Ester basestock vaporisation from thin oil films

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ABSTRACT

Volatile materials, released by lubricants, relate to various engineering, occupational and workmanship aspects. Most tests (flash point, NOACK, TGA etc.) assess thermodynamic evaporation without focusing on prolonged oxidation and hydrolysis, which can also produce volatiles, especially in unsaturated esters. A thin film test was adapted for long-term (2000 h+) vaporisation studies in dry or humid atmosphere. Rapeseed oil and oleate esters showed initial weight gain due to peroxide formation at 50–130°C. Only afterwards release of volatiles began and approached 5%wt. in rapeseed oil. FTIR demonstrated significant oxidation even in cetane. Antioxidants had only slight effects on rates and tendencies, while 20% relative humidity clearly accelerated vaporisation. Acidity buildup was much faster in oleyl alcohol than in stearyl alcohol despite similar vaporisation trends. Although decomposition appeared much slower than the combined rate of oxypolymerisation and saponification, such film-based methodology represents a powerful tool to investigate long-term vaporisation tendencies of lubricants. © 2017 John Wiley & Sons, Ltd.

INTRODUCTION

Lubricant basestocks with recognised low volatility are gaining popularity due to reduced fire hazards, slower oil consumption, better odour, improved workmanship and other measurable or perceivable factors. Oil volatility is conventionally assessed using flash points, TGA,¹ NOACK volatility test (CEC L40-T-87, DIN 51581 or ASTM D5800), gas chromatographic distillation (ASTM D2887) and similar techniques. These methods are soundly established and served well to compare thermodynamic evaporation rates of different oils. However, the fact that fluids can slowly decompose and...
release volatile constituents due to oxidation, hydrolysis, catalytic cleavage and other chemical reactions is not addressed in existing standard tests. Many lubricants, including engine oils and industrial fluids, are exposed to metal surfaces as thin films for very long durations, and significant amounts of volatile emissions might be released due to decomposition reactions, primarily oxidative scission and hydrolysis. While vaporisation of acids is limited by their ionic nature, other products of hydrolysis and oxidation might be much more volatile than original ester basestocks. Decomposition products of oils and fat derivatives are thoroughly studied in food science due to their immense significance to odour and flavour. For example, hundreds of volatile compounds are produced in frying oils, and temperatures as low as 50°C are already sufficient to cause their emission. Food research mostly focuses on qualitative identification of volatile compounds, rather than of the rates of their emissions. Nevertheless, if vegetable oils and other unsaturated esters are used as lubricant basestocks, it is obvious that in long term many compounds of lower mol.wt. can be produced with high probability of their vaporisation.

Depending on the lubricant application, frequently vapourised material does not condense back into the lubricant reservoir, but collects elsewhere, especially if the lubricated system is not closed. Condensed degradation products are often quite different than a lubricant itself and might lead to unexpected impacts. Obviously, the larger is the volume of long-term volatile emissions, the higher are the risks of negative influence on equipment, working environment or personnel. Typically, workmanship and engineering decisions, which deal with volatility of a specific lubricant, are drawn based on flash points, NOACK results and distillation curves, none of which really address long-term decomposition.

Unfortunately, the volumes of long-term vaporisation are not specifically measured in standard oxidation tests, whose durations might be quite long, in particular Baader, TFOUT, UOT etc. Consequently, systematic comparative studies of long-term decomposition tendencies of various basestock types are not readily available. The perception still dominates that flash point, distillation curve and other standard test data correlate satisfactorily with long-term volatile emissions. As a result, high mol.wt. basestocks, especially vegetable oils or poly alkylene glycols, which perform well in standard tests, are often viewed as nearly non-volatile, and their volatile emissions are considered negligible. However, our earlier publication reported surprising differences between long-term vaporisation losses of synthetic, biobased and mineral basestocks, most of whom had been considered low volatility. In that study only oxidative degradation was taken into account without considering the impact of humidity due to test method and equipment limitations. Obviously, hydrolysis is capable to decompose ester linkages and produce degradation products of lower mol.wt. The main objective of this report is to adapt the experimental methodology in order to investigate the long-term volatility of oils under dry or humid atmosphere. Another purpose is to accommodate thicker oil films, which should improve accuracy and repeatability of the measurements. Since oil films degrade much faster than bulk liquids due to abundant oxygen, humidity and metal surfaces, in this study, an attempt is made to provide an accelerated methodology to quantify the extent of volatile emissions in basestocks and formulated lubricants due to chemical decomposition. Capabilities of the test are further expanded in this investigation by introducing FTIR in order to demonstrate the compatibility of the thin film methodology with spectroscopic and chromatographic techniques. Such experimental tool can be a valuable instrument for enhancing engineering, occupational, formulation and other developments, which might benefit from the actual numbers on how much volatile emissions could be released in lubricated systems over long periods of operation.
EXPERIMENTAL

Materials

Laboratory grade acetone, isopropanol and xylene (Avsista, Lithuania) were used for washing and titrations. KOH and phenolphthalein (Avsista, Lithuania) were used for acidity determination. The coupons for degradation tests were manufactured in-house from low carbon steel (98.8%wt. Fe, 0.8%wt. Mn and 0.4%wt. Si) and represented the cylinders of 17 ± 1 mm in diameter. Deionized water for humidity chamber operation and acidity titrations was produced in-house by reverse osmosis system Demiwa 10 Rosa (Watek, Czech), resulting in conductivity below 1 μS cm⁻¹.

