Studies on the Volatility of Synthetic and Mineral Oil Base Fluids Using Thermogravimetric Analysis (TGA)

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Abstract

This report examines volatility characteristics of hydrocarbon base fluids using thermogravimetric analysis (TGA). The lubricants chosen for this study include samples from API groups II, III, and IV. The demand for improved lubricants has driven research on this topic. Adoption of low volatility lubricants by industries has the potential for an unprecedented positive impact on the environment. Kinematic viscosity alone was a poor method for determining volatility. Isoviscous group II and III chemically modified mineral oils (CMMOs) generally exhibit greater volatility than group IV synthetic polyalphaolefins (PAOs). Significant volatility differences were observed between air and inert atmospheres for the same samples. Advantages of the TGA test for measurement of lubricant volatility are discussed.

Introduction

Environmental and governmental restrictions have forced industries to examine alternative methods of reducing emissions and oil consumption. Cleaner burning and improved lubricants has been proven to aid in reducing these. Studies have shown that reducing oil volatility is essential to improving lubricants. An understanding of the relationships between the molecular structure of lubricant base fluids and the properties and performance of these materials is directly related to reducing oil volatility.

Previous studies of degradation and weight loss of lubricants have been examined using Thermogravimetric Analysis (TGA) [1-6]. They indicate that lubricants degrade thermally when components boil off due to volatilization or by the changes in fluid structure at elevated temperatures. Comparison of the volatilization profiles of base fluids can give useful volatility information about each fluid.

Studies have reported that typical operating temperatures for bearings, gears and piston rings rarely exceed 150°C [7]. The automotive industry is designing for more fuel efficient and low emission vehicles which have resulted in engines running at much higher temperatures. This is partly attributed to industry's use of smaller engines and smaller oil sumps to reduce weight. Additionally, exhaust gas recirculation (EGR) has become more popular and contributes to elevated temperatures potentially exceeding the 150°C temperature. Lubricant volatility restricts the maximum operating temperatures of these components. A study of lubricant fluid thermal and oxidative stabilities will need to address this issue.

Based on reported temperatures in combustions engines, it is likely that lubricants are exposed to temperatures above 150°C. It is possible that for short periods of times, lubricants will

experience temperatures as high as 480°C. However, components of these fluids have been reported to boil off at temperatures even below 150°C [8].

Lubricants with continuous exposure to elevated temperatures, as seen in combustion engines, break down, decreasing their life expectancy. Deposits from these fluids cause increases in stresses and wear, reducing the performance of the engine. These high temperatures are sufficient to break covalent bonds and permit reactions that would not occur at lower temperatures.

Volatility

Volatility is an expression of a lubricant's evaporation tendency [9]. This is commonly associated with oil consumption in crankcase applications and is related to environmental issues. High volatility fluids boil at lower temperatures and are exhausted into the environment. As the lighter components of high volatility fluids evaporate, the viscosity of the remaining fluids increases contributing to the resulting lubricant "going out of spec." A 5W30 oil that exhibits excess losses may become a 10W40 oil after less than 1000 miles.

The standard method for testing volatility is the NOACK volatility test (DIN 51581, CEC L40-T-87, ASTM D5800). This test is used by both European and U.S. OEM's and industry organizations that include volatility in their specifications. It should be noted that the test lacks the ability to distinguish true volatility from chemical reactions occurring simultaneously at elevated temperatures. However the test still provides valuable information on oil volatilities.

Additive volatility can also affect lubricant performance. Studies are being conducted to evaluate additives to determine their volatility characteristics under anaerobic and aerobic conditions.

In this study, the volatility and TGA weight loss of commercial hydrocarbon based fluids were evaluated in ultra high purity nitrogen and air. Oxidation is a concern when considering lubricant volatility in air. Under identical heat treatments, molecular bonds degrade much faster in air than in nitrogen.

The objectives of this study were:
- To use TGA to test the volatility of various lubricants in air and in the absence of air.
- To determine if significant differences are observed in volatility due to the presence of air (O_2).
- To determine if significant differences are observed in volatility due to type of lubricant, lubricant viscosity, and structure.
- To discuss how lubricant volatility and choice of lubricant can affect the environment.

