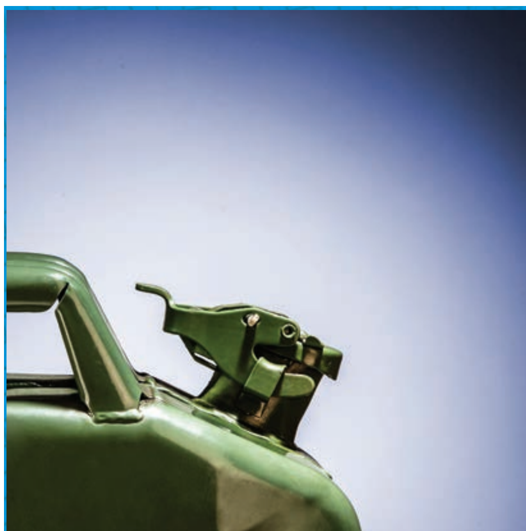

Measuring the Influence of Antioxidant Additives on Oxidation Stability for Fast and Economical Dosage of Antioxidants in Spark-Ignition Fuels

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Additives are added to fuels to improve their stability and performance. For spark-ignition fuels the correlation of oxidation stability to antioxidant concentration can be determined with a Rapid Small Scale Oxidation Stability Tester to prevent the excessive use of valuable antioxidant materials and operate cost-effectively. This approach is a fast, safe and user-friendly alternative to the traditional bomb method (ASTM D525 / EN ISO 7536).
The Rapid Small Scale Oxidation Stability Tester measures the induction period of spark-ignition fuels in compliance with ASTM D7525, which can be used as an indication of the oxidation and storage stability. Compared to other oxidation and storage stability test methods, this approach uses a small sample and gives test results in a short time period. The article will provide information on the performed tests as well as the results and their discussion.

Introduction

Oxidation stability is an integral part of the standard specification for spark-ignition fuels (ASTM D4814 / EN 228). Typical gasoline is primarily composed of naphtha (cycloalkanes), paraffins (alkanes) and olefins (alkenes). As refiners seek to maximise the production of high-value products from low-value stocks, there is an increased pressure to include catalytically cracked naphtha component streams with high olefin content into the gasoline blending pool. In particular, the unsaturated components are inherently unstable and subject to deterioration due to oxidation, which can cause undesirable fuel characteristics such as darkening, formation of polymers and reduced induction periods. Aging of gasoline can occur both during storage and use in an engine with hydroperoxides as initial reaction products, which - followed by a series of subsequent reactions - give rise to aldehydes, acids and polymers. Ultimately, these oxidation products are responsible for an acidity increase leading to rusting and corrosion, oil thickening leading to loss of viscosity control and appearance of insoluble materials leading to filter and nozzle blocking. The primary use of antioxidant additives is to extend the induction period and lifetime for which gasoline can be stored before undesired oxidation products are formed. However, the response of a gasoline to an antioxidant in terms of increased induction period and thus oxidation stability depends on both the antioxidant and the fuel composition. In order to achieve the best possible results for a certain fuel blend a thorough screening of antioxidants and their concentration is inevitable to accomplish the most cost-effective solution.

RSSOT – Rapid Small Scale Oxidation Test (ASTM D7525)

The RSSOT – Rapid Small Scale Oxidation Test was developed as an alternative to the standard test method for oxidation stability of gasoline ASTM D525, which is the traditional bomb method. This new test method measures the induction period of spark ignition fuels, including those containing alcohols or other oxygenates under accelerated oxidation conditions by an automatic RSSOT instrument. A typical test is conducted with a small sample volume of 5 mL which is introduced into a test cell and charged with oxygen to 500 kPa at a temperature of 15°C to 25°C. The measurement is started by heating the test cell to 140°C and lasts until the break point is reached, which is defined as the pressure in the test cell which is 10% below the maximum pressure of the test run. The induction period, which can be used as a measure of the oxidation stability, is specified as the time elapsed between starting the heating procedure of the test cell and the break point (pmax-10%), which is commonly measured in minutes (Figure 1).

