol in CCl_4 is given as 3645 cm^{-1} [26]. The N-H frequency of Benzenamine, N-phenyl- in CCl_4 is given as 3432 cm^{-1} [27]. These values are in good agreement with the results obtained. Note that these structures are representative cores of commonly employed phenolic and aminic antioxidants. Actual antioxidants would additionally contain alkylated substituents, to impart solubility with paraffinic lubricant base stocks.

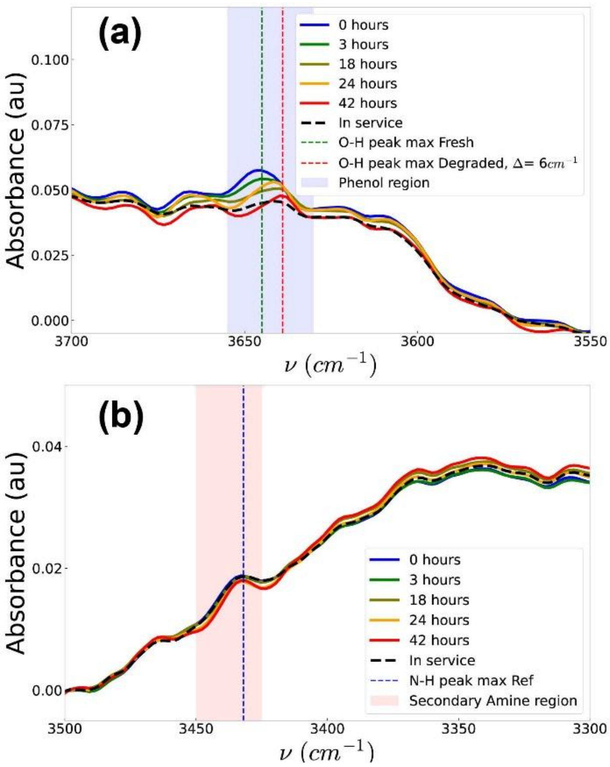

Fig. 3. FTIR plots of GT46 oil antioxidant features. (a) FTIR spectra of GT46 samples at various degradation times between 3700 cm-1 and 3550 cm-1, in the phenolic region highlighted in blue. (b) FTIR spectra of GT46 samples at various degradation times between 3500 cm-1 and 3300 cm-1 in the aminic region highlighted in red.

A common usage of FTIR in condition monitoring lubricants is to look at the formation of oxidized species, in particular formation of carbonyl (C=O) modes which typically appear between 1800 cm^{-1} -1670 cm^{-1}. The intensity of the carbonyl modes can be used to semi-quantitative trend lubrication oxidation, using the Direct Trend method described in ASTM E2412. Fig. 4 (a) shows the carbonyl region for the GT 46 samples (b) is a plot of the samples corresponding oxidation numbers at their respective degradation time. A monotonic increase in oxidation number is obtained for the samples with increasing degradation time. The data is well described by a linear fit, which is plotted as a dashed red line. Based on the obtained linear relation, the in-service sample has an oxidation number that should be equivalent to a degradation to that of an 8.6 hour sample degraded at 170°C.

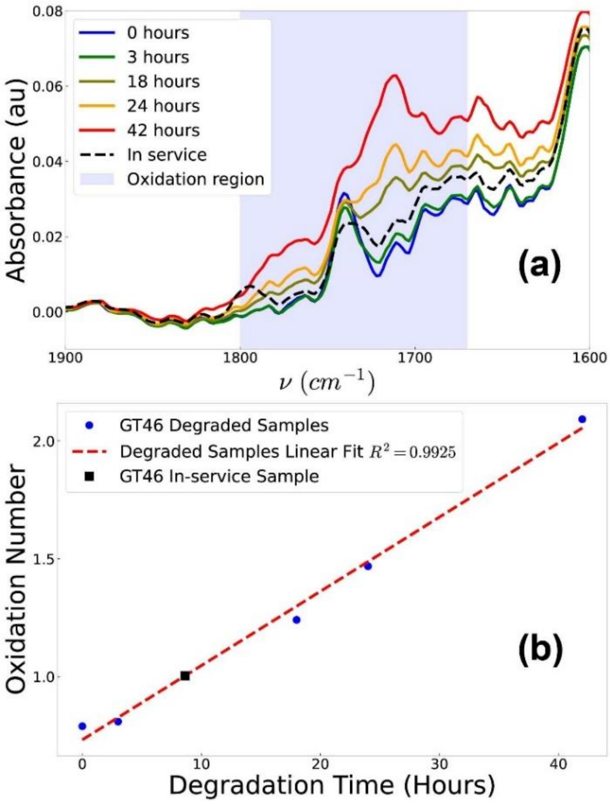

Fig. 4. FTIR plots and processed oxidation of GT46 oil oxidation features. (a) FTIR spectra of GT46 samples at various degradation times between 1900 cm-1 and 1600 cm-1, in the oxidation region highlighted in blue. (b) Plot of oxidation number vs Degradation time.

To gain further quantitative insights into the antioxidant degradation rates of GT 46 lubricant, samples were sent for LSV measurements. The LSV data in terms of amine % and phenol % are tabulated along with the computed oxidation numbers in Table 2. As per convention in LSV, the reference (0 hour) GT46 sample has amine % and phenol % set to 100. The LSV results confirmed the presence of phenolic and aminic antioxidants, in agreement with FTIR observation. The results show monotonic decreases for both the aminic and phenolic levels with increasing degradation time, with the phenolic levels depleting prior to the aminic levels. This is in general agreement with what is typically observed in lubricant systems and has been explained in terms of amine-phenol synergy, whereby the phenol will regenerate the aminic antioxidant. A depletion rate of the amine that is greater or comparable to that of the phenol may occur in cases where there is high water content that effectively blocks hydrogen abstraction. The depletion of antioxidants is also inversely related to the increase of FTIR oxidation number. This is an intuitive result, as the depletion of antioxidant scavengers increases the probability that peroxy radicals or other reactive oxygen species will oxidize the base oil, leading to the formation of carbonyl (C=O) functional groups.

Table 2. Tabulated Results from LSV and Oxidation Number (ASTM E2412).

GT46 Degr. Time (hours)	LSV Phenol %	LSV Amine %	Oxidation Num.
0	100	100	0.79
3	63	92	0.81
18	20	70	1.24
24	8	54	1.47
42	3	22	2.09
In-Service	69	*100*	1.00

Note that the In-service sample also showed an LSV amine % of 100. This was confirmed to be an artifact from the lab LSV metric output, which sets a ceiling of 100% to the amine sample based on the area of reference (0 hour) sample. Upon inspection of the raw amperograms, the area of the in-service sample was confirmed to be greater than that of the reference sample. This stems from the fact that the fresh reference sample and in-service sample may not come from the same lubricant batch. For this reason, conclusions should not be made regarding the LSV phenol levels in comparison with the degraded sample.

Fig. 5 plots the sample LSV % levels against degradation times. The phenol % and amine % LSV scores can be well described by simple functions. The phenol % vs degradation time data shown in (a) is well described by an exponential decay model, which is typical of first-order reactions. By contrast, the amine % LSV data in (b) appears to decay linearly, which matches other reports [16]. (c) shows the total LSV %, which is defined as the area of the phenol and amine peaks in the amperogram, divided by the total area of the reference sample [21]. This metric, although not typically used and defined, is a proxy for the total antioxidant level in the lubricant. It is also well described by an exponential decay model.

