Application of ASTM Test Methods to Analyze the Oxidation Properties of Automotive Gasoline in Various Test Conditions

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Abstract

Determination of oxidation properties of petroleum products is important to determine their reactivity in the presence of air, moisture, and organic compounds. Petroleum products are unstable as they form gum upon aging in the presence of air which is directly related to oxidation of gasoline. As the oxidation occurs in the system, the molecules of oxygen decrease resulting in the pressure drop in the system. Additionally, the presence of sulfur and other organic molecules can accelerate the oxidation in gasoline. The current method ASTM D525 Standard test method for oxidation stability of gasoline (Induction Period Method) covers the determination of the stability of gasoline under accelerated oxidation conditions and ASTM D130 Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test was applied to determine the oxidation condition of gasoline in the presence of sulfur contamination. In this study ASTM D130 and D525 was performed to determine the oxidation properties of gasoline sample in the presence of air, moisture and additives. Scanning Electron Microscopy (SEM) imaging techniques were used to compare the rust formed in the Cu-strips during the oxidation process.

Keywords: Copper corrosion, gum formation, gasoline, oxidation

1. Introduction

Crude petroleum oil needs to go under variety of testing before being used in the market since the oxidation properties of the petroleum products must be stable when used in internal combustion engines. Often times various organic molecules such as parafins, olefins and sulfur present in the crude petroleum products can initiate oxidation reