ELGI Paper - Venice 2016

The Evaluation of Oxidation Resistance of Lubricating Greases using the Rapid Small Scale Oxidation Test (RSSOT)

S. J. Nolan and R. Savin

Abstract

ASTM D7545 is an established fuel industry test that measures the Oxidation Stability of Middle Distillate Fuels using the Rapid Small Scale Oxidation Test (RSSOT). This test equipment was recently evaluated by the ELGI Biobased Working Group (WG) in conjunction with the ELGI Railway WG using grease samples from Round Robin studies to evaluate other recognised oxidation tests, such as the traditional ASTM D942 test, Pressure Differential Scanning Calorimetry (PDSC) and a Modified Rotary Pressure Vessel Oxidation Test (RPVOT). However, ASTM D942 requires careful preparation of the apparatus to ensure that the measured pressure loss is not compromised by oxygen leakage, and it takes 100 hours to complete the test. This paper shows that the RSSOT apparatus delivers accurate and repeatable results for lubricating greases in a time-efficient manner, (minutes rather than days) yet discriminates their oxidation performance in line with traditional and other oxidation tests.

Introduction

In 2009 a joint ELGI - NLGI Working Group was formed to consider appropriate test methods to measure the oxidation and low temperature performance of Bio-based lubricating greases. These greases have gained an increasing market share due to increasing consumer recognition of the need for environmentally acceptable lubricants, (EAL) and increasing legislation driving change towards sustainable and biodegradable lubricants. To develop effective products it is necessary to measure their performance in commonly used standard industrial tests that were originally designed to measure the performance of mineral-oil based (non-biodegradable) grease products. These tests are often unreliable, operator sensitive (poor repeatability) and lab-to-lab agreement (poor reproducibility) leading to erratic and misleading results if not carried out in duplicate or triplicate tests, which adds cost and time.

The objective for bio-based lubricant manufacturers is to develop robust products with proven performance in key areas such as oxidation resistance and low temperature performance. Since new laboratory equipment is now available for the determination of oxidation and low temperature performance, these have been evaluated against the older methods to determine their suitability for use. If suitable, these tests could then be standardised in new test methods suitable for evaluating the physical performance of bio-based products going forward, which could be used for product specification and quality control purposes.

Oxidation causes a breakdown of the chemical and physical properties of materials. For example, samples with fats and oils can become rancid, exhibiting an increase in acidity that can lead to corrosion and rusting. Oils can thicken, becoming more viscous and affecting their lubricating properties. Sludge can also form, blocking nozzles and filters, further compromising lubrication. Lacquering can effect cooling and friction properties, and dyes can undergo discolouration.

To slow these processes, antioxidants are added to inhibit the oxidation reaction. In order to use the most effective of these additives and the optimal dose for a particular application, a means of performance assessment is required.

Oxidation stability testing is necessary for

- Development of new products
- Evaluation of potential new additives
- Shelf-life investigation & prediction
- Quality control of incoming goods
- Quality assurance before product release
- Assessment of storage conditions
- Controlled accelerated ageing

This paper focusses on work carried out to determine the most suitable oxidation test(s) for bio-based greases in terms of ease of use, repeatability, reproducibility, equivalence of results (i.e. read-across), suitability for product development and quality control.

Suitable Oxidation Test Equipment for Greases

The most commonly used oxidation test methods for greases are tabulated below. Note the ASTM D7545 is an RSSOT test currently used for Fuels:

Test	"OPVOT"	"RPVOT"	"PDSC"	"RSSOT"
Procedure	**ASTM D942**	**ASTM D2272 mod**	**ASTM D5483**	**ASTM D7545**
Date of Test	1947	2012	1993	2014
Sample	20 g total (4 g x 5 glass dishes)	20g (grease) in 30g (silicone oil)	approx. 2.0 mg (SFI pan)	4 to 5 g (1 x glass dish)
Temperature	99°C	150°C	155°C, 180°C or 210°C	140°C Programmable
Test Duration	100 hours	Measured (minutes)	Measured (minutes)	Measured (minutes)
Test Gas	Oxygen	Oxygen	Oxygen	Oxygen
Test Pressure	110 psi (758 kPa)	90 psi (620 kPa)	500 psi (3500 kPa)	(101 psi) 700 kPa
Result	Pressure loss (measured) after typically 100 hrs	Induction Time (IT) to reach 25 psi (4%) pressure drop in minutes	Oxidation Induction Time (OIT) in minutes	Time to desired Pressure loss (nominally 10%)
Repeatability	Varies; 2 to 10 psi	N/A	0.42√m (± 8%)	N/A
Reproducibility	Varies; 3 to 20 psi	N/A	0.71√m (±13%)	N/A
Issues	Operator skill Leakage! Timing (ON / OFF) Duration, 100 hr	Sample dilution Silicone oil impact	Sample loading Surface area Blow off!	None