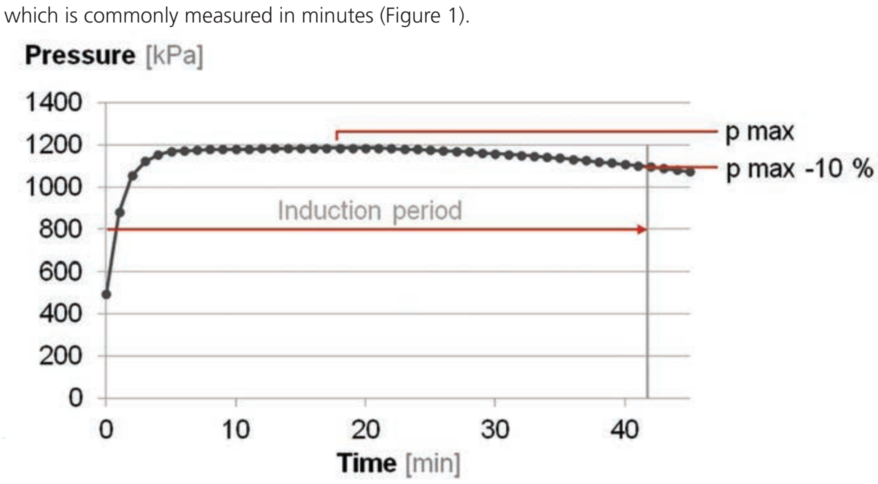

Figure 1: RSSOT / ASTM D7525 induction period, which is defined as the time elapsed between starting the heating procedure of the sample pressure vessel and a pressure drop of 10 % from p-max.

The fundamental parameters influencing the induction period of the RSSOT are the applied temperature and oxygen pressure within the sample vessel. Using fuel samples, the influence of both parameters was investigated independently (Figure 2). The pressure dependence was investigated at 140°C with oxygen pressures ranging from 100 kPa up to 800 kPa. The test results show that the measured induction period for fuel samples has no significant dependence on the applied oxygen pressure in the sample vessel. In contrast, the investigation of the temperature dependence from 110°C up to 160°C in 10 °C increments at 700 kPa has revealed that the RSSOT induction time is highly dependent on the applied test temperature and that the rate constant k increases with temperature. The Arrhenius plot shows a linear correlation of the rate constant against the applied test temperature with the general conclusion that the RSSOT induction period of a fuel sample is approximately cut by half for each temperature increase of 10°C.

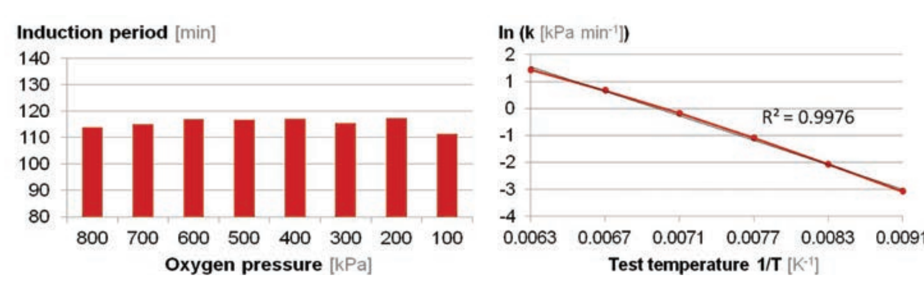

Figure 2: Left: Pressure dependence of RSSOT induction period for fuel samples. Right: Arrhenius plot of RSSOT rate constant against test temperature for fuel samples.

In comparison to the RSSOT, the standard test method for oxidation stability of gasoline ASTM D525 is typically conducted with a large sample size of 50 mL in an oxidation pressure vessel at lower temperatures of 100°C and an oxygen pressure of 700 kPa. The break point for the ASTM D525 is defined as the point in the time-pressure plot that is preceded by two following pressure drops of 14 kPa each within 15 minutes. The corresponding induction period is defined as the time elapsed between application of temperature and break point. Although the ASTM D7525 and ASTM D525 are in some respects similar, the differences in test temperature, sample size and break point definition make the RSSOT method a faster, safer and more user-friendly alternative (Table 1).

Table 1: Comparison of the RSSOT / ASTM D7525 with ASTM D525

Method	ASTM D7525	ASTM D525
Sample size	5 mL	50 mL
Test temperature	140 °C	100 °C
Oxygen pressure	500 kPa	700 kPa
Break point	pmax-10%	2 following Δp of -14 kPa each within 15 min
Induction period	Time between application of temperature and break point	Time between application of temperature and break point

Thanks to the higher test temperature and smaller sample size the ASTM D7525 test method reaches the break point approximately 15 to 25 times faster than with ASTM D525. Moreover, the break point definition of the ASTM D525 with two following timed pressure drops of 14 kPa can lead to tests where the break point criterion is never reached und thus no induction period can be measured. The clear definition of the ASTM D7525 break point as pmax-10% eliminates this problem and an induction period is obtained in all tests. Additionally, in contrast to the ASTM D525, no additional safety measure like a burst-disc is needed because of the apparatus design of the RSSOT. The eruption of a burst-disc during a test can be a major hazard to the surrounding laboratory staff and laboratory environment.

These advantages make the RSSOT ideal for the fast optimisation and release of gasoline.

