

## SHORT-TERM AND LONG-TERM VOLATILITIES OF FILMS FROM POLYOL ESTER AND ETHER-BASED OILS OF VARIOUS MOLECULAR WEIGHTS

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**Abstract:** Viscosity and volatility parameters are very important for many technical applications, such as adhesives, lubricants or coatings. Often low viscosity and low volatility is desirable and various esters of oils from industrial crops are more appropriate than hydrocarbons. Short term evaporation can be quantified by thermogravimetric analysis (TGA), standard protocol of NOACK volatility or even flash point. But standardized tests of prolonged degradation do not address vaporization. In this study short and long-term volatilities of esters from industrial crops were compared to hydrocarbons and ethers using thin film methodologies. It turned out that mostly components of low molecular weight are responsible for NOACK results. Long term volatility is more dependent on decomposition reactions, which take place due to hydrolysis, oxidation and other degradation processes. Double bonds and ether linkages lead to higher long-term volatile emissions. Decomposition trends must be considered when selecting oils for applications, where low volatility and migration is important.

**Keywords:** Industrial crops; basestocks; viscosity; degradation.

### 1. INTRODUCTION

Industrial recognition of acylation, metathesis and other advanced synthetic methods in oleochemical technology has resulted in commercialization of a variety of new compounds, such as estolides [1], macrodiols, olefins [2], multifunctional esters [3] and many others. Frequently they can be produced by chemically or biocatalytically converting oils from industrial crops without competition with the food production. In some cases, like Camelina, Crambe [4] and some other non-food oilseeds, sizeable quantities of technical fluids can be obtained from soil of relatively poor quality, which is not suitable for food cultures. Such precedents are very beneficial to advancement of innovative biorefinery concepts, constitution of new value chains and overall progress in bioeconomy.

Many applications of technical fluids impose strict specifications on their volatilities and viscosities. A broad range of techniques can be used to evaluate dynamic and kinematic viscosities along with many other rheological parameters. It is very customary to measure and report viscosities for newly developed fluids even when it is not formally required. On the other hand, methodologies for quantitative evaluation of volatility are less systematic. Since volatility is very important for fuels and other petroleum products, several methodologies are developed to evaluate petrochemical fluids by distillation of their fractions with different molecular weights (mol. wt.). However, commercial oleochemical products rarely render themselves to distillation. Typically, only their boiling and flash points are reported for safety reasons, without engaging into more detailed investigations of their volatilities.

Relationship between flash points and fluid volatility is not straightforward. Fluids, which are difficult to ignite, might be quite volatile but still have high flash points, e.g. tetrachloroethylene (m.p. -22°C, b.p. 121°C, flash pt. 122°C), octadecafluorooctane (m.p. -25°C, b.p. 105°C, flash pt. 100°C), etc. Therefore, thermogravimetric analysis (TGA) is often used to evaluate the amounts of volatile constituents. Small amount of samples, rapid measurement times, good inter-laboratory repeatability

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and many other advantages make TGA widely used for quality control and academic research. However, b.p., flash points or TGA data describe only thermodynamically driven evaporation, when compounds of lower mol. wt. move into the gas phase to equilibrate their partial pressure. In many cases decomposition-driven emissions are also important, especially when fluids oxidize, hydrolyze or otherwise degrade during long-term field usage.

Decomposition-driven volatility is particularly significant in unsaturated oleochemicals. In many cases their odors and emissions are primarily caused by oxidative scission of polyunsaturated chains. Some degradation tests, such as Rancimat, even determine oxidative stability by evaluating volatile emissions. When measuring flash points or even under TGA, such degradation is not a major factor, but in field usage oxidative scission might be the main reason of volatile losses. Gradual reduction of oil volume, buildup of slime around reservoirs, odor emissions and many other factors are directly related to long-term vaporization of fluids. Fuels, lubricants, rust preventives, process oils and many other technical fluids can be affected by degradation, leading to significant volatile losses.

Therefore, one must account for the differences between short-term and long-term vaporization. TGA under so called NOACK regime can be used as a method to test short-term vaporization. NOACK regime is designed to compare volatilities of lubricant basestocks. The original procedure ASTM D5800 measures volatile losses of a fluid sample, placed into a container of specified dimensions, heated to 250°C and exposed to the controlled air stream over the container for 60 min. Several variants of the NOACK tests exist, three of them being described in ASTM D5800 with the sample volume in the container varying from 60 ml to 120 ml. Therefore, the TGA procedure has received significant recognition [5] For evaluation of long-term vaporization, thin film degradation tests can be performed [6], [7]. Oil films are exposed to abundant metal surface and availability of air oxygen, therefore their degradation proceeds much faster than in bulk. Consequently, emission of volatile decomposition products can be measured gravimetrically.