Stearyl alcohol was supplied by KAO Chemicals (Japan) as Kalcol 8098. Oleyl alcohol was purchased from Merck (Germany). Monoacyl glycerol (MAG) was supplied by Lambent (USA) as Lumulse GMT K. A sample of rapeseed fatty acid methyl esters (FAME) was acquired from Mestilla biodiesel manufacturer (Lithuania) reportedly meeting EN 14214 standard requirements. Substituted phenol antioxidants (AO) Irganox 1076 and Irganox 1010 were acquired from BASF (Switzerland). See Table I for additional properties.

Methods

Thin film degradation test represents the main experiment of this study. Its key principles are described in the previous report, while the most critical changes are discussed in detail in the Section. A forced-draft oven with humidity control HCP-108 by Memmert GmbH (Germany) was used. Precision balance ALJ-160-4NM by Kern Analytical Instruments GmbH (Germany) was used to weigh low carbon steel coupons with ±0.1 mg accuracy. The coupons were polished with the 2000 grit sand-paper (SiC) before each sample application. Using a pipette, sample oils were applied in a form of homogeneous films of 500 μm ± 2% thickness onto the coupons. The layer of stearyl alcohol flakes, which are waxy solid at room temperature, was applied with a spatula and spread uniformly. The accuracy of the film thickness was verified every time after application by weighing the coated coupon. Film thicknesses of...
20 and 100 μm were used only in one experiment, as listed in Table II. After oil deposition, coupons were moved into the oven with equilibrated temperature and relative humidity (RH). After the film degradation, the coupons were removed from the oven and weighed to determine volatile losses. In some cases, the coupons were placed back into the oven to continue the degradation, deducing the time outside the oven. Such removal — weighing — reheating cycle was performed not more often than every 4 h. After the final heating cycle, the coupon was immersed into isopropanol to wash off the residual film for acidity measurements. When most of the film was not soluble, it was assumed solid. In all those cases, the films appeared solid visually, and their surface would not restore its shape, if indented with spatula while still being heated.

Infrared spectra were recorder on Perkin Elmer FTIR Frontier Dual range MIR-FIR spectrometer (courtesy Vilnius University). The coupon, which was coated with sample oil, was placed onto the tray of GladiATR by Pike Technologies (USA). After pressing the film with the diamond crystal, the spectra were recorded at 32 scans.

Acidity of the samples was measured titrimetrically by adapting the AOCS official method Cd 3d-63 ‘Acid value’. Fresh KOH solution in isopropanol at 0.1% mol. was prepared every day and used to titrate the degraded sample, which had been washed off the coupon. The washed coupon was dried, weighed and the acidity was calculated as mg of KOH per 1 gram of degraded sample, which remained after volatile emissions, i.e. not the original sample. Obtained experimental values were calculated into % weight change and plotted against the test durations. Least squares methodology was employed to correlate the measured values to the test duration by utilising the Excel 2013 software. Most used percentages were calculated on weight-to-weight basis, unless indicated otherwise.

In this text, the term ‘evaporation’ is attributed to the material losses due to solely thermodynamic phase transition from liquid to gas and not due to chemical reactions, which produce the materials of lower mol. wt. (oxidation, hydrolysis, metathesis, thermocatalytic scission etc.). When just chemical process or both thermodynamic and chemical processes are considered, the terms ‘vaporisation’ and ‘volatile emissions’ are used interchangeably.

RESULTS AND DISCUSSION

Thin film test adaptation

A number of thin film test procedures have already been utilised for oxidation studies; however, they rarely focus on volatile losses. Most widespread standard tests RPVOT, TFOUT, Baader, Rancimat

