CRC Report No. CM-136-20

DEVELOP PRECISION STATEMENTS FOR OXIDATION STABILITY TEST METHODS ASTM D525 AND ASTM D7525/ CORRELATION STUDY BETWEEN INSTRUMENTS BETWEEN OPERATING RANGE 240-1440 MINUTES

Final Report

June 2024

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Final Report

Project CM-136-20

Submitted to:
Coordinating Research Council
5755 North Point Parkway, Suite 265
Alpharetta, GA 30022
Attention: Dr. Chistopher Tennant

Prepared by:
Dr. Travis Kostan, Sr. Research Analyst
Valerie Rios, Supervisor-R&D

Southwest Research Institute® (SwRI®)
San Antonio, TX

June 2024

Approved by:

Kevin Shannon, Manager-R&D
Fuels and Lubricants Technology Department
Fuels and Lubricants Research Division

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FOREWORD

This report covers development and testing conducted by Southwest Research Institute (SwRI) for the Coordinating Research Council (CRC). The project, performed under CRC contract CM-136-20, was initiated in June of 2022 and testing was terminated in September of 2023 based on pilot study results. The internal SwRI project number was 08.27486. The SwRI project manager was Kevin Shannon, assisted in testing by Laboratory Supervisor Valerie Rios. Statistical analysis was conducted by Dr. Travis Kostan.

TABLE OF CONTENTS

LIST OF FIGURES AND TABLES

LIST OF FIGURES

LIST OF TABLES

1.0 EXECUTIVE SUMMARY

This report documents a project conducted by SwRI on behalf of the Coordinating Research Council (CRC). The goal of the project was to determine the feasibility of a correlation equation between two oxidation stability test methods, ASTM D525, *Standard Test Method for Oxidation Stability of Gasoline (Induction Period Method)* and ASTM D7525, *Standard Test Method for Oxidation Stability of Spark Ignition Fuel – Rapid Small Scale Oxidation Test (RSSOT)*. The data obtained from the correlation study would also be used to update the precision statement of D525 per ASTM D6300.

Research in the beginning of this project found four other correlation studies indicating a D525 result of 240 minutes would result in a D7525 result in the 15-25 minute range, while one other study indicated a 40-minute crossover point. The potential for a sample dependency on the correlation led the group to decide to first pursue a smaller scale pilot study in order to determine the likelihood of success of the larger project before conducting the full-scale Interlaboratory study (ILS).

Four samples were obtained, which were created from the 2x2 combinations of two non-oxygenated fuels which were labeled high stability component 1 and 2 (HSC-1 and HSC-2) with two low stability components (LSC-1 and LSC-2). Various blend percentages were tested to try to, at a minimum, obtain results which bracketed the D525 240-minute time on each sample, so that the D7525 time equivalent to 240 minutes in D525 could be estimated. The results are shown below in Table 1. The "A" and "B" following the fuel name indicate that these results are on a different batch of the fuel components.

TABLE 1: PILOT STUDY RESULTS

Fuel	% HSC	% LSC	D7525	D525
Fuel 1	98%	2%	14.00	108
			15.26	
	98%	2%	18.33	134
	99%	1%	22.03	>1440
Fuel 2A	60%	40%	18.85	191
Fuel 2B	50%	50%	20.68	204
	60%	40%	24.05	261
	60%	40%	28.25	not run
	70%	30%	32.36	>1440
Fuel 3A	60%	40%	17.91	125
Fuel 3B	60%	40%	21.06	not run
	60%	40%	21.70	189

	70%	30%	64.38	>1440
Fuel 4A	98%	2%	16.71	86
Fuel 4B	98%	2%	16.90	not run
	98%	2%	21.93	85
	99%	1%	31.35	>1440