Oils from industrial crops are frequently transformed chemically into free acids, alcohols or esters with or without unsaturation. It is difficult to assess a large variety of chemical categories with different mol. wt., which often contain multiple or mixed functionalities. Therefore, only simple representatives are selected for this study. Two mineral oils are also included for comparison, since they are the competitive petroleum-based fluids being replaced by oleochemical representatives. There are several mechanisms of decomposition: oxidative, hydrolytic, microbial, etc. In this study only oxidative decomposition is considered, employing ambient air without specifically studying hydrolytic effects, which might also be quite significant [7]. Oleic moiety is selected to represent unsaturated derivatives, concurrently with squalene and squalane. The latter has similar properties to those of paraffinic oils, so its testing results might correlate to abundant technical data on mineral oils.

## 2. EXPERIMENTAL

Mineral oil RL208 was acquired from Weber Reference Oils (Germany), diester 2EH dodecanedioate from TCI Chemicals, FAME from Bliska (Poland). Squalane, squalene, oleic acid and oleyl alcohol were purchased from Merck (Germany). Their key properties are listed in Table 1.

**Table 1.** Measured viscosities and volatilities with theoretically determined mol.wt. of test samples.

Oil name	Abbreviation	Molecular weight, g/mol	Viscosity at 40 °C, mm <sup>2</sup> /s	NOACK volatility, %
NOACK calibration oil	RL208	n.a.	38.6	13
Paraffinic mineral oil	300SN	n.a.	61.4	10
C <sub>30</sub> H <sub>62</sub>	squalane	423	18.1	11.2
C <sub>30</sub> H <sub>50</sub>	squalene	411	10.1	11.4
di-2-ethylhexyl-1,12-dodecanedioate	diester	455	n.d.	5.2
Technical oleic acid	oleic a.	282	n.d.	n.a.
Technical oleyl alcohol	oleyl alc.	268	n.d.	78
Rapeseed fatty acid methyl esters	FAME	296	4.5	66

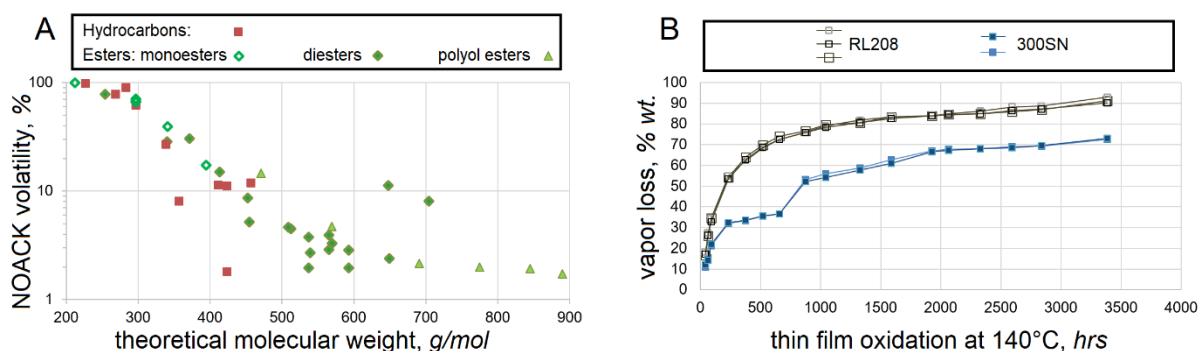
Initially the temperature was ramped at 50°C/min rate until reaching 235°C, then ramping was reduced to 5°C/min. At 249°C, which was reached after 7 to 8 min of ramping, the isothermal regime was

imposed. Weight loss readings after 8'00" from the heating initiation were recorded as NOACK values. Mineral oil-based reference liquid RL208, originally blended by Shell Global Solutions Deutschland GmbH (Germany) was used for calibration, averaging  $13.0 \pm 1.6\%$  wt. loss in 9 runs.

Long-term vaporization tests were performed using methodology, described previously [6, 7]. Low carbon steel coupons were coated with 500  $\mu\text{m}$  thick films of test fluids and heated in a forced-draft oven (Memmert GmbH, Germany) at 90, 120 or 140°C. The coupons were weighed periodically to determine weight loss due to sample vaporization using the balance ALJ 160-4AM (Kern & Sohn GmbH, Germany).

### 3. RESULTS AND DISCUSSION

Short-term volatility of the fluids was evaluated using the NOACK method. Only the samples with known chemical identities were used so mol. wt. could be calculated theoretically. Dependence between NOACK volatility and mol. wt. is shown in Fig. 1A.