| Test duration, h | Film thickness ↓ | 21–22 | 38–44 |
|-----------------|-----------------|-------|-------|
|                 | Loss, %wt.      | Rate mg cm⁻² | Loss, %wt. | Rate mg cm⁻² |
| 500 μm          | 8.6 ± 2.3       | 2.0 ± 0.5 | 18 ± 1.1 | 4.5 ± 0.3 |
| 100 μm          | 27 ± 4.0        | 2.0 ± 0.3 | 37 ± 3.0 | 3 ± 0.3 |
| 20 μm           | 73 ± 12         | 1.8 ± 0.3 | n.d.     | n.d.     |
and others are not designed to quantify volatile losses. This capability has been utilised in thin film-based microoxidation family of tests,\textsuperscript{9–11} such as Koehler Instruments K-29200. However, test equipment employs a sample pan with rectangular profile and favours fluid accumulation around the brim. Consequently, the oil film thickness increases greatly when travelling from the pan center to the edge (Figure 1). Another film-based oxidation test, PDSC, in principle can also be adapted for volatility measurements. In one of PDSC variants, SFI pan can hold an oil drop in sessile placement. However, if a larger droplet, c.a. 30 mg, is placed on the pan, it barely resembles a film, while its weight is still too small to be accurately measured in order to account for volatile losses. Also, repeatability of oil tests in SFI pans has been quite poor\textsuperscript{10} due to spillages or droplet instability.

The concept of flat test coupon for thin film oxidation has already been successfully employed, as reported previously.\textsuperscript{7} However, in that study the coupon could not hold a film thicker than 100 μm even in case of high viscosities because of its spilling over the edge. In the current investigation, the spillage problem is resolved by polishing the coupon sides, as suggested previously,\textsuperscript{12} leading to a mirror quality finish of the coupon walls. Special care is taken to avoid any accidental rounding of the coupon edge, maintaining a sharply perpendicular cross-section between horizontal and vertical surfaces. It does not seem intuitive at all that highly smooth coupon walls could be helpful in preventing the film spillage from the surface. Nevertheless, such measures dramatically improve the capability of the coupon to hold larger samples and assure that film thicknesses in excess of 500 μm could be easily retained even for low viscosity fluids, such as biodiesel or other FAME mixtures.\textsuperscript{13}

It must be noted that changing the film thickness from 50 to 500 μm in theory should not affect the absolute rate of evaporation, since the surface area has not changed. The results of oleyl alcohol heating at 90°C from the films of three different thicknesses are shown in Table II. For the most part, demonstrated tendencies agree with the expectation that the rate of evaporation in terms of material loss (mg cm\textsuperscript{-2}/C\textsubscript{0} 2) does not depend on film thickness.

During early stages of heating, the evaporation rates are quite similar, producing 2 mg cm\textsuperscript{-2} of oleyl alcohol vapour at 90°C. After a large portion of the sample evaporates, the film becomes thinner, and the relative variation of its thickness is much more pronounced. In extreme cases, the film begins to pool, exposing empty areas of the coupon surface. Consequently, the absolute rates of vaporisation go down somewhat in thinner films.

However, the variation of vaporisation losses in relative terms is much greater, e.g. 8.6% wt. vs 73% wt. for 500 and 20 μm films, respectively, in ~21 h at 90°C. Obviously, the loss affects the relative sample size much less significantly for thicker films. Therefore, if measured in %wt., the values are very dependent on film thickness with volatile emissions from thinner films at much higher percentages.

The limitation of minimum film thickness must also be considered, especially in 20 μm films. Earlier study\textsuperscript{14} showed that at room temperatures oil films thinner than 5 μm could not be maintained on steel discs due to surface tension forces. Depending on surface roughness and accidental contamination

Figure 1. Oil film placement cross-sections in thin film oxidation tests (from left): microoxidation pan\textsuperscript{9}; SFI pan\textsuperscript{10}; and coupon in this study. [Colour figure can be viewed at wileyonlinelibrary.com]
(e.g. dust), oil pooling can begin even in much thicker films, especially at higher temperatures, which reduce oil viscosity. Film pooling produces dry zones on the test coupon and leads to the smaller area of liquid surface. When testing 20 μm films such discontinuities were observed after about 20 h of heating, making the absolute rates of vaporisation somewhat lower. After longer heating, the influence of oxidative polymerization (i.e. oxypolymerization) became more evident, which can be observed by the difference between the absolute rates of 500 and 100 μm films after ~40 h.

Nevertheless, repeatability of tests in thicker films appears acceptable, if appropriate precautions are taken. Measured values of TAG vaporisation in Figure 2, based on three runs at 120°C and five runs at 130°C, show that accuracy can be better than 0.5%wt. in 500 μm films. It is worth noting that Figure 2 shows a magnified scale of vaporisation losses, and the measurement fluctuations would not be so visible at 10%wt. or larger scale. Due to better accuracy, the initial film thickness of 500 μm has been selected for all further experiments in this investigation. Test durations can be extended much further as long as adequate temperature control and prevention against dust contamination is assured. In this investigation, some measurements approach 2000 h durations, but even longer tests are possible as well, making the thin film test a great instrument in studying long-term vaporisation.