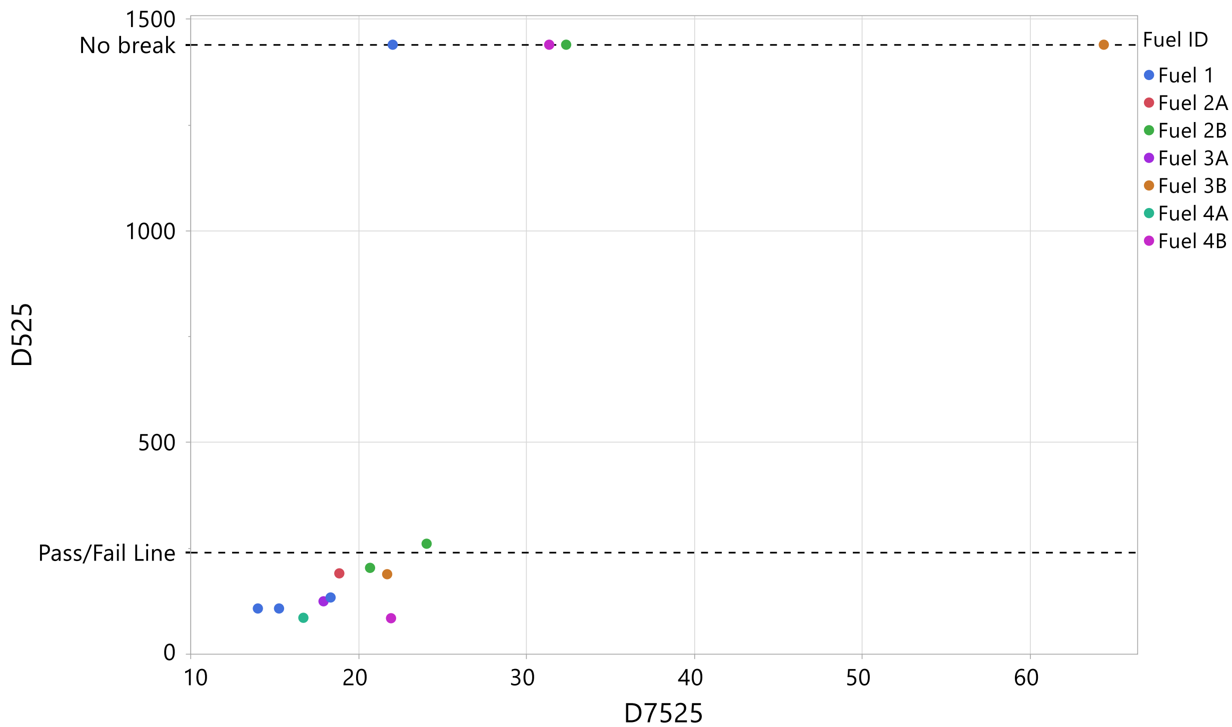

FIGURE 1: PLOT OF D525 VS. D7525 FOR PILOT STUDY

The data revealed several problems which would ultimately lead to the decision to not move forward with the full ILS and correlation study. First, there was ultimately only one sample for which there was an observed break point above 240 minutes in D525. It was clear that it would not be possible to blend samples with fine enough resolution to confidently find the equivalent D7525 result corresponding to 240 minutes in D525. This lack of ability to obtain samples between 240 and 1440 minutes would also prevent these samples from being appropriate for the ILS precision updates.

It is notable that Fuel 2 in this study was the same high and low stability components from the previous research which suggested a 240 minutes D525 result could produce a result near 40 minutes in D7525. With new batches of the same fuel components, the current study produced a 24.05-minute D7525 result which paired with a 261-minute D525 result, which is much more aligned with the crossover point suggested by other fuels in previous research and for fuels in this study. This could mean several things. There could be a lab bias component at either lab for one or both of the test methods. Additionally, it seemed clear that different batches of fuel components can change results, as seen in this pilot study testing. At this point, the group decided to conclude the testing and terminate the project, as it seemed highly unlikely that the project goals could be accomplished with these samples.