Methodology

As mentioned previously, the NOACK volatility test is the standard method for testing volatility. The test is performed by maintaining a sample at 250°C for 60 minutes under a prescribed air flow. The fluid's volatility is then calculated from the weight difference before and after the test.

Another common method of testing oil volatility is the use of gas chromatography (GC). The disadvantages are that GC is conducted in an inert atmosphere and does not truly subject the oil to real life conditions.

The TGA test takes aspects of both NOACK and GC tests and combines them. The test is safe like the GC test and provides real life conditions like the NOACK test. Additionally the test is fast and easy to use. The TGA test uses very small sample sizes and is an extremely accurate and repeatable method for measuring oil volatility [10].

Experimental

Lubricant base fluids were obtained from commercial sources. All samples were stored at room temperature in the dark in tightly sealed bottles with little head-space.

Mineral oil base fluids were selected to represent API groups II and III and synthetic polyalphaolefin base fluids were selected to represent API group IV.

Results reported here for NOACK volatility were obtained from the manufacturer of each base fluid. The repeatability of the NOACK test (ASTM D5800) [11] is reported to be +/- 5%, and reproducibility is +/- 10%.

TGA experiments for this study were obtained using a Perkin-Elmer 7HT instrument. All experiments were performed using the same platinum pan to maintain a consistent surface to volume ratio for each measured sample. This is important because the rate of evaporation of a sample depends on the surface available for the molecules to escape from the liquid. The sample (~8-14 mg) was added to the platinum pan. The atmosphere was either ultra high purity nitrogen or air at calibrated flow rate of 100 ml/min.

The temperature was ramped from 30-400°C at 10°C/minute. The temperature was held at 400°C for 15 minutes before the program completed. Experiments performed in nitrogen were purged for 120 minutes at 30°C to eliminate air from the TGA prior to beginning the temperature program. It was noted that there was no loss of sample during the purging process.

TGA repeatability is being determined from replicate experiments and will be reported later.

Results and Discussion

Base lubricant fluids are designated by API group classification as described in **Table 1**.

Table 1: API Group Classifications

Base Stock Group	Sulphur, wt.%		Saturates, wt.%	Viscosity Index
Group I	> 0.03	and/or	<90	80 - 120
Group II	≤ 0.03	and	≥ 90	80 - 120
Group III	≤ 0.03	and	≥ 90	> 120
Group IV		All Poly-alphaolefins (PAO)		
Group V		All Base Stocks Not Included in Groups I-IV		

API groups are classified based on sulphur and saturate content and viscosity index. Several properties and performance features of the base fluids are summarized in **Table 2**. Data was taken at selected parts of the TGA curve with a temperature programmed TGA which is also shown in **Table 2**.

Table 2: Properties and Performance Features of the Base Fluids

Lubricants	Group	KV	VI	NOACK	Lubricants	Group	KV	VI	NOACK
PAO 4	IV	3.9	124	13.6	651-0150	2	4.07	93	29.38
PAO 6	IV	5.75	143	7.4	651-0141	2	4.119	97	28.52
C-4R	III	4.174	129	14.7	651-0130	2	5.719	93	17.54
C-5R	II	4.676	118	14.5	651-0159	2	6.087	111	8.14
C-7R	III	6.891	145	4.1	651-0143	2	4.133	101	28.26
C-100R	II	4	98	27.39	651-0160	2	4.162	103	27.17
C-220R	II	6.5	101	9.56	651-0172	3	4.16	123	14.8
P 1008	II	4.2	113	15	651-0149	3	4.178	129	14.28
P 1810	II	5.7	97	14	651-1946	3	5.9	127	9
					651-0124	3	6.501	129	7.25

Isoviscous series were created to objectively compare the samples. These series are shown below in **Tables 3-5**.

Table 3: Series 1 having kinematic viscosities between 3.9 – 4.2 cSt

Sample	PAO 4	651-0172	C-4R	651-0149	C-100R	651-0150	651-0141	651-0143	651-0160
Group	IV	III	III	III	II	II	II	II	II
Kinematic Viscosity (100°C), cSt	3.9	4.16	4.17	4.178	4	4.07	4.119	4.133	4.162

Table 4: Series 2 having kinematic viscosities between 5.7 – 5.75 cSt

Sample	PAO 6	P1810	651-0130
Group	IV	II	II
Kinematic Viscosity (100°C), cSt	5.75	5.7	5.719

Table 5: Series 3 having kinematic viscosities between 5.75 – 6.9 cSt

Sample	PAO 6	650-1946	651-0124	C-7R	651-0159	C-220R
Group	IV	III	III	III	II	II
Kinematic Viscosity (100°C), cSt	5.75	5.9	6.501	6.89	6.087	6.5

Both the TGA and NOACK tests were relevant methods for examining the volatilization of the lubricant components. The TGA experiment uses thin film evaporation which models applications where circulating oil passes over metal surfaces. Bulk oil that sits in the sump vaporizes in a similar manner to the NOACK apparatus [12]. The tests should provide realistic data that models typical lubricant applications.

NOACK Volatility

Kinematic viscosity alone was not an accurate method for predicting NOACK volatility (R^2=0.5485) as shown in **Figure 2**. For example, fluids in series 1 (3.9-4.2 cSt) had NOACK volatility ranging from 13-30%. Fluids in series 2 (5.7-5.75 cSt) exhibited NOACK volatility range of 6-18%. Kinematic viscosities in these ranges cannot be used to differentiate lubricant fluids.

However, if API group number is known, kinematic viscosity becomes a better indicator of NOACK volatility. The R^2 values for the trend lines in **Figure 2** indicate that viscosity is a good predictor of volatility for group III and IV oils. This is not true with group II oils; however **Figure 2** suggests that as viscosity increases, the correlation to volatility becomes stronger (indicated by the reduced scatter.)

Directly comparing isoviscous oils by API group indicates that the lowest NOACK volatilities were exhibited by group IV PAOs (**Figure 2**). In a similar manner, group III oils showed lower NOACK ratings than group II oils. The lower NOACK ratings exhibited by group IV synthetic hydrocarbons indicates that these could potentially provide formulations that are more energy conserving.

Figure 2 illustrates that more viscous fluids generally have lower NOACK volatilities. This is apparent by the negative slopes of the trend lines. API group II oils exhibit a greater reduction in volatility with increasing viscosity when compared to group III and IV oils.