**Weight changes during heating**

Improved sensitivity of the test is very helpful in quantifying the changes of film weight, especially when little evaporation is expected. Behavior of low volatility oils is of particular interest, because of the expectation that oils must not evaporate at zero vapour pressures or temperatures significantly below boiling point. Early into the test under these conditions such oils in fact do not evaporate at all, as shown in Figure 3 for FAME at 50°C (chart A) and TAG at 90°C (chart B).

To the contrary, cetane showed rapid evaporation at 50°C and especially at 90°C, taking 144 and 4.5 h, respectively, for the liquid phase to disappear completely. Compared with cetane, mol.wt. of FAME is just 24% larger (226 vs 296 g mol⁻¹, respectively) with reportedly higher boiling point (287°C vs ~400°C), but FAME evaporation is many times slower, and it could not even be detected at 50°C during early stages. Just as in case of TAG at 90°C, the initial weight gain due to peroxide formation is evident. Such weight increase, rather than any volatile losses, is observed, because double bonds, which are present both in FAME and TAG, are susceptible to allylic substitution reactions by...
free radicals and rapid abstraction of ambient oxygen. In thin films diffusion, limitations are much smaller compared with bulk liquids; therefore, peroxide formation is rapid and easily detectable by weight gains in FAME and TAG.

So the early stages of thin film tests are in full agreement of the perception that neither FAME nor vegetable oils evaporate at 50°C, the latter staying non-volatile even at 130°C (Figure 2b). However, if heating is continued long-term, thermodynamic evaporation might not be the only driving force of the volatile emissions. Just as autodispersion theory predicts, peroxide decomposition generates many derivatives, including lower mol. wt. compounds, which result in release of volatiles. Subsequently, weight gains in FAME or TAG films are eradicated by vaporisation of the chemical reaction products, and in long term the volatile losses are much more abundant than any buildup of peroxides. Although thermodynamic evaporation of TAG even at 120°C was negligible, long-term volatile emissions approached 5%wt. before TAG solidification after 28 h of heating due to oxypolymerization reactions. FAME evaporation was not detectable at 50°C, but much higher rates could be measured at 90°C. Nevertheless, the whole volume of FAME film could not be vaporised, as opposed to cetane, which evaporated completely. Concurrently, with oxidative scission and hydrolysis, reactions of oxypolymerization also take place in unsaturated esters. Resulting compounds of higher mol. wt. are obviously much less likely to evaporate and stay within the film volume. Consequently, even after

Figure 3. Temperature influence on vaporisation of the following: (a) cetane and FAME under humid atmosphere and (b) rapeseed oil (TAG) under dry atmosphere. Except of FAME at 50°C, tests were discontinued after no liquid phase was present due to vaporisation or solidification. [Colour figure can be viewed at wileyonlinelibrary.com]
nearly 1500 h heating at 90°C, a significant portion of the original FAME film remained in the liquid phase (despite very high viscosity) with volatile losses stabilising around 70%wt.

These observations show that considerable amounts of unsaturated ester basestocks can be lost as volatiles despite negligible evaporation initially. Since the influence of double bond oxidation is crucial, antioxidants (AO) can be expected to have a major effect on the rates of long-term vaporisation. Hydrolysis can also produce low mol.wt. fragments in ester basestocks, nearly independently of unsaturation. Therefore, influence of RH should also be taken into account.

Influence of antioxidants (AO) and humidity on volatile losses

Since oxidative scission is a very important cause of long-term volatile losses in TAG, effects of several AO on vaporisation was screened. Two phenolic AO were tested the most extensively: AO1 with one substituted phenol moiety and AO4 with four substituted phenol moieties in a molecule (Table I). Both of them are widely recognised as effective free radical scavengers. Addition of 1%wt. of these AO showed some inhibition of vaporisation rates (Figure 4).

Effectiveness of both AO at 90°C and 120°C was clearly quantifiable, yielding somewhat lower volatile emissions than those of uninhibited TAG. Nevertheless, the AO did not make a dramatic difference and by no means could neither AO1 nor AO4 be recognised as an effective measure to prevent long-term vapourisation. Furthermore, at 160°C the advantage of AO formulations in suppressing long-term volatile emissions was even less evident. Preferential vaporisation of AO themselves or their depletion products might explain such ineffectiveness. Since both AO are quite heavy in terms of mol. wt. (Table I), it would be somewhat surprising, if they could vapourise much easier than TAG, in particular AO4. Poor AO performance might be explained more convincingly by assuming that AO undergo decomposition into more volatile fragments during oxidation. A more elaborate experimental arrangement would be needed to investigate such scenario further.