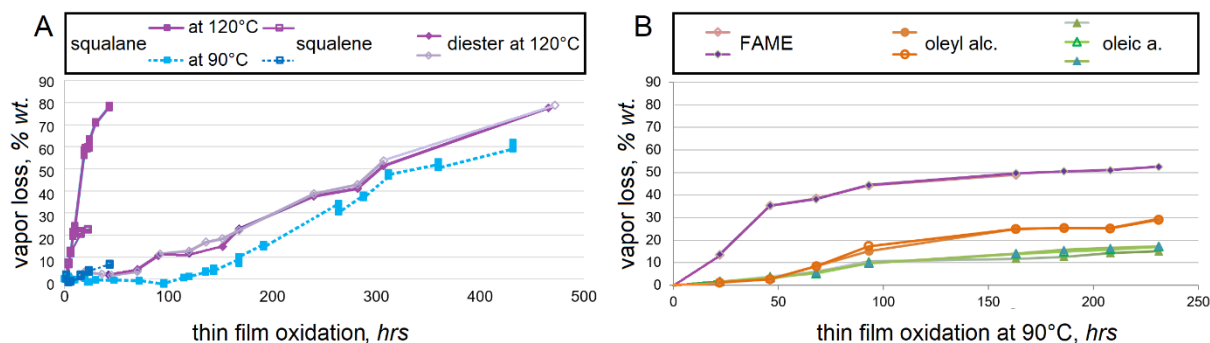


**Figure 1.** A) NOACK volatilities of hydrocarbon and ester-based oils with calculated mol. wt. B) long-term vaporization of two mineral oils (triplicate and duplicate runs) at 140°C.

Since chromatographic or mass-spectral analyses were not performed, some compounds could retain significant amounts of impurities, which could result in additional volatile emissions. Therefore, from this data alone it would be too speculative to draw quantitative correlations. But a very strong influence of mol. wt. on NOACK volatility is clearly evident. No effect of saturation or unsaturation could be observed. Table 1 shows that NOACK volatilities of fully saturated squalane and highly unsaturated squalene are nearly identical, the data points also represented in Fig. 1. This confirms the expectation that NOACK volatility is not significantly affected by oxidative decomposition and reflects only thermodynamically-driven short-term volatility. The same should be expected from b.p. and flash point measurements, because oil samples in these are usually heated to lower temperatures for less than 1 hr.

Mineral oils RL208 and 300SN recorded NOACK volatilities of 13 and 10% respectively at relatively high temperature up to 250°C. However, when tested under long-term oxidation conditions, these oils lost most of their volume to volatile emissions, despite much lower test temperature of 140°C, see Fig. 1B. The runs were discontinued after nearly 5 months of testing when the samples solidified due to oxypolymerization. This shows that the difference between amounts of material, lost during evaporation, and that lost during long-term decomposition, can be dramatically different.

Influence of unsaturation on long-term volatility was evaluated by comparing squalane and squalene at 90 and 120°C, see Fig. 2A. At 120°C the rates of vaporization were not too different between squalane and squalene. The latter solidifies rapidly, therefore, only the initial trends could be compared. Interestingly, the diester of quite similar higher mol. wt. vaporized much slower than the hydrocarbons, suggesting that polarity of esters reduced evaporation rates. At 90°C significantly faster vaporization could be observed from squalene, approaching 10% in ~50 hrs with more than 150 hrs needed for squalane. This agrees with the expectation that unsaturation accelerates decomposition rates. On the other hand, the rates of their volatile emissions at 120°C were surprisingly similar.



**Figure 2.** A) long-term vaporization of hydrocarbons and saturated diester (duplicate) of similar mol. wt. B) long-term vaporization of ester, alcohol and acid (multiple runs) of similar mol. wt. at 90°C.

Compared to double C=C bonds, hydroxyl or carboxy functional groups may not affect oxidative decomposition reactions as significantly. But they still might have a strong effect on evaporation, see Fig. 2B. Despite somewhat higher mol. wt. FAME vaporizes much faster than oleyl alc., while oleic a. has the slowest rate of vaporization. The latter has the best capability of forming hydrogen bonds, which is also a significant factor in oleyl alc. Therefore, their evaporation is much slower than that of FAME. Observed trends are quite intuitive, however, they give a clear quantitative comparison between representatives of different oleochemical categories and can be a valuable tool to assess long-term volatility effects without the need of prohibitively long testing.

#### 4. CONCLUSIONS

- TGA, NOACK, boiling point and flash point procedures measure only thermodynamically-driven short-term volatile emissions. Thin film degradation tests can compare long-term volatilities, which are caused by decomposition reactions.
- Most of oil volume can be lost through long-term decomposition. Even fully saturated esters and hydrocarbons can lead to nearly 100% volatile emissions, driven just by oxidative decomposition. Mist formation, hydrolytic and microbial degradation might also be important.
- Double bonds, hydroxyl, carboxy, ester and other functional groups along with molecular weights have significant effects on evaporation and decomposition.

#### 5. ACKNOWLEDGMENTS

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