**Figure 2: NOACK Volatility versus Kinematic Viscosity**
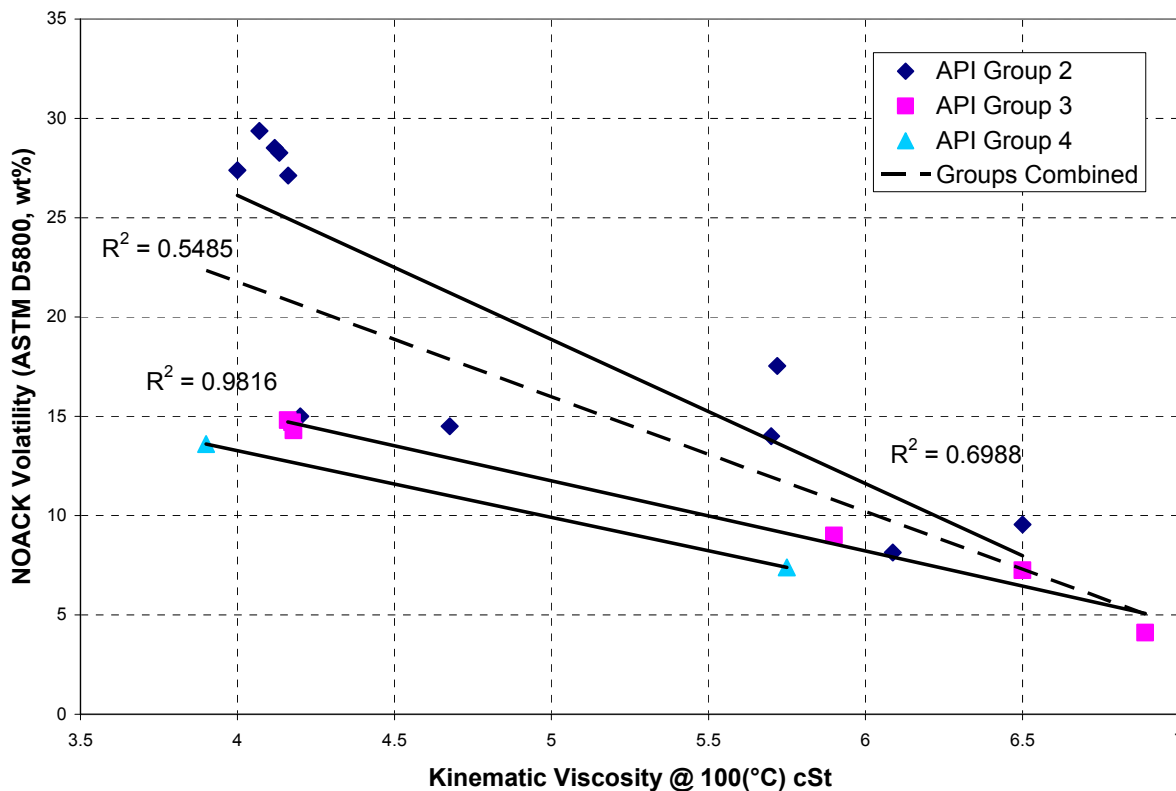
TGA

Accuracy, repeatability, and small sample size are a few advantages of using TGA as a method for measuring volatility characteristics of lubricant fluid. The procedure can be run virtually unattended. Some experimental cautions must be considered when using the TGA test. It has

been reported that pan shape influences the position of the TGA curve [13]. Therefore, the best comparisons are those made on the same instrument with the same pan. If the pan shape is not altered, repeatability is good. The shape of the pan affects the surface to volume ratio of the test sample which affects the evaporation rate and consequently the TGA curve. The quantity of gas (inert or air) passing over the sample also affects the position of the curve.

Comparing lubricants in their respective isoviscous series, it was noted that volatility generally increased when comparing TGA tests in air to tests run in nitrogen. Under identical temperature prescriptions, it required significantly less time for the samples to vaporize in air. This is attributed to oxidation and more cracking of the molecules in the lubricant fluid that occurs in the presence of air. The presence of oxygen causes chemical reactions that are not present in the inert atmosphere of nitrogen. In an inert atmosphere, weight loss is entirely due to vaporization until higher temperatures are reached.

The TGA tests indicate that volatility generally decreases with increasing viscosity. Comparing the curves in **Figure 3**, it took longer for the more viscous oil to completely vaporize in nitrogen. Heavier hydrocarbons found in more viscous fluids take longer to vaporize, therefore decreasing the volatility of the lubricant.