Though there does appear to be a sample dependency on the correlation between test methods, it seems possible that with enough data a go/no-go type of limit could be established for D7525 as an alternative to D525 in future gasoline specifications. This would be a number of minutes in D7525 for which one could have a certain confidence, such as 95% or 99%, that if a result exceeded that value in D7525, the same sample would exceed 240 minutes in D525. Except for one result from previous research which could not be reproduced in this study, all previous data and this pilot study data seems to indicate that approximately 25 minutes in D7525 is very likely to be above 240 minutes in D525. However, without any reason to discard the previous research and consider it invalid, one must consider the possibility that certain samples tested at certain labs might still see results near 40 minutes in D7525 which can fall below 240 minutes in D525. If a go/no-go limit is desired, it is recommended that additional data be collected in the future. D7525 data in the 20-35 minute range with corresponding D525 results on the same sample would be the most valuable to help determine the appropriate go/no-go limit.

2.0 INTRODUCTION

In the 1930's, ASTM D525 was developed to predictively monitor the oxidative stability of gasolines at the refinery and during storage to ensure they were fit for purpose. When conceived in 1939, D525 was state of the art when non-oxygenated and sometimes unstable thermally cracked gasolines existed. However, in today's technological environment, the D525 induction period accelerated stability test is now a cumbersome and lengthy test to run which also comes with safety issues associated with pressurizing a 50 mL sample of flammable gasoline with pure oxygen and then immersing the sample in a 100 °C heated bath or block heater. The test is run until a "break point" is reached, defined as the number of minutes until a pressure drop of 14 kPa in 15 minutes is succeeded by a pressure of not less than 14 kPa in 15 minutes. Current ASTM D4814 spark ignition fuel stability requirements include a minimum of 240 minutes in the D525 test. A test with no break point is generally run for 1440 minutes before being terminated. Many test laboratories find that this testing is too lengthy and have concerns about the safety risk of pressurizing a flammable material with oxygen.

There is a strong desire by many laboratories to move to ASTM D7525, otherwise known as the Rapid Small-Scale Oxidation Test (RSSOT). This test involves smaller quantities of fuel, is inherently safer, and has a significantly shorter test length. However, while both tests intend to determine oxidation stability, the test metric used to determine the break point in the D7525 is different than D525. Rather than defining the break point by a rate of pressure drop as in D525, D7525 records the maximum pressure and defines the break point as the number of minutes until a 10% drop from maximum pressure is reached. Therefore, this project sought to understand whether a reasonable correlation equation could be developed between the two test methods, such that D7525 might be considered as an alternative to D525 in future modifications to gasoline specifications. As a secondary objective, both methods are in need of updated precision statements, a task which could be accomplished with data obtained from the correlation study.

To accomplish the project goals, sufficient data would be generated such that the data collected on each method would individually meet the requirements of an ASTM precision study as given by ASTM D6300.

3.0 PRELIMINARY RESEARCH AND THE NEED FOR A PILOT STUDY

During the initial stages of the project, the project team researched and compiled other studies which had been conducted to assess the correlation between D525 and D7525. Data from five different studies were obtained. Each study was conducted by blending varying amounts of a low stability fuel component into a fuel in order to achieve a range of results. Data from these studies is shown below in Table 2.

TABLE 2: PRELIMINARY RESEARCH ON OTHER D525/D7525 COMPARISONS

Fuel 1

D525 (mins)	D7525 (mins)
174	15.1
175	15.6
218	13.1
232	12.4
266	18.8
289	19.2
285	21.5
312	20.9
334	20.0
351	19.6
352	20.1
354	19.7
363	20.9
374	20.3
383	22.2
390	21.0
395	20.4
399	20.2

Fuel 2

D525 (mins)	D7525 (mins)
60	10.00
55	10.30
75	11.43
70	12.95
90	14.80
90	17.31
120	21.35
190	24.45
200	38.80

Fuel 3

D525 (mins)	D7525 (mins)
199	13.55
244	13.93
271	14.63
348	15.45
453	17.60

Fuel 4

D525 (mins)	D7525 (mins)
57	7.96
133	13.98
224	21.85
261	25.75

Fuel 5

D525 (mins)	D7525 (mins)
600	26.38
645	29.30
690	30.51
795	36.13

The data raised concern amongst the group, as it indicated a potential sample dependency on the correlation. The data indicated that samples around 240 minutes in the D525 would produce anywhere from around 10 minutes to 40 minutes, depending on which sample was being used to study the correlation. After discussion, the committee decided on conducting a smaller scale pilot study in a single lab prior to conducting the full interlaboratory study (ILS) on the two test methods. If the results of the pilot study indicated a low probability of success in the larger study, the project could be halted, and ultimately time and resources would be saved.