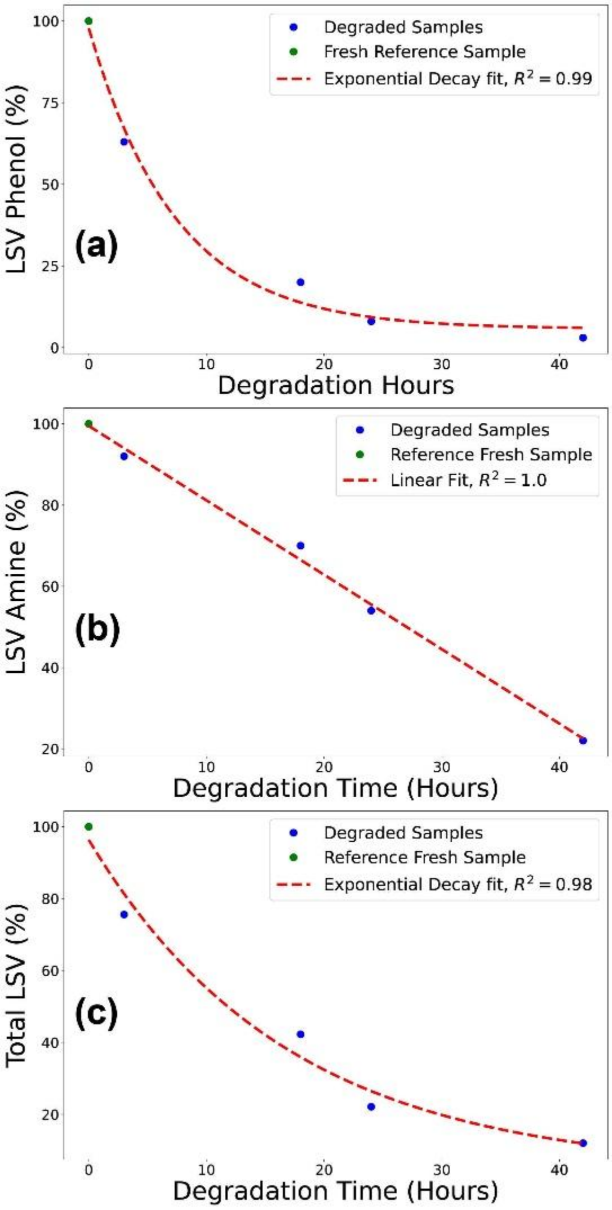

Fig. 5. Plots of GT 46 LSV scores vs. sample degradation time. (a) LSV Phenol decay. (b) LSV Amine decay. (c) Total LSV (Areas of Phenol and Amine divided by reference total.)

4.1 Amine phenol synergistic effects

It is well understood that using two or more antioxidant molecules can have synergistic effects [28, 29]. For instance, using a primary antioxidant and a secondary antioxidant is effective as the former can scavenge radical peroxides and the latter radical hydroperoxides. Certain commercial lubricants contain two primary antioxidants, one consisting of amine, and the other a phenol. The commonly attributed reason is that in such systems the lower-cost phenolic antioxidant can serve to regenerate the higher cost but higher efficacy aminic antioxidant, optimally extending the overall useful life of the oil [8]. Economic considerations aside, the chemical details of this synergy and how it manifests itself in terms of the experimental observations are relevant in the context of antioxidant depletion monitoring methods.

Industrial aminic antioxidants generally have a lower one electron oxidation potential than phenolic antioxidants, and antioxidant ability is correlated with lower oxidation potentials [30]. This difference in oxidation potential is reflected in terms of the standard linear sweep voltammetry ASTM method, whereby the aminic oxidation peak is observed prior (at a lower voltage) to the phenolic peak (higher voltage) [31, 32]. This may partially explain the higher observed aminic reactivity observed in literature, where diphenylamine has an inhibition rate nearly double that of the sterically hindered phenol at 100 °C [33].

However, due to the synergistic effects in amine-phenol systems, phenolic antioxidants are always depleted before aminic antioxidants. The phenol has a lower bond dissociation energy which allows the regeneration of the (secondary) amine to be thermodynamically favorable [34]. The regeneration mechanism is explored in the following sections.

4.2 Chemical Kinetics model

To better understand whether simple models accurately describe the chemical kinetics of phenol-amine lubricant systems, a chemical kinetics analysis was completed. Following a similar approach as Omrani et al. [35], a set of rate equations (2-5) are written out in terms of the amine (AmH), Phenol (PhH), aminyl radical (Am•), phenoxy radical(Ph•), peroxy radical (ROO•) and hydroperoxide (ROOH).

$$AmH + ROO\bullet \overset{k_1}{\rightarrow} Am\bullet + ROOH \quad (2)$$

$$Am\bullet + PhH \overset{k_2}{\rightarrow} AmH + Ph\bullet \quad (3)$$

$$PhH + ROO\bullet \overset{k_3}{\rightarrow} Ph\bullet + ROOH \quad (4)$$

$$Am\bullet \overset{k_4}{\rightarrow} \emptyset \quad (5)$$

Reactions (2) and (4) describe hydrogen abstraction (atom transfer) from an amine or phenol to a peroxy radical as previously discussed in a general sense in equation (1). Reaction (3) describes the regeneration of the aminic antioxidant by the phenol. As discussed previously, this reaction proceeds due to the greater thermodynamic stability of the Ph• compared to Am•).

The symbol ∅ in (4) represents a decay pathway to non-radical products of Am• which are no longer considered. This reaction is needed as a sink so that Am• competes to react with other radical species to eliminate, instead of being indefinitely available for reaction with a phenol as in (2). Formally, (4) is a simplification, as another radical reactant, (e.g. ROO•, Am•, etc) is required to create ∅ (non-radical product(s)). A corresponding reaction also exists as a sink for the Ph• but it is not required in this simple picture as the species is only a product in (2) and (3) and not a reactant.

The differential rate equations can be written as equations (6-8):

$$\frac{d[AmH]}{dt} = -k_1[AmH][ROO\bullet] + k_2[Am\bullet][PhH] \qquad (6)$$

$$\frac{d[PhH]}{dt} = -k_2[Am\bullet][PhH] - k_3[ROO\bullet][PhH] \qquad (7)$$

$$\frac{d[Am\bullet]}{dt} = k_1[AmH][ROO\bullet] - k_4[Am\bullet] - k_2[Am\bullet][PhH] \qquad (8)$$

This set of differential rate equations can be solved numerically. The value of $[ROO\bullet]_0$ is fixed as a constant, such that $[ROO\bullet]=[ROO\bullet]_0$ and assumed to be present in large excess. This assumption is tied to excess oxygen availability given ambient atmospheric conditions. Starting concentrations of AmH and PhH are set to 1.0 (Normalized relative concentration), and the starting concentration of [Am•] is assumed to be 0.

4.3 Steady State Approximation

It is possible to go one step further to simply the rate equations invoking a steady state approximation (SSA) for the intermediate Am•. Formally this step is to set the rate of change of [Am•] to zero. In essence this means that the rate of formation and depletion are equal. This assumption can be made as the aminyl radical is very reactive and therefore short-lived. This approximation is also made as most industrial researchers will not have the capability to measure the transient aminyl concentration, and it has the added benefit of further simplifying the equations into simpler analytical forms. Then equation (6) can be rearranged to:

$$\frac{d[Am\bullet]}{dt} = 0 = k_1[AmH][ROO\bullet]_0 - [Am\bullet](k_2[PhH] + k_4\,) \qquad (9)$$

By further algebraic rearrangement the following expression is obtained:

$$[Am\bullet] = \frac{k_1[AmH][ROO\bullet]_0}{(k_2[PhH] + k_4\,)} \qquad (10)$$

Then by substitution of [Am•] into equations (7) and (8) It is possible to generate equations (11) and (12).

$$\frac{d[AmH]}{dt} = \frac{-k_1k_4[AmH][ROO\bullet]_0}{(k_2[PhH] + k_4\,)} \qquad (11)$$

$$\frac{d[PhH]}{dt} = -[ROO\bullet]_0[PhH]\left(\frac{k_1k_2[AmH]}{(k_2[PhH] + k_4\,)} + k_3\right) \qquad (12)$$

Like (6-8), equations (10-12) can also be solved numerically. This allows us to assess the validity of the steady state approximation and the values of k_1-k_4 can then be determined from a fit to normalized LSV amine and phenol data from Table 2.

Solving the rate equations in equations (9)-(11) was done numerically, and the resulting rate equations were fit to the LSV for the phenol amine and as shown in Fig. 6. (a) Shows that the rate equations can fit the obtained data and have similar forms to the simple linear and exponential equations fit in Fig. 5. At this point, no attempt to derive any further quantitative information regarding the rate constants given the limited dataset was made. The goal is simply to validate why phenomenological simple models can successfully describe the decay of the phenol and amine. The second insight provided by this exercise pertains to the relative rates. In this model, rates k_2 and k_4 must be comparable for there to be a linear amine loss. If $k_2 \gg k_4$, then the amine concentration would remain constant until the phenol is significantly depleted. In other words, the rate of amine regeneration cannot keep up with the loss of Am• specified in (5). A depletion rate of amine that is greater or comparable to that of phenol may occur in cases where there is high water content that effectively mitigates the hydrogen abstraction process in equation, creating a scenario where $k_4 \gg k_2$ (3).