Measuring the influence of antioxidant additives on gasoline with high olefin content

A "raw" gasoline with an olefin content of approximately 40% and a commercially available antioxidant were used for this investigation. The influence of the antioxidant additive on the induction period was screened for concentration from 0 ppm up to 50 ppm and tests were done in parallel using both test methods ASTM D7525 and ASTM D525 (Table 2). The results show that with the ASTM D7525 a short induction time of 23.55 minutes is obtained with 0 ppm of antioxidant, which can be gradually prolonged up to 17.60 minutes with an antioxidant concentration of 50 ppm. As expected the ASTM D525 has a much longer induction time of 199.34 minutes with 0 ppm antioxidant, which likewise for the ASTM D7525 is prolonged with increasing concentration of antioxidant additive. Overall, the measured induction periods were approximately 20 times faster with the RSSOT in comparison to ASTM D525.

Table 2: Influence of antioxidant additives on the induction period of gasoline with high olefin content

Antioxidant (ppm)	ASTM D7525 (min)	ASTM D525 (min)
0	13.55	199.34
5	13.93	243.50
10	14.63	271.00
25	15.45	348.00
50	17.60	453.00

Plotting the induction periods of ASTM D7525 and ASTM D525 against each other shows a linear correlation with an excellent data fitting of $R^2 = 0.98$ (Figure 3, left). In ASTM D4814 the limit for automotive spark-ignition engine fuels is set to a minimum induction period of 240 minutes using ASTM D525 as the test method, or 360 minutes for the EN 228 test method. Correlating these minimum ASTM D525 induction periods to ASTM D7525 the minimum induction period with the RSSOT has to be approximately 14 minutes for ASTM D4814, or 16 minutes for EN 228. To assess the influence of the antioxidant, the additive concentration was plotted against the ASTM D7525 induction period. The linear slope with a fitting of $R^2 = 0.99$ indicates an excellent correlation between RSSOT induction period and antioxidant additive concentration. Using this plot the minimum needed antioxidant concentration to meet the limits defined in the specifications ASTM D4814 and EN 228 can be determined. The ASTM D4814 oxidation stability criterion of 240 minutes induction period with ASTM D525 correlated to 14 minutes induction period with ASTM D7525 and can be met with 6 ppm of antioxidant concentration. The EN 228 oxidation stability criterion of 360 minutes induction period with ASTM D525 correlated to 16 minutes induction period with ASTM D7525 and can be met with 30 ppm of antioxidant concentration.

Ultimately, these results show that the ASTM D7525 allows fast product optimisation and helps to prevent excessive use of antioxidant additives to get the most cost-effective solution.

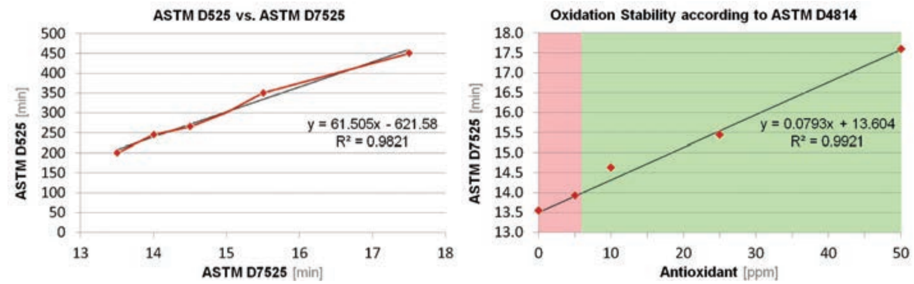

Figure 3: Left: Plot of ASTM D7525 induction period against ASTM D525 induction period for a gasoline with an olefin content of approx. 40%. The linear slope with a fitting of $R^2 = 0.98$ indicates an excellent correlation between both methods with the induction period of ASTM D7525 being approximately 20 times shorter in comparison to the induction period of ASTM D525. Right: Plot of ASTM D7525 induction period against antioxidant concentration for a gasoline with an olefin content of approximately 40%. The linear slope with a fitting of $R^2 = 0.99$ indicates an excellent correlation between induction period and antioxidant additive concentration. Colors indicate the correlated compliance of the gasoline oxidation stability with ASTM D4814. Green: in compliance. Red: no compliance

Conclusion

Oxidation stability is an integral part of the standard specification for spark-ignition fuels (ASTM D4814 / EN 228) and the use of antioxidant additives is indispensable to fulfill the requirements, especially for the increasing number of gasoline blends with high olefin content. The test data has shown that the ASTM D7525 (RSSOT) allows for fast, safe and user-friendly assessment of antioxidant influence on the induction period and thus oxidation stability of fuels. Moreover, the ASTM D7525 has an excellent correlation with the standard test method ASTM D525, while measuring the induction period approximately 20 times faster. This makes the ASTM D7525 the ideal industry procedure for product optimisation and release of gasoline.