Table 1: Comparative Test Procedures used in Oxidation Tests

ASTM D942: "Bomb" Oxidation test (OPVOT)

This test has been used for many years to assess oxidation performance requirements for greases, and is well known throughout the grease industry. However, it takes considerable effort to set-up and run a test, and requires 100 hours (4 days and 4 hours) to obtain a result. There is a risk of the seal leaking throughout the test giving poor results, and a subsequent need to either repeat the test or run duplicate samples in the first place. This makes the test timely and expensive to run requires a scheduled start time (Monday, Thursday or Friday morning). The D942 (OPVOT) test is therefore not well suited to Research and Development (R&D) and Quality Control (QC) requirements.

ASTM D2272: Modified Rotary Pressure Vessel Oxidation Test (RPVOT)

This test was included for evaluation in the 2012 ELGI Rail WG RR. A grease sample (20g) is diluted with silicone oil (30g) to make a liquid mixture suitable for testing. Test pressure is similar to OPVOT, but test temperature is significantly higher which reduces the IT time to minutes. There is concern that sample manipulation may lead to irrelevant results and poor precision.

ASTM D5483: Pressure Differential Scanning Calorimetry (PDSC)

PDSC is an expensive analytical test apparatus that has been used by major companies to determine the oxidation resistance of lubricating oils and greases. For grease tests there is the added complexity of obtaining a smooth surface film on the sample in the test pan. Operator expertise is required to ensure the pressurisation steps do not cause the test pans to be blown off their test sites at the start of the test, requiring a repeat test. The price and general lack of availability of this test equipment to grease manufacturing companies are issues that could make global adoption of this approach unlikely.

Rapid Small Scale Oxidation Test (RSSOT)

<u>Test Principle – RapidOxy (RSSOT)</u>

The Rapidoxy is a RSSOT instrument. It accelerates the oxidation process for a sample at an elevated temperature when exposure to excess of oxygen.

In a small sealed test chamber the sample is exposed to pure oxygen under pressure (up to 700 kPa) at a chosen temperature (up to 200 °C). The temperature is kept constant and the pressure is continuously traced until a defined pressure drop is detected. It allows the determination of oxidation stability for various products and assists in the prediction of how fast a sample will oxidise and experience the associated loss in functional quality.

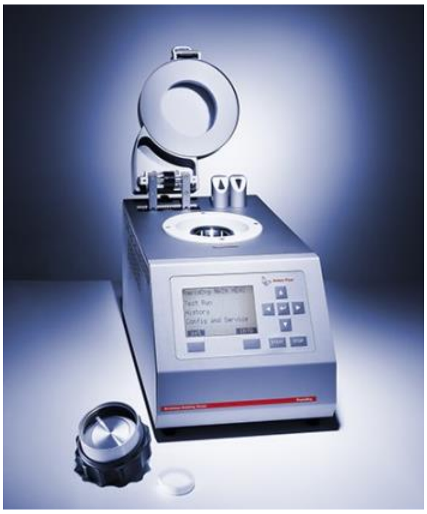


Figure 1: RapidOxy (RSSOT) apparatus

Induction Period & Break Point

Typically, once the oxidation process starts the rate of oxidation increases rapidly in a chain reaction. Therefore, once underway, full oxidation will follow rapidly. Since this behaviour is predictable the test only needs to run until the induction or break point for the purposes of oxidation stability measurement.

The time elapsed between starting the heating procedure of the sample vessel and the moment when the formation of oxidation products rapidly increases in known as **the induction period**.

The end of the induction period is indicated by a defined pressure drop (i.e. p max -10 %) indicating the rapid consumption of oxygen. This is known as the **break point**.