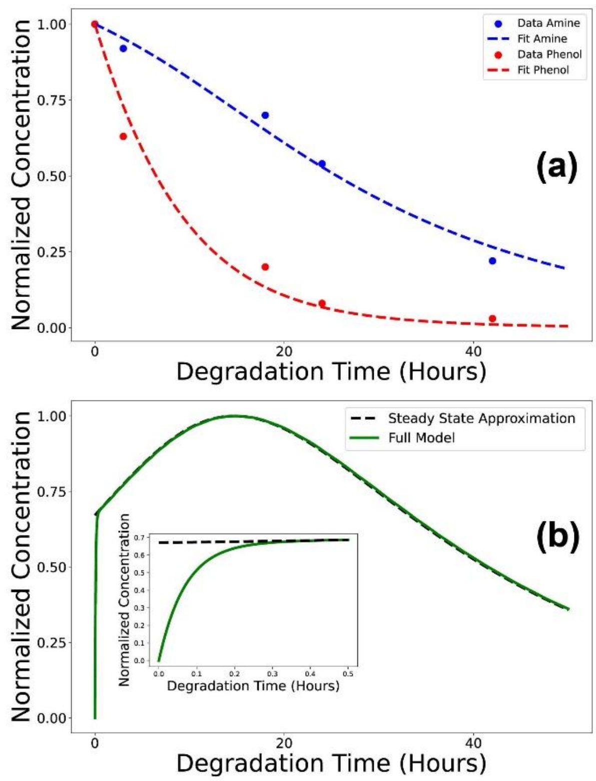

Fig. 6. Kinetic models fit GT 46 LSV scores vs. sample degradation time. (a) LSV Phenol and Amine decay plots. (b) Plot of the aminyl (Am•) concentration using steady-state approximation and full rate equations. Inset: Plot of the aminyl concentration reaching the steady state concentration as computed by the full rate equation at early times.

The differences between the steady state approximation instead of the full rate equation treatment is also evident based on a plot of [Am•] shown in **Error! Reference source not found.** (b). Using the rates k_1-k_4 obtained from the fit, the concentration of [Am•](t) converges to the steady state approximation obtained in equation (10). The major difference is shown in the panel inset, where the steady state approximation assumes that there is a starting concentration of [Am•] at t=0, whereas the full rate equation assumes that its starting concentration is 0 and gradually increases over an induction period of 0.5 hours. This demonstrates that for our purposes, the steady state approximation is effective to describe the general kinetics of the intermediate over the course of the reaction but is not strictly correct at early reaction times.

4.4 Limitations of LSV/ Future Work

Although the LSV measurements were outsourced to a commercial laboratory, there are important considerations of the method that should be highlighted.

A common pitfall of the LSV methodology is in ensuring that the correct fresh reference oil from the same batch as the in-service and/or degraded samples is used. As shown in this work, there can be batch to batch variability in antioxidant concentration, and so the relative antioxidant concentration of 100% is only meaningful if a correct reference is employed. Data analysis from the laboratory should also be scrutinized, as their report output will also bound to antioxidant sample levels from 0%-100%, even if the measured peak current is greater than the reference sample. Although not disclosed here by our laboratory provider, experimental factors such as electrode preparation, potential window selection, sweep rate and electrolyte preparation need to be considered and fixed throughout the series of measurements. In some systems there is a possibility of peak overlapping between antioxidant species further complicating data analysis. Possible improvements to the LSV method can be realized in terms of using differential pulsed voltammetry, which can improve measurement sensitivity by modulating the applied voltage. It should be noted however, that the latter is not currently an ASTM approved method.

In the absence of amine regeneration via the phenol, under high-temperatures degradation simulating aviation engines aminic antioxidants have been observed to decay with first-order kinetics [36, 37]. This would be consistent with the kinetics model presented in the previous section where equation (4) is removed. However, in the case of diphenylamine another regeneration pathway going through a nitroxide intermediate have been reported [38]. This regeneration pathway mitigates the decay of the aminic antioxidant, at the cost of oxidizing the base oils. As discussed previously, the formation of carbonyls can be trended through FTIR oxidation number. Whether the nitroxide regeneration pathway changes the diphenylamine decay from exponential (first order) to linear (appearing zeroth order) or not under the conditions employed in this work is something that would need to be experimentally verified. To verify this, the procedure used in this work can be employed on a suitable turbine oil only containing a diphenylamine antioxidant.