Hydrolysis represents another chemical mechanism, which generates lower mol.wt. products in ester basestocks. The extent of this decomposition mechanism was tested in FAME by introducing 20% RH into the test atmosphere at 90°C (Figure 5). The data show that higher humidity increases the rate of volatile emissions from FAME. Since hydrolysis of simple esters yields an alcohol and an acid, in case of FAME, free fatty acids (FFA) and methanol must be produced. The latter is expected to evaporate

Figure 4. Influence of 1%wt. phenolic antioxidants AO1 (hollow diamonds) and AO4 (filled diamonds) on TAG (rectangles) vaporisation under dry conditions at 90°C, 120°C and 160°C. Tests terminated after film solidification. [Colour figure can be viewed at wileyonlinelibrary.com]
nearly instantaneously at 50°C or higher temperatures. Since mol.wt. of methanol comprises ~11% of that of FAME (32 vs 296 g mol⁻¹), the gravimetrical difference between dry and humid results in Figure 5a is not very large. Nevertheless, the data are sufficient to show that humidity significantly accelerates the volatile emissions of biodiesel.

Effects of RH can be studied in complex esters as well. However, in case of TAG, hydrolysis initially produces FFA and diacyl glycerols, ensued by MAG and terminated by free glycerol. Any of these are not nearly as volatile as methanol at 90°C. Above the boiling point of water, it becomes problematic to control RH, so humid atmosphere investigations at temperatures above 90°C have not been pursued in this study. Effects of RH on TAG volatile emissions have not been studied either due to unlikely evaporation of diacyl glycerols. Nevertheless, evaporation of MAG and alcohols at 90°C is quite probable, as discussed later.

FTIR Spectroscopy of degraded films

Since many analytical techniques require only minor amounts of sample, the oil volumes from the thin film test can be used for analysis in various spectroscopic, titrimetric, solvational, chromatographic and other assays. In this study, films of cetane and FAME were analyzed on FTIR in order to investigate the degradation trends in more detail using conventional peak identification²⁰ and to observe the extent of oxidation and hydrolysis. FTIR spectra of fresh and degraded cetane films is presented in Figure 6 and Figures S1–S3.

The vibrational features due to the alkyl chain of cetane appear in the C-H stretching region. The symmetric and asymmetric stretching modes of methylene groups, νₛ(CH₂) and νₘₐₐ(CH₂), can be observed at 2852 and 2920 cm⁻¹, respectively. The asymmetric stretching mode of CH₃ moieties, νₘₐₐ(CH₃), as well as the corresponding symmetric mode, νₛ(CH₃), are also visible at 2957 and 2873 cm⁻¹, respectively. In addition to spectra in Figure 6, magnified peaks are displayed in Figure S1. In the low frequency region, the cetane methyl groups are presented as asymmetric deformation band at 1465 cm⁻¹ and the symmetric band at 1379 cm⁻¹. The former band is frequently overlapped by the CH₂ scissor vibration occurring at 1480–1440 cm⁻¹. For n-alkanes, such as cetane, a

Figure 5. Influence of humidity on vaporisation (a) and acid buildup (b) in FAME at 90°C under dry atmosphere and 20% RH. Acidity was not tested beyond 300 h. [Colour figure can be viewed at wileyonlinelibrary.com]
band due to CH$_2$ wagging vibrations occurs near 1304 cm$^{-1}$. The peak at 721 cm$^{-1}$ can be attributed to the CH$_2$ rocking vibrations. All these peaks are magnified in Figure S2.

Degradation temperature was held at 50°C in order to limit the extent of cetane vaporisation. FTIR shows that just in 4 h exposure significant amounts of oxidised material is built up in the cetane film. Peaks at 1729 and 1740 cm$^{-1}$ are present only in oxidised films and demonstrate formation of carbonyls very clearly. Buildup of hydroxyls is evident above 3080 cm$^{-1}$, with detectable bands at approximately 3250 cm$^{-1}$, caused by appearance of hydrogen bonding (Figure S3). New peaks at 1203, 1216 and 1230 cm$^{-1}$ can also be attributed to oxidation products. When comparing the films after 4 and 31 h degradation, only minor spectral differences can be observed, which seems a bit unusual. Intuitively, more oxidised material should be produced by further degradation with absorption bands of higher abundance at 1203–1230 cm$^{-1}$, 1729–1740 cm$^{-1}$ intervals and around 3250 cm$^{-1}$. However, this is not evident from FTIR data, which suggest that many oxidation products are lost through volatile emissions. Substantial vaporisation of cetane at 25%wt. in 31 h favors these assumptions.