The RSSOT instrument completes the test once the break point is reached, reporting the induction time for the sample (in minutes). The longer the induction period the better the sample resists oxidation.

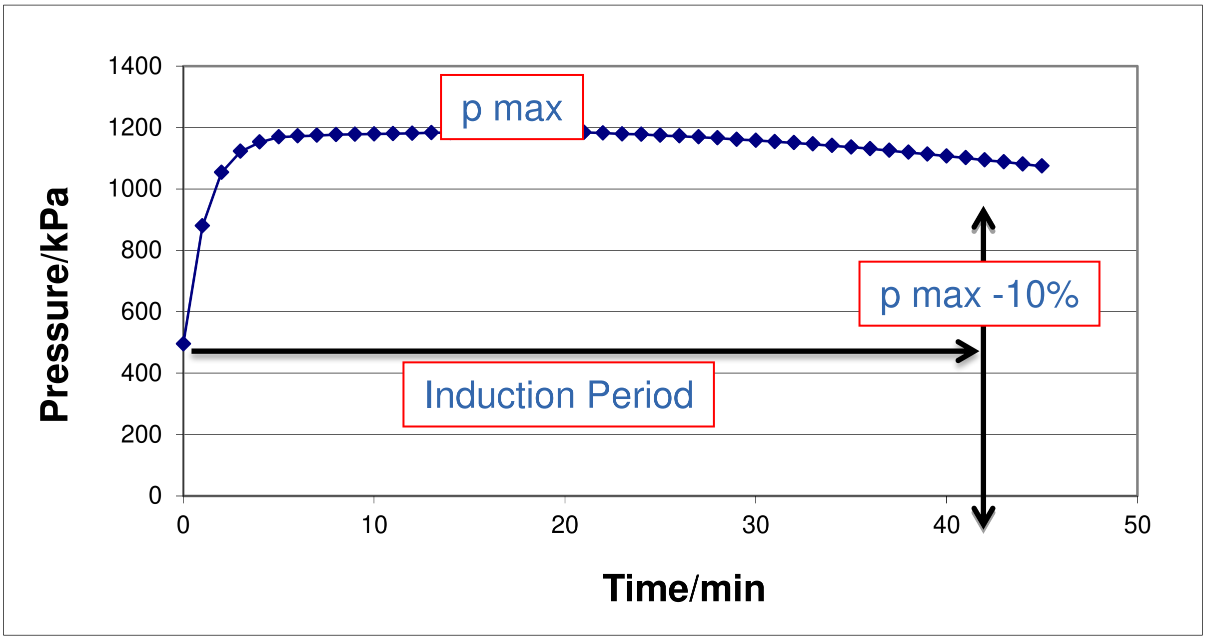


Figure 2: RSSOT test process chart

Test Variables - Pressure Dependency

The effect of the chosen test pressure on the result is important variable to understand. To evaluate this, a sample was tested at a range of difference pressures. The data shows that there is no significant effect in the induction time caused by the applied test pressure.

Fülldruck in kPa	Pmax-10% minutes decimal
800	113.76
700	115.10
600	116.97
500	116.70
400	117.10
300	115.48
200	117.40
100	111.31

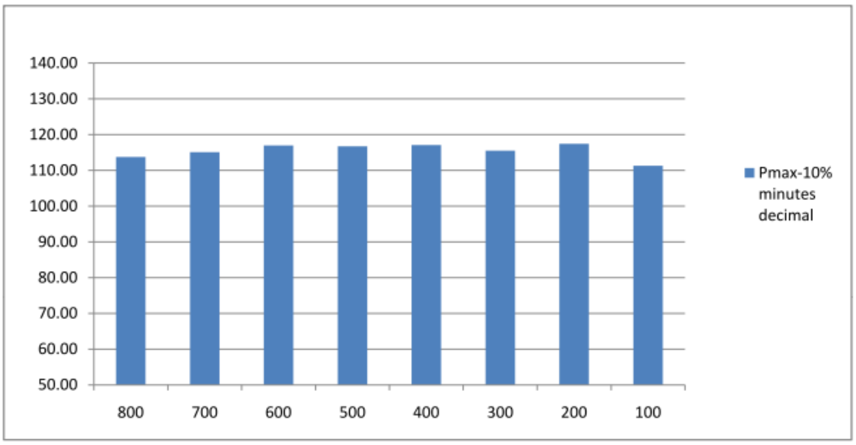


Figure 3: Effect of various applied test pressures on RSSOT oxidation induction period

Test Variables - Temperature Dependency

It is important that the relationship between test temperature and induction time is understood. Accelerated aging and the temperature dependence of chemical reactions can be predicted by the work of Arrenius.

It is important that the RSSOT can be predicted to this equation, allowing the user to develop test methods with confidence. Arrhenius plots are often used to analyse the effect of temperature on the rates of chemical reactions.

A sample was tested at a range of temperatures. An Arrhenius plot displays the logarithm of kinetic constants plotted against inverse temperature.

Test Temperature [°C]	**p max -10 %** (minutes decimal)
110	1172.98
120	415.30
130	159.30
140	68.25
150	31.72
160	16.15

Table 2: RSSOT Test Temperature versus Oxidation Induction Period

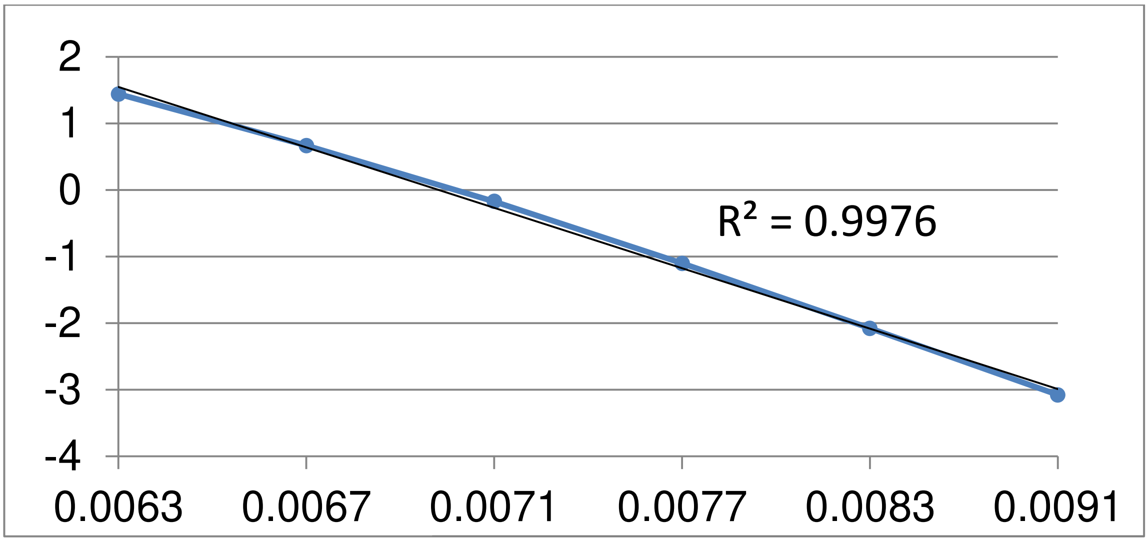


Figure 4: Arrhenius Plot in [k (kPa min-1)] - note Temperature 1/T [K]

A straight line relationship is observed, showing that a 10°C temperature increase leads to a halving of the test time. When developing test methods this allows the user to predict induction period and optimise test procedure.

Advantages of the RSSOT method

- No sample preparation, simply place into the sample dish
- No need of hazardous materials for fat extraction
- Suitable for liquid, solid and semi-solid samples
- Faster results, saves time and money
- Small sample volume, typically only 5 mL

The RSSOT apparatus was engineered to improve traditional oxidation stability test methods for gasoline, diesel, biodiesel and biodiesel blends which are time consuming and labour-intensive so cannot be used for spot checking product quality or for process monitoring and control. The RSSOT test offers very fast test cycles (generally 1 - 2 hours), improved user safety, easier sample handling, small sample sizes (region of 5 ml), fast and simple cleaning procedure as well as a fully automatic operation including oxygen charging and relief. It provides clear and understandable results and delivers significant improvements in repeatability and reproducibility compared to traditional oxidation tests.