This work also reveals that if performed carefully, LSV offers a good compromise between cost and ability to perform kinetic measurements, which is typically the domain of HPLC or other chromatography methods. The lack of separability in LSV is mitigated by the fact that there is a sufficient difference in oxidation potential between the antioxidant and its degradation products. In the optimal case, the amperogram peaks can be well-resolved. Examples of this are in the N-Phenyl-1-naphthylamine (PAN) system where formed oxidation byproducts are located at a lower oxidation potential than the parent antioxidant. [39] In this case, LSV is effectively able to disentangle the various populations. In cases where it is unable, it may still be useful as an indicator of antioxidant potential of the lubricant, as the first oxidation products of antioxidants also have antioxidant ability [8]. Nevertheless, to validate the kinetics obtained by LSV, studies involving HPLC would be useful to accurately measure antioxidant levels [36, 38]. Future work may explore this avenue.

4.5 Online Implementation

While LSV is an effective offline technique for antioxidant tracking, due to its use of electrolyte consumables and electrode maintenance it is not directly amenable to online implementation. One approach to provide online measurement is to use a suitable technique that directly probes antioxidants, requires no consumables, is robust to environmental factors of temperature and vibration, and that provides a high sampling rate (at least 1 measurement per hour) and high time resolution (<1s) for near-real time measurement. One possible technical approach that can meet these general requirements is fluorescence spectroscopy. Antioxidants, due to their aromatic structures, are fluorescent molecules. Fluorescence spectroscopy can be used in online format using fiber optic cables and require no consumables. Fluorescence of antioxidants has the inherent advantage of being high frequency (~10^{15}-10^{13} Hz), that do not couple with typical machinery vibrations (1-3000 Hz). Fluorescence lifetimes for antioxidant molecules are typically in the order of nano-microseconds, allowing for high temporal resolution. An example of an implementation is described in more detail in prior publications [23, 24]. In terms of practical implementation aspects, fluorescence is better suited to steady state temperature conditions where the antioxidant photoluminescence quantum yield is stable. Other important experimental measurement considerations include the fluorescence measurement geometry to avoid inner-filter effects, excitation-source selection and careful consideration of spectrometer sensitivity and spectral resolution. Spectrometer integration time and averaging needs to be properly set to ensure high signal to noise and avoid detector saturation. Particularly, in terms of fiber-based fluorescence systems, selection of fiber optic properties, such as numerical aperture, fiber diameter, and material properties such as hydroxyl content also need to be considered.

The current work used the setup as previously described to measure the fluorescence signal from the GT46 sample set. A processed metric, termed the normalized fluorescence score was computed. Previous work on in-service samples demonstrated that normalized fluorescence correlated reasonably well for in-service turbine samples [24]. Fig. 7 shows the correlation between the LSV results and Normalized Fluorescence scores for LSV phenol, LSV amine and LSV total in panels (a), (b) and (c) respectively. The phenol and total LSV data show good agreement with a linear fit.

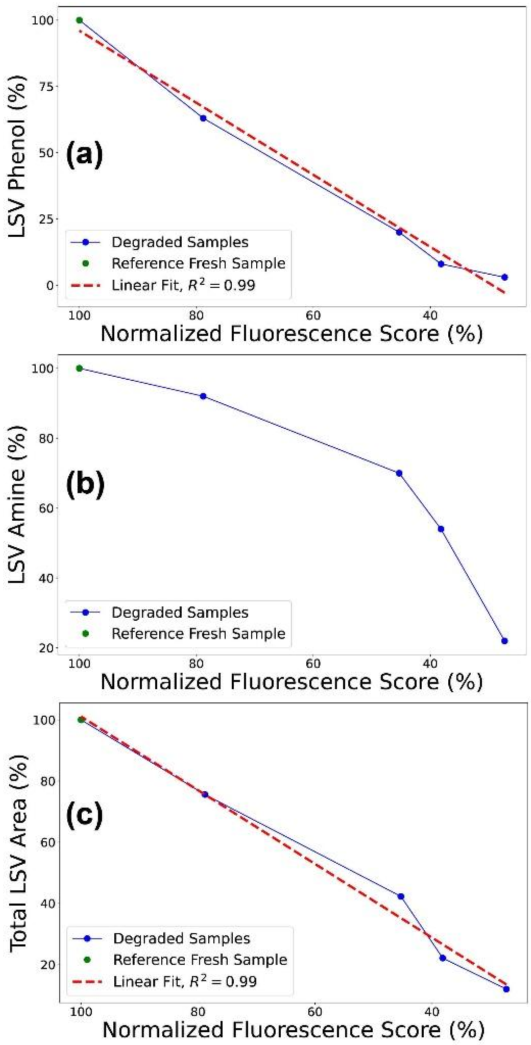

Fig. 7. Plots of GT 46 LSV scores vs. normalized fluorescence score %. (a) LSV Phenol vs Fluorescence.