Since FAME is less volatile than cetane, FTIR of its films were recorded at both 50°C and 90°C (Figure 7). Its spectra are more complex. First of all, even the fresh ester has much broader chemical diversity, because methyl oleate comprises just around 60% of the sample, the rest being esters of various trans-unsaturated and poly-unsaturated FA along with numerous manufacturing byproducts (free FA, glycerides, tocopherols etc.). In addition, compared with cetane, FAME is much more reactive due to double bonds, ester linkages and various other constituents. Consequently, many more degradation pathways are available for FAME in the thin film test, especially at 90°C. In the alkyl region, the bands of methyl and methylene groups are observed in nearly identical locations as for cetane spectra at 2853, 2873, 2923 and 2957 cm$^{-1}$ along with additional peaks (Figure S4). The band at 3007 cm$^{-1}$, clearly visible as a small shoulder in Figure 7, is caused by the stretching vibration of CH cis-olefinic groups. However, after heating at 90°C for 70 h, the peak disappeared, because of isomerization from cis- to trans- double bonds in unsaturated FA.$^{21}$
In the region from 1800 to 1700 cm\(^{-1}\), observed peak at 1740 cm\(^{-1}\) can be attributed to the stretching of C=O, typical of esters. However, after longer duration of film degradation, additional peaks appeared in its vicinity. Significant increase in absorbance around 1710–1720 cm\(^{-1}\) suggests appearance of H-bonded carboxyls, which are typical in concentrated FFA (Figure S5). Some increase in absorbance around 1760 cm\(^{-1}\) is evident after 70 h degradation at 90°C, which is attributable to carboxyls without hydrogen bonding. Appearance of these peaks suggests that significant amounts of acids build up in FAME during degradation, accompanied by formation of ketones with absorbance at 1720 cm\(^{-1}\) and possibly other secondary oxidation products.\(^{21}\) Ketones can be produced during allylic substitution reactions at the double bond sites, when hydroperoxides decompose into secondary alcohols and ketones.\(^{16}\) Carboxyl formation via hydroperoxide decomposition cannot be ruled out, but this route is more complex because of secondary alcohol oxidation into ketones, rather than aldehydes turning into acids. Therefore, acidity buildup most likely comes from FAME hydrolysis, although more systematic approach is necessary to provide more accurate rates of these competing mechanisms, for example, by comparing the rates of absorbance increase at 1710–1760 cm\(^{-1}\) in high purity methyl oleate and methyl stearate.

Degradation does not seem to dislocate the bands in the region of 700–1500 cm\(^{-1}\). As in cetane spectra, CH\(_2\), CH\(_3\) bending and CH\(_2\) rocking vibrations modes are fixed at 1463, 1362 and
724 cm\(^{-1}\), respectively (Figure S5). The band at 1434 cm\(^{-1}\) is likely caused by the methyl ester group (CO–O–CH\(_3\)) and another characteristic peak at 1197 cm\(^{-1}\) may also correspond to the (C–O) ester linkage.\(^{22}\) The peak at 1245 cm\(^{-1}\) could be the result of the O-H deformation, and the small band around 1000 cm\(^{-1}\) could be attributed to the C–CH\(_2\)–O due to the presence of glycerol.\(^{23}\)

Also, some degradation products are formed probably without any heating, just by the application of thin FAME film onto the steel coupon. Thin film and abundance of steel surface create favorable conditions for some degradation of FAME and other esters at room temperature. Consequently, only some increase in absorbance can be observed in FAME 50°C samples. Degradation is more obvious in spectra of 90°C samples with increasing absorbance in 800–1500 cm\(^{-1}\) region. As discussed, a duplet develops at 1740 cm\(^{-1}\), which suggests that oxidised double bonds affect the vibrational characteristics of ester linkage, resulting in peak broadening. Significant broadening is observed in vibrational bands of methyl and methylene bonds, Figure S6, which implies that diverse functional groups are formed in their vicinity. Increase of absorbance above 3100 cm\(^{-1}\) is much more apparent than in case of cetane (Figure 7). This implies not only faster oxidation, but much higher probability of hydrolysis, which should lead to carboxyl formation. Vibrational nodes of carboxyls produce much higher absorbance than those of hydroxyls in cetane. However, a clear distinction between oxidation and hydrolysis cannot be drawn from these FTIR spectra of studied FAME. Higher purity of methyl oleate would be much more appropriate for FTIR studies of chemical pathways of oxidative and hydrolytic degradation. The purpose of this particular FTIR investigation is primarily to confirm the possibility of direct spectroscopic analysis of degraded oil without the need of its dissolution. Obviously, dissolved specimens can also be tested not only by FTIR but also by using a great variety of other techniques as well, including titrimetry, which is presented later.

**Alcohol vaporisation and acidity**

Ester basestocks can hydrolyze into a variety of alcohols and acids. Polyoil esters can produce a number of partial esters and free acids, while dibasic esters can produce free alcohols and acidic esters. Even in refined vegetable oils, diacyl glycerols and MAG are present at significant levels, often exceeding 5%wt. as calculated from acidity specifications on the assumption that under 1%wt. oleic a. concentration 2.0 mg KOH are consumed per 1 g oil. In dibasic ester basestocks, oleyl moiety is sometimes utilised. Therefore, volatile emissions of oleyl alcohol and stearyl alcohol were compared at 90°C, which gave more details on the influence of unsaturation. MAG, rich in FFA, was also included as an important product of vegetable oil hydrolysis (Figure 8).