In 2012 a Round-Robin study was carried out by the ELGI Biobased WG to determine the oxidation performance of eight grease samples (G1 through G8) using the ASTM D942 (OPVOT), RPVOT and PDSC techniques, (See Table 3). Independently of the Rail WG, these samples were used by two ELGI Biobased WG participants in RSSOT tests to determine whether the RSSOT could be a suitable test candidate for a new RR oxidation study for Bio greases. The RSSOT test method used a glass or PTFE dish filled with the test grease sample (approx. 5 g) and the surface smoothed using a palette knife to ensure each sample surface is equivalent. The dish was then placed into the RSSOT test cell and closed using a seal to prevent leakage. Test pressure (700 kPa) and temperature (140°C) were selected and the test initiated. The measured RSSOT result is the time in minutes to achieve a 10% pressure drop at test temperature. RSSOT results were very favourable.

Comparative Oxidation Performance - 2012 RR Results versus RSSOT:

Sample (RR)	ASTM D942 kPa	kPa	Mean	RPVOT mod. (min)		Mean	PDSC OIT (min)		OIT (min)		OIT (min)		RSSOT (min)		
							155°C	180°C	155°C	180°C	150°C	210°C		140°C	150°C
G1	50	20	**35**	599	739	**669**		51.6		57.2			299	**323.4**	
G2	65	25	**45**	463	738	**601**		33.9		47.55		6	277	**318.7**	
G3	670	703	**687**	50	55	**53**	9.5		4.65		13		62	**63.4**	
G4	660	648	**654**	54	35	**45**	12.2		10.75		16.2		73	**69.1**	
G5	110	69	**90**	354	622	**488**		50	9.2			3	202	**249.4**	
G6	673	648	**661**	41	36	**39**							35	**32.4**	
G7	N/A	225	**225**	57	75	**66**	9.7		9.55				90	**95.8**	
G8	238	360	**299**	55	62	**59**			6.75				119	**128.4**	**64.5**

Table 3: ELGI WG Round-Robin 2012 results with additional RSSOT data

The raw data for each grease sample (G1 - G8) in each oxidation test is tabulated above, (Table 3).

For ASTM D942 (OPVOT) lower results equate to better oxidation performance, but for all the other tests higher results equate to better performance. In order to review the effectiveness of each test in discriminating the relative performance of the eight RR samples, the results were normalised to make comparison easier, (Table 4) - values in RED are at 180°C, values in BLUE are at 155°C.

Sample	D942	RPVOT	PDSC OIT	RSSOT
G1	35	669	**54.0**	311
G2	45	601	**41.0**	298
G3	687	53	**7.1**	63
G4	654	45	**10.8**	71
G5	90	488	**9.2**	226
G6	661	39	N/A	34
G7	225	66	**9.6**	93
G8	299	59	**6.8**	124

Table 4: Normalised Results

Sample	D942	RPVOT	PDSC OIT	RSSOT	MEAN
G1	1	1	**1**	1	**1.00**
G2	2	2	**2**	2	**2.00**
G5	3	3	**5**	3	**3.50**
G7	4	4	**4**	5	**4.25**
G8	5	5	**6**	4	**5.00**
G4	6	7	**3**	6	**5.50**
G3	8	6	**7**	7	**7.00**
G6	7	8	No Data	8	**7.67**

Table 5: Ordered level of Oxidation Performance

The results were then ordered in terms of best to least performers, (Table 5).

ELGI WG RR 2012 versus RSSOT - Consensus Oxidation Performance Order

Figure 5: Discrimination of Oxidation Performance according to the Test Method used.

In Figure 5 it can be seen that G1 is the best performing grease followed by G2 as second best, (rated equally by all tests). Similarly, G3 and G6 are the least performing greases, even though no PDSC data is available for G6 it is rated as the least performing based on the three other tests used. We find some disagreement in the order of performance between tests, but for D942 (OPVOT) RPVOT and RSSOT tests only two results out of eight are out-of-line with the consensus order, whereas for the PDSC test three results out of seven are out-of-line with the consensus order.