(b) LSV Amine vs Fluorescence. (c) Total LSV % vs Fluorescence.

Compared to the study conducted with in-service samples obtained previously [24], the fluorescence score exhibits excellent correlation ($R^2 > 0.99$) for the linear cases. It should be noted that the oils considered in this study were single antioxidant systems, compared to the mixed phenol-amine GT46 oil in this work. Although this is ideal lab degraded data, this clearly establishes that a fluorescence spectroscopy derived condition indicator effectively tracks antioxidant depletion. A likely source of error in the previous study may have also stemmed from the issue of not having matched LSV reference samples to the specific in-service sample lubricant batch, as was observed in the case of the provided in-service GT46 sample. Other sources of error could pertain to non-uniformity of oil degradation in real world systems, sampling methods and delay between sample acquisition and measurement. These factors have been carefully mitigated in the current study in terms of constant temperature and homogeneity imparted by our heating mantle setup, ensuring that representative samples were drawn across a span of degradation times and that external lab LSV measurement took place within 10 days of sample degradation.

In terms of LSV, the condemning limit is usually set to 25% of remaining amine antioxidant for mixed phenol aminic systems [16, 19, 21]. Therefore, for practical implementation of online oil condition monitoring, the most important consideration is to correlate fluorescence with LSV amine %. Monitoring depletion of phenol and the total LSV area can still offer additional insights and validation checks and may offer easier interpretability for online measurement during antioxidant replenishment.

5. CONCLUSION

This paper investigated turbine oil condition monitoring, particularly in the context of antioxidant depletion. Antioxidants are particularly important given that antioxidant depletion indicates significant oxidation that will lead to formation of varnish and organic acids. Thus, antioxidant depletion is a good condition indicator that precedes increases in other commonly used metrics such as AN, MPC ΔE or FTIR oxidation number. This work also showed that under laboratory settings, high quality measurements of antioxidant depletion can be obtained using the standard LSV technique that agrees with FTIR oxidation number trends.

This paper also looked at the question of typical antioxidant compositions in turbine systems. Turbine lubricants contain phenol antioxidants, amine antioxidants or a mixture of both. This work looked at a commercial GT46 lubricant mixture that contains both antioxidants as evidenced by both FTIR and LSV measurements. Results in this work agreed with previous observations that in combined phenol amine systems, phenols will deplete significantly faster than amines. This was attributed to synergistic effects that lead to phenols effectively regenerating amines. Core assumptions underpinning phenol amine synergistic effects were examined and then explored further in terms of a set of kinetic rate models. The kinetic rate models could be used to fit LSV data for both amine and phenol depletion and provide further insight as to why an exponential decay model well describes phenol decay, whereas amine decay is well described by a linear decay model. This work suggests a path forward to performing more detailed kinetic studies also supported by HPLC measurements. Future research will focus on online implementation results as well as more in-depth studies of amine, phenol and mixed amine-phenol systems. By extending the procedure to a larger number of lubricants in these respective categories it will be possible to evaluate whether the simple LSV kinetic models developed in this work can be further generalized.

LSV is inherently ill-suited for online integration due to use of reagents and electrode fouling concerns requiring frequent cleaning. However, if LSV is used instead as a method to calibrate an online sensor, then a useful near real-time lubricant condition indicator correlated to antioxidant level(s) can trend. This work showed that LSV data can be used to calibrate fiber-based fluorescence spectroscopy, which is a technique that is well-suited for online sensing of machinery in real-world conditions. Fluorescence spectroscopy can also offer a broader monitoring solution than LSV, detecting other lubricant failure modes such as fuel contamination. While online fluorescence does not negate the value of performing offline FTIR and/or LSV measurements, it has the potential to become an effective, compact and cost-effective tool that provides operators with useful high temporal resolution feedback regarding antioxidant levels between periodic oil analysis intervals. This work suggests that fluorescence-based condition monitoring is viable under laboratory degradation settings. Ongoing and future work will focus on validating this premise in gas turbine lubricant systems. Implementing an effective predictive maintenance strategy will require reliable and accurate online monitoring as a foundation.

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