3.1 Pilot Study

The purpose of this study would help answer two important questions:

1) Does the pilot study data further confirm the data from the previous research that there is a sample dependency on the correlation between D525 and D7525.
2) For the D525 precision study, can appropriate blend proportions of high and low stability fuel components be found such that samples are obtained which produce D525 results across the range of the method, i.e. from at or below 240 minutes to near 1440 minutes. This is needed to produce an appropriate precision statement.

With these goals in mind, two non-oxygenated fuels were obtained, along with two low stability fuel components, such that four combinations of high and low stability component were available, as shown below in Table 3. One of the four combinations, “Fuel 2” in this study, was the same as Fuel 2 from Table 2. This combination was of particular interest, since it appeared to show the largest difference in the two-method correlation from the previous research, with a D7525 result of 38.8 minutes still producing a D525 result less than 240 minutes.

TABLE 3: FUEL COMBINATIONS FOR PILOT STUDY

Fuel	High-Stability Component	Low-Stability Component
Fuel 1	HSC-1	LSC-1
Fuel 2	HSC-2	LSC-2
Fuel 3	HSC-1	LSC-2
Fuel 4	HSC-2	LSC-1

The pilot study began testing samples on D7525 only, since the test uses a smaller quantity of fuel and is quicker to run than D525. The goal was to determine by trial-and-error the starting point for blend percentages such that a D7525 result would be within the 10-20 minute range. The data from previous research indicated that this range was mostly likely to produce D525 results close the 240-minute area of interest. Once the ratio was determined, sample volumes large enough to run both test methods on the same blend would be made. The first four results on each fuel are shown below in Table 4.

TABLE 4: FIRST FOUR PILOT STUDY RESULTS

Fuel	% High-Stability Component	% Low-Stability Component	D7525 (mins)	D525 (mins)
Fuel 1	98%	2%	18.33	134
Fuel 2	60%	40%	18.85	191
Fuel 3	60%	40%	17.91	125
Fuel 4	98%	2%	16.71	86

At this point it was discovered that an insufficient volume of HSC-2 and LSC-2 were sent to conduct the pilot study. Therefore, there was a delay in testing until additional quantities of each could be obtained. Since these components make up one or both part of Fuels 2-4, once the new samples were obtained, D7525 was re-run in order to verify similar performance using the new batches of HSC-2 and LSC-2. At the same time, another blend of Fuel 1 using the same blend percentages as the first test was made to obtain a repeat test for both the D7525 and the D525. This would allow some indication of the variability in the blending process using the same batch of blend components. The results of these four tests along with their comparison to the first run is shown below in Table 5.

TABLE 5: REPEATED D7525 TESTS WITH NEW BATCHES OF BLEND COMPONENTS

Fuel	% High-Stability Component	% Low-Stability Component	D7525 1st Run (mins)	D7525 2nd Run (mins)	2nd run New Batch Blend Components
Fuel 1	98%	2%	18.33	14.00	None
Fuel 2	60%	40%	18.85	28.25	HSC-2 and LSC-2
Fuel 3	60%	40%	17.91	21.06	LSC-2
Fuel 4	98%	2%	16.71	16.90	HSC-2

There were several interesting observations made from the repeat testing. First, it appeared that the new batch of the low stability component LSC-2 might be less severe than the original batch. This can be seen from the fact that both Fuel 2 and Fuel 3 got notably higher results with the new batch than with the original, while Fuel 4, which only changed the high stability component, gave a nearly identical repeat result. Though only a single data point is available, it is also interesting to note the potential interaction in the low stability component with the high stability component, as Fuel 2 saw an increase of nearly ten minutes in the D7525 repeat, while Fuel 3 only saw an increase of just over three minutes. For reference, though not a true repeat by ASTM standards, the repeatability of D7525 at 20 minutes is about 2.4 minutes.