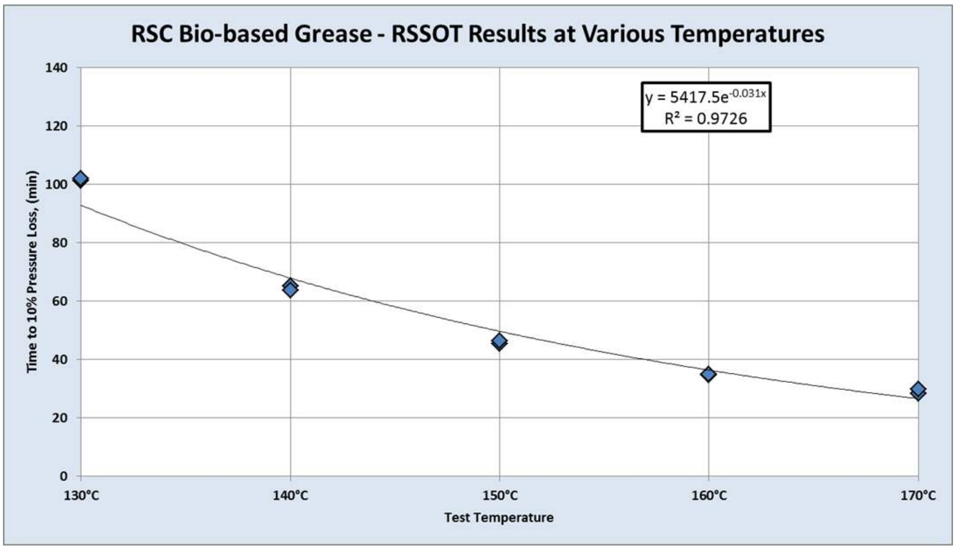
This RR study found that, in general terms, all of these tests can discriminate good oxidation performance from poor, but PDSC is more likely to misalign their relative order of performance.

How effective is the RSSOT test?

a) Repeatability

For a test to be effective it must deliver repeatable results when carried out by the same operator using the same equipment and the same test sample. This is the repeatability precision measurement (r).

In Figure 2 an experimental bio grease sample has been tested in the RSSOT apparatus twice at five different temperatures. The results are plotted and tabulated below, (Figure 6). The plot shows very good repeatability, where the two data points at each test temperature virtually overlap. The trend line shows an exponential equation fits very well with the data, and illustrates the effect of increasing / decreasing the test temperature on the rate of oxidation. This could be a valuable tool for R&D purposes.

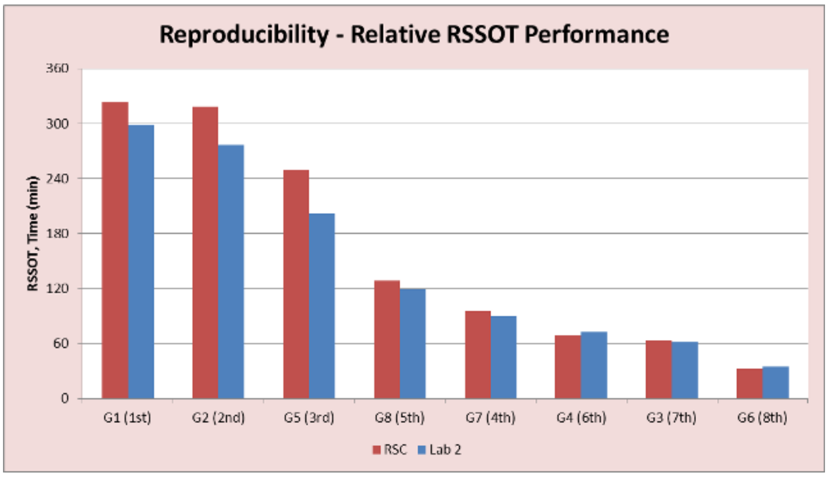


Test Temp	Result/ mins
130°C	101.20
130°C	102.08
140°C	65.06
140°C	63.56
150°C	45.31
150°C	46.40
160°C	34.61
160°C	34.95
170°C	28.18
170°C	29.68

Figure 6: Repeatability Data for Bio Grease at various temperatures, individual test data tabulated.

b) Reproducibility

Another very important requirement for an effective test is reproducibility, (R) such that if another laboratory were to run the same sample in the same test equipment using the same procedure, but a different operator, they should get similar results.