It is evident that at 90°C thermodynamic evaporation of both stearyl and oleyl alcohols proceeds at appreciable extent. Oxidative scission in stearyl alcohol is unlikely, hydrolysis essentially not possible; therefore, most of its volatile emissions are produced by thermodynamic evaporation. Emission rates in oleyl alcohol are similar during the early stages of heating. However, later, its vapourisation slows down and remains much lower until film solidification after ~280 h. In contrast, stearyl alcohol film has not solidified even after 700 h heating at 90°C. As a matter of fact, the film of stearyl alcohol was solid at room temperature initially, but after ~300 h heating, its film already remained liquid when cooled to ambient as a result of decaying purity.

Absence of quantifiably higher volatile emissions in oleyl alcohol suggests that its oxidative scission or other possible decomposition mechanisms (e.g. metathesis) do not represent a dominating degradation mechanism, and their extent is probably much lower than that of concurrent processes, which result in higher mol wt. products. Volatile emissions from oleyl alcohol just before solidification are
much lower than those of stearyl alcohol after ~230 h. This implies that higher mol.wt. derivatives, which do not evaporate, are produced at much higher rate in oleyl alcohol. These processes in stearyl alcohol are less likely; therefore, it continued evaporating faster.

Eventually, the rate of stearyl alcohol evaporation went down, but it would be premature to assume that oxypolymerization was the primary cause of the slowdown. Acidity of the alcohols has also increased (Figure 8b), which implies another mechanism of chemical degradation. Abundant dissolved oxygen and metal surface can catalyze oxidation of hydroxy groups into aldehyde and carboxy derivatives. Rapid increase of acidity suggests that stearyl alcohol can undergo such transformation, with stearic acid, a probable intermediate product. Oxidation of oleyl alcohol, with much faster acidity buildup, is more complex because of concurrent peroxide formation and decomposition processes, which also produce significant amount of carboxylic derivatives. Availability of metal surfaces then results in high probability of metal salt and soap formation reactions, with eventual production of Fe stearates and more complex organo-metallic derivatives.24 The stearates have much higher mol.wt. not only because of Fe atom but also due to distearate and tristearate congeners; the same analogy applies to more complex organo-metallic derivatives. So their evaporation at 90°C is not likely at all.

While soap formation from FFA is quite evident, appearance of organo-metallic derivatives in the case of cetane is quite unexpected. As measured, its volatile losses at 50°C or 90°C exceeded 100%wt., with terminal runs actually averaging at 100.9% and 101.2%, respectively (Figure 3a). This can only be explained by chemical reactions of steel surface with degradation products of cetane, which produce sufficiently volatile organo-metallic derivatives. In such manner, not only all cetane was vaporised from the surface, but amazingly, nearly 1%wt. of all volatile emissions from cetane were comprised of metallic constituents, if compared with C, H and O in terms of elemental composition. This observation also indicates that in thin film environment even such an inert molecule as n-alkane still undergoes significant degradation, and its volatile emissions cannot be considered as solely thermodynamic evaporation. Evidently, loss of metal from the surface bears strong implication of corrosion processes as well.

Volatile emissions of MAG appeared much lower (Figure 8a) despite quite abundant FFA in the original sample at ~20%mol. In case mol.wt. are similar, carboxylic acids generally evaporate much slower due to stronger hydrogen bonds compared with alcohols. Same explanation applies when comparing evaporation of alcohols and hydrocarbons or esters. Slow increase in acidity was quite surprising in MAG tests. Acid buildup was barely quantifiable and stayed within 50 ± 10 mg KOH/g
throughout the whole test. Since MAG contains free hydroxy groups, which are capable of forming an ester linkage with carboxy group, some intra-esterification could have taken place. However, it is too speculative to assume any additional chemical mechanisms without data from spectroscopic, chromatographic or other analytical methods.

Major acidification was observed in FAME as well (Figure 5b). Its rate was somewhat lower than that of oleyl alcohol (Figure 8b), as it should be expected due to the absence of hydroxy groups. Furthermore, the amount of poly-unsaturated double bonds, which are much more prone to oxidative scission, was significantly higher in FAME than in oleyl alcohol, approximately 25 vs 5% mol., respectively. This comparison highlights the contribution of hydroxy group oxidation in oleyl alcohol under dry conditions. However, at 20% RH, acidification of FAME is nearly as intensive as that of oleyl alcohol, suggesting that under humid conditions esters are likely to hydrolyze and produce acids.