Figure 3: Comparison of Group II Oils with Different Viscosities in Nitrogen
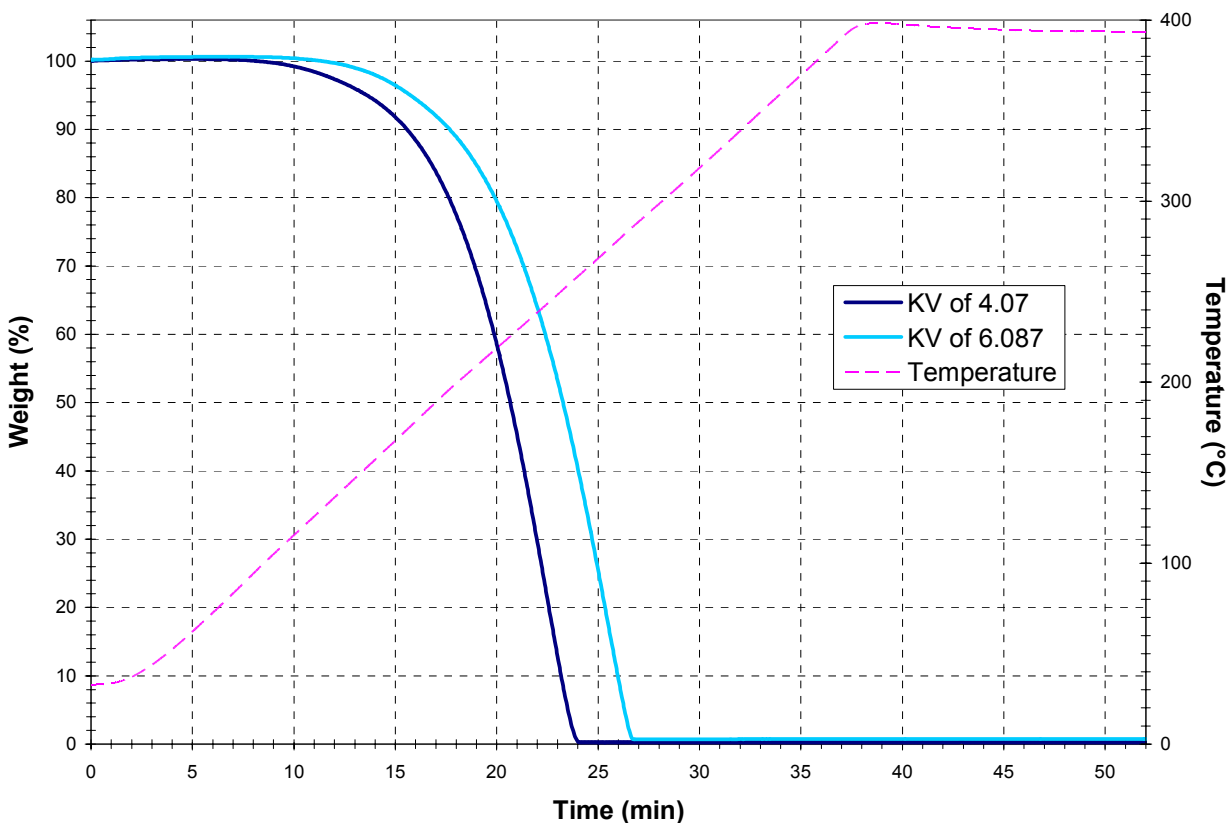
TGA Deposits

The actual amount of deposit is a function of several variables including application and operation life of the lubricant. Deposit measurements were taken as the remaining material at a specified temperature. This is equivalent to a run time using a standard experiment as is the case for the TGAs represented in **Figure 3**. For comparison purposes, a 39 minute runtime was chosen in this study. Deposit amounts are shown in **Table 6**.

Table 6: Deposit Amounts (%) for Air and Nitrogen Tests

		Air	Nitrogen			Air	Nitrogen
Lubricants	*Group*	*% Deposit by TGA*	*% Deposit by TGA*	*Lubricants*	*Group*	*% Deposit by TGA*	*% Deposit by TGA*
PAO 4	IV	0.9688	0.0482	651-0150	II	1.7172	0.2701
PAO 6	IV	2.8022	0.5599	651-0141	II	1.7147	0.3263
C-4R	III	1.1310	0.3789	651-0130	II	2.7751	0.5015
C-5R	II	2.3991	0.3519	651-0159	II	4.0547	0.7348
C-7R	III	4.8176	0.3556	651-0143	II	1.4118	0.5345
C-100R	II	1.7857	0.0000	651-0160	II	1.6636	0.5492
C-220R	II	4.2303	0.4082	651-0172	III	1.7397	0.4023
P 1008	II	0.7637	0.3570	651-0149	III	1.4329	0.5039
P 1810	II	2.9190	0.3163	651-1946	III	3.7248	0.5226
				651-0124	III	4.9689	0.4433

Also shown in **Table 6** is that deposits in air are significantly higher than deposits in nitrogen. The only difference between the tests was the gas flowing over the sample; therefore the increased deposit observed must be attributed to the oxidation occurring in air. The increased deposits were also observed visually after the TGA tests were completed. Tests run in air required acetone to remove deposit from the pan between tests. **Figure 4** illustrates that deposits were found to generally increase with kinematic viscosity of the fluid. This increase was greater in the presence of air. This implies, but does not prove that hydrocarbon molecular weight contributes to this effect.