Sample	RSC	Lab 2
G1 (1st)	323.4	299
G2 (2nd)	318.7	277
G5 (3rd)	249.4	202
G8 (5th)	128.4	119
G7 (4th)	95.8	90
G4 (6th)	69.1	73
G3 (7th)	63.4	62
G6 (8th)	32.4	35

Figure 7: RSSOT Reproducibility data for ELGI WG 2012 RR greases, test data tabulated

Figure 7 shows the RSSOT results for all ELGI WG 2012 RR grease samples from two different laboratories. The actual results are tabulated, but it is clear from the plot that reproducibility is also very good, since both laboratories produced fairly similar results and discriminate all eight greases equally in terms of their relative oxidation performance. This level of reproducibility means that better agreement between laboratories should be possible going forward, and shows the RSSOT test would be suitable for use in setting Specification and Quality Control requirements.

c) Comparative Oxidation Performance over a Temperature Range

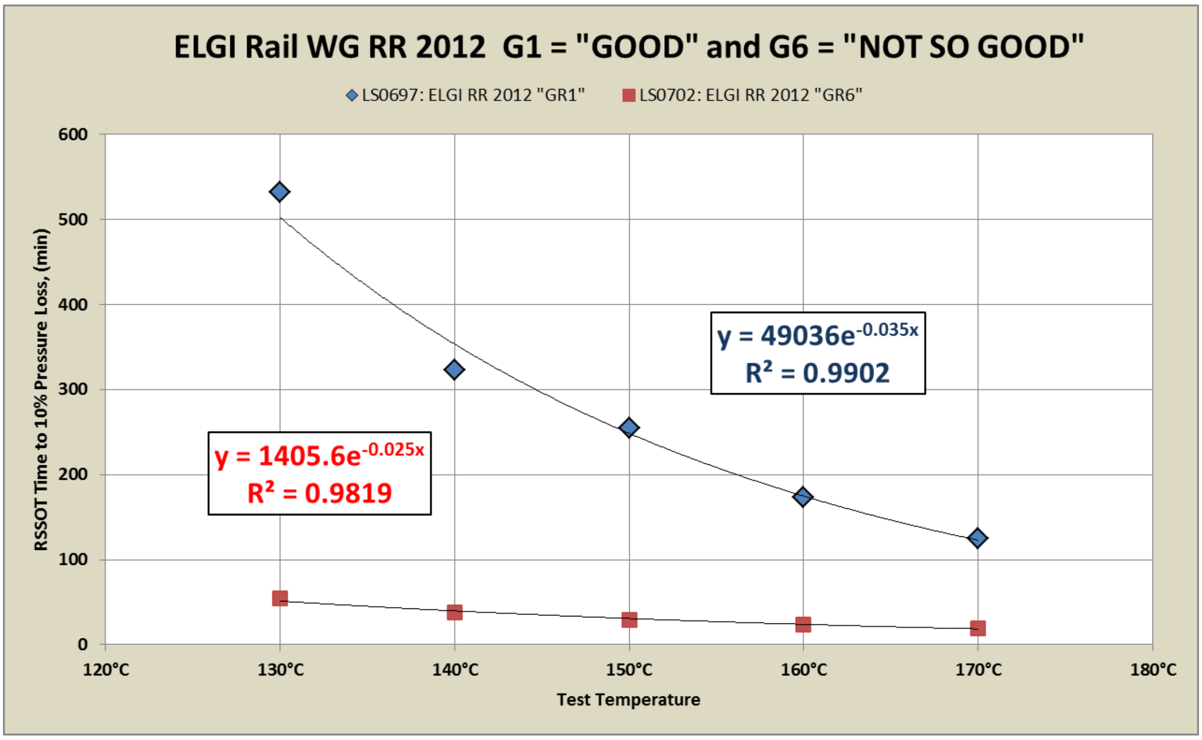


Figure 8: Comparison of Oxidation Performance

IN Figure 5 the ELGI WG RR samples were ordered according to their relative oxidation performance. G1 was found to be the best performing grease and G6 was found to be the least performing grease.

Figure 8 shows the results from RSSOT tests carried out on both samples at various temperatures to determine whether the test temperature had a variable impact on their relative performance; and it is clear that this is not the case for these samples. Again we find a good relationship between the rate of oxidation and temperature change, with a strong exponential relationship for the curves. However, from the plot it is clear that G1 performs better at 170°C than G6 does at 140°C.

d) Antioxidants - Additive Impact

For R&D purposes it is necessary to evaluate the performance of various antioxidants in a grease to determine the best candidate, the required treat-rate and cost implications. If ASTM D942 (OPVOT) test performance is stipulated a study of this type could take a very long time to complete with significant testing costs. Since our previous tests have shown that the RSSOT orders the level of oxidation performance in-line with the ASTM D942 test, it is now possible to evaluate various antioxidants rapidly in the RSSOT, determine their optimum treat rate and make proposals for the most cost effective formulation in a very short time.