Suitability of the test for long-term volatile emission measurements

Long-term vaporisation of lubricant basestocks has already been reported earlier for thinner oil films c.a. 50 μm. Current observations at 500 μm films are fully in line with the previous conclusions, as compared with the volatile emissions from several esters, mostly caused by oxidative decomposition. It must be noted that relatively thick films of 500 μm in this test provide much higher accuracy. Even more, introduction of humid atmosphere gives the possibility to account for hydrolytic degradation. Hydrolysis and saponification have been particularly puzzling for ester basestocks. Rate of hydrolysis is highly affected by steric hindrance and intramolecular stresses of the ester linkage, so it is almost impossible to accurately predict hydrolytic stability just by knowing chemical composition of an ester basestock. The thin film test provides an excellent tool to monitor the effects of hydrolysis, which is rather problematic in currently used tests, such as ASTM D2619 ‘standard test method for hydrolytic stability of hydraulic fluids (beverage bottle method)’. These tests are not fast (e.g. 48 h in D2619) and suffer from repeatability issues due to problematic degree of mixing between the sample and water. Their resemblance to field applications is also questionable, because frequently hydrolysis is caused by humid air rather than mixing with water, especially in oil films. The thin film test provides a tool to differentiate the hydrolytic stability within several hours, which is more important, and more rationally represents actual causes of lubricant hydrolysis. In field, engine oils, hydraulic fluids and other lubricants usually form films, which are exposed to humidity and moisture at more significant extent than during bulk mixing of water droplets.

Vaporisation of hydrolysis products highlights one more aspect for ester-containing lubricant performance. Based on MAG data, FFA such as oleic acid are not very volatile at 90°C; however, somewhat higher temperatures might vaporise them. Alcohol fragments can be volatilized even easier, in case mol.wt. is similar. Many esters, including MAG, are also used as friction modifiers and other types of lubricant additives, polymerised esters in particular. Eventually, volatile products of ester hydrolysis condense somewhere in lubricant systems as films, pools, droplets or similar. None of these represent bulk liquid; therefore, the thin film methodology is again quite viable in studying their further degradation. Accumulated decomposition products might engage in many unwanted technical processes, especially corrosion. This highlights the importance of good understanding of decomposition mechanisms and rates, when developing a lubricant basestock. This thin film methodology represents a simple but fast, accurate and reliable measurement of vaporisation rates, which is much more informative than results of traditional volatility tests, such as NOACK, TAG or flash point. Therefore, thin film tests can be very useful in predicting the volatile emissions from lubricants or their basestocks. If
supplemented with additional techniques, for example, titrimetry, colorimetry, spectroscopy, chromatography, microscopy or other, such film-based methodology represents a powerful tool to investigate long-term vaporisation tendencies of lubricants and industrial oils.

CONCLUSIONS

A previously used thin film test was modified to accommodate larger samples, expose them to humid atmosphere and integrate a detailed chemical analysis. Capitalizing on improved accuracy and analytical capabilities, several ester and fatty alcohol fluids were screened, and the following findings were observed:

- The thin film test can accurately measure long-term vaporisation rates of various basestocks.
- Additional titrimetric, solvational, spectroscopic and other analytical techniques can be incorporated into the test to monitor acidity, metal dissolution, solidification, corrosion, buildup of degradation products etc.
- Influence of hydrolysis can also be investigated by controlling the RH in the test atmosphere.
- Long-term vaporisation can be substantial in unsaturated esters, despite zero vapour pressure at test temperatures. In vegetable oils, which are considered low volatility, long-term vaporisation can exceed 5%wt.
- In unsaturated esters, acidity builds up rapidly, but it can also increase in saturated esters due to hydrolysis or oxidation of available hydroxyl groups.
- Acidic degradation products are likely to form organo-metallic compounds with metal surface, such as Fe soaps.
- In monounsaturated ester basestocks, the combined rate of oxypolymerization and saponification appears to dominate concurrent decomposition processes, such as oxidative scission.
- Long-term vaporisation rates are high enough even in non-volatile lubricants, and it is necessary to consider how these emissions might affect equipment, personnel and environment.

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**SUPPORTING INFORMATION**

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**Figure S1.** FTIR peak identification for fresh and degraded cetane spectra in the interval of 2800–3000 cm⁻¹
**Figure S2.** FTIR peak identification for fresh and degraded cetane spectra in the interval of 700–1800 cm⁻¹

**Figure S3.** FTIR peak identification for fresh and degraded cetane spectra in the interval of 3000–3600 cm⁻¹

**Figure S4.** FTIR peak identification of fresh and degraded FAME spectra in the interval of 2800–3100 cm⁻¹

**Figure S5.** FTIR peak identification of fresh and degraded FAME spectra in the interval of 600–1800 cm⁻¹

**Figure S6.** FTIR peak identification of fresh and degraded FAME spectra in the interval of 3000–3600 cm⁻¹