Figure 4: Deposit versus Kinematic Viscosity
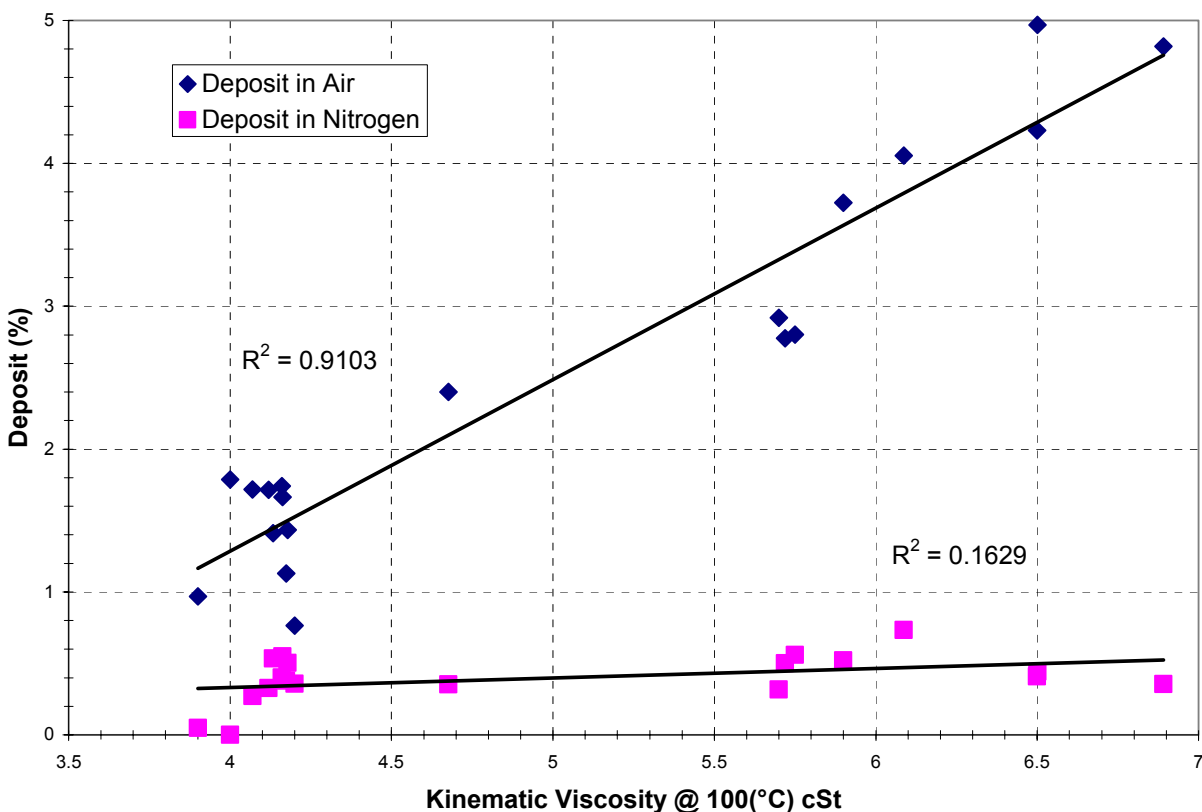
Conclusions

- The results of these studies indicate the importance of using more than one test to measure lubricant volatility. The NOACK test is really an oxidation test which is a sufficient method of measuring volatility for specific applications. The TGA test measures volatility which can be used to model applications that are not possible with the NOACK test. Using both tests in conjunction allows for more accurate and comprehensive results.

- It was found that CMMOs are generally more volatile than isoviscous group IV synthetic PAOs. The increased volatility may result in a greater mass of hydrocarbon released to the environment by CMMOs.

- Kinematic viscosity alone was not a good method for determining volatility. However, if API group number is known, the correlation between viscosity and volatility is good.

- Volatility generally increased when comparing TGA tests in air to tests run in nitrogen.

- Volatility generally decreases with increasing lubricant viscosity.

- Deposits in air were greater than those in nitrogen for all fluids tested.

Future Work

Volatility studies should be conducted on different pan materials. For simulations of in-use applications, pans should be made of materials identical to equipment components.

Studies should continue to test volatility in oxygen free atmospheres to determine structures of volatile components of base fluids.

Additive volatility affects lubricant performance. Studies are being conducted to evaluate additives to determine their volatility characteristics under anaerobic and aerobic conditions.

Acknowledgements

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