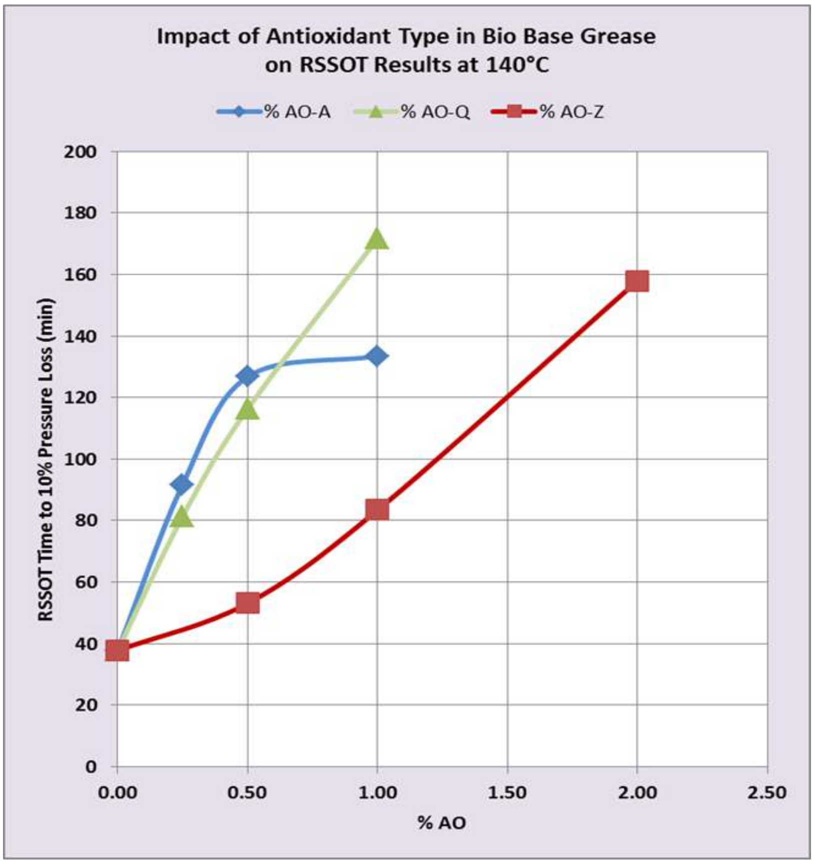


Figure 9: Impact of three different antioxidants on a Bio base grease

Figure 9 shows how three different antioxidants perform at different treat-rates in a Bio Base Grease in the RSSOT test at 140°C. The three chosen treat-rates correlate to their recommended, halved and doubled treat-rates.

It can be seen that all the antioxidants are effective, but that AO-A and AO-Q are more effective at a lower treat-rate than AO-Z which requires a higher treat-rate to achieve similar results. This data was derived from tests carried over a two day time frame. To achieve similar AO profiling using ASTM D942 would require several weeks to complete depending on the number of OPVOT vessels available.

Clearly the RSSOT is a quicker route to take.

Conclusions

The work carried out in this study and the results acquired from recent ELGI Biobased and Railway WG RR studies show:

- The RSSOT test is effective in measuring the oxidation performance of greases
- Correlation with “traditional” grease oxidation tests is very good
- Repeatability, r is very good
- Reproducibility, R is very good
- RSSOT is precise and accurate
- Possible to derive oxidation rate curves for greases over a range of temperatures
- Test is easy to do – no sample manipulation or risk of leaks
- Several tests can be carried out in one day, longer tests overnight
- Possible to run R&D projects in a week! (e.g. additive approval, thickener impact, etc…)
- Suitable for additive evaluation and treat optimisation studies
- Speed of test make it suitable for Quality Control purposes
- Proposal for new IP test method to be developed with Energy Institute
- High potential for use in condition monitoring of greases leading to a better understanding of the working life of a grease in service
- Potential for use in the determination of the Shelf-life of greases.
- **RSSOT is perfectly suited to grease oxidation performance testing**