Considering the stated repeatability equation given in D7525 is $r = 0.3903 * X^{0.6}$, the repeated value of 14.00 of Fuel 1 was outside the repeatability as well, which was not a total surprise and likely an indication of the variability of the blending process. This was important information to consider for future testing. Large enough quantities would need to be made to run both methods on the same blend, and failure to do so could severely impact any conclusions about the correlation between the two methods. Using the same blend, the D7525 result on Fuel 1 was repeated again and also sent for D525 testing. The third D7525 result on Fuel 1 was 15.26 minutes, and the D525 result was 108 minutes.

With sufficient quantities of both high and low stability components now on hand, blend proportions of high and low stability components were adjusted to try to obtain results on all four samples which bracketed the 240-minute time in D525. Each blend sample was made with enough volume to run both test methods on the same blend. The full set of pilot study results are shown below in Table 6. The letter "A" or "B" following the fuel name is used to distinguish between tests run on the first or second batches of HSC-2 and LSC-2. For each fuel, results are ordered based on the D7525 result. The data are plotted in Figure 2.

TABLE 6: PILOT STUDY RESULTS

Fuel	% HSC	% LSC	D7525	D525
Fuel 1	98%	2%	14.00	108
			15.26	
	98%	2%	18.33	134
	99%	1%	22.03	>1440
Fuel 2A	60%	40%	18.85	191
Fuel 2B	50%	50%	20.68	204
	60%	40%	24.05	261
	60%	40%	28.25	not run
	70%	30%	32.36	>1440
Fuel 3A	60%	40%	17.91	125

Fuel 3B	60%	40%	21.06	not run
	60%	40%	21.70	189
	70%	30%	64.38	>1440
Fuel 4A	98%	2%	16.71	86
Fuel 4B	98%	2%	16.90	not run
	98%	2%	21.93	85
	99%	1%	31.35	>1440

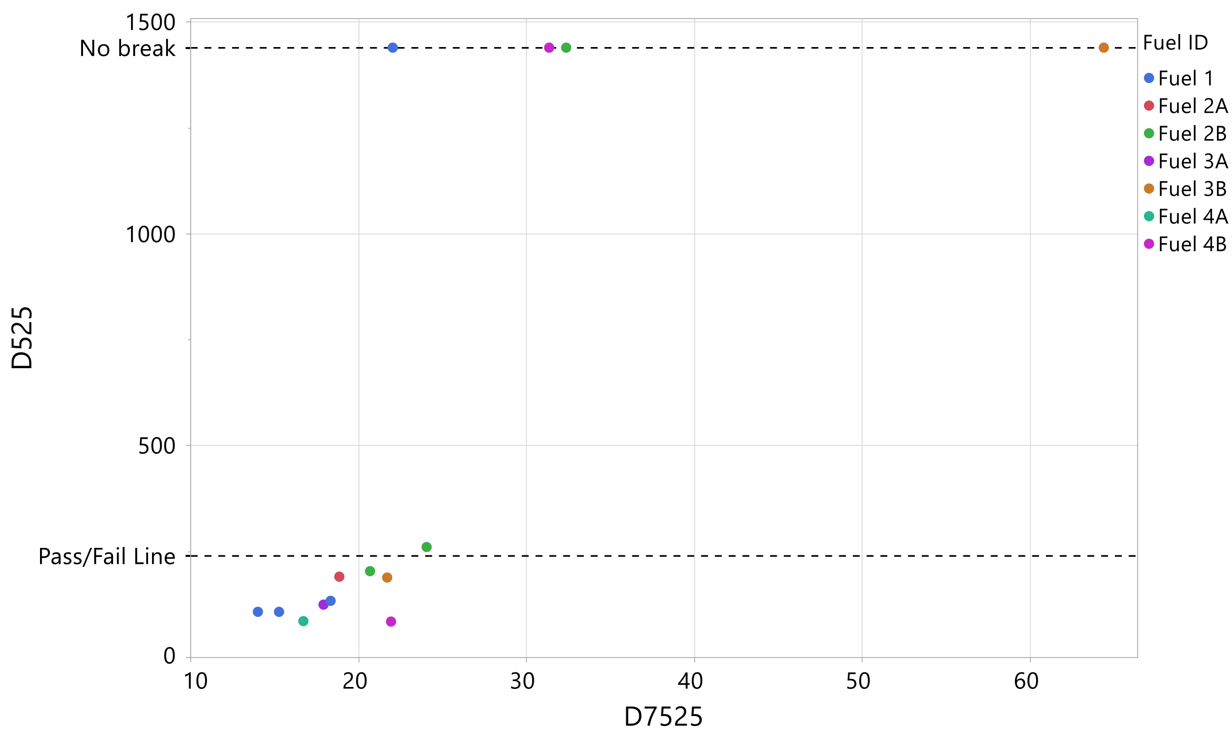

FIGURE 2: PLOT OF D525 VS. D7525 FOR PILOT STUDY

The data revealed several problems which would ultimately lead to the decision to not move forward with the full ILS and correlation study. First, there was ultimately only one sample for which there was an observed break point above 240 minutes in D525. For Fuel 1 and Fuel 4, when going from 2% to 1% of LSC-1, the D525 result went from very unstable, with a total of four results all below 150 minutes, to results which showed no break point (>1440 minutes). It was clear it would not be possible to blend samples with fine enough resolution to confidently find the equivalent D7525 result corresponding to 240 minutes in the D525. A similar story was seen with Fuel 3, where going from 40% LSC-2 down to 30% LSC-2 increased the D525 result from 189 minutes to have no observed break point. Only for Fuel 2 was there an observed break point above 240 minutes in D525, which was a 261-minute result. This sample produced a D7525 result of 24.05 minutes. Interestingly enough, this was the same high and low stability component from which showed a result of 38.8 minutes in D7525 still falling below 240 minutes in D525. This could mean several things. There could be a lab bias component at either lab for one or both of the test methods. Additionally, it seemed clear that different batches of fuel components can change results, as seen in this D7525 pilot study testing.

At this point, the group decided to conclude the testing and terminate the project, as it seemed highly unlikely that the project goals could be accomplished with these samples. Even if there was the ability to blend 35% LSC-2 into Fuel 2 and Fuel 3 to get more data near 240 minutes, there didn't appear to be any path forward which would allow appropriate samples to be obtained for the two precision studies, which would require obtaining samples which well cover the full range of the test methods.

4.0 CONCLUSIONS AND NEXT STEPS

This project studied the feasibility of a correlation equation between two oxidation stability test methods, ASTM D525 and D7525. Additionally, there was a desire to use the data from the correlation study to update the precision of D525. Early research revealed concerning sample dependency on the correlation and caused the team to first consider a smaller scale pilot study. Results indicated that, for the four samples used in the study, it would not be possible to blend with enough resolution to obtain adequate data to accomplish the project goals. There was also some level of sample dependency on the correlation as indicated by the previous studies. The four samples in this project suggested that 240 minutes in D525 was expected to result in D7525 results between 20 to 25 minutes.

Though there does appear to be a sample dependency on the correlation between test methods, it seems possible that with enough data a go/no-go type of limit could be established for D7525 as an alternative to D525 in future gasoline specifications. This would be a number of minutes in D7525 for which one could have a certain confidence, such as 95% or 99%, that if a result exceeded that value in D7525, the same sample will exceed 240 minutes in D525. Except for one result from previous research which could not be reproduced in this study, all of the previous data and this pilot study data seems to indicate that approximately 25 minutes in D7525 is very likely to be above 240 minutes in D525. However, without any reason to discard the previous research on Fuel 2 and consider it invalid, one must consider the possibility that certain samples tested at certain labs might still see results near 40 minutes in D7525 which can fall below 240 minutes in D525. If a go/no-go limit is desired, it is recommended that additional data be collected in the future. D7525 data in the 20-35 minute range with corresponding D525 results on the same sample would be the most valuable to help determine the appropriate go/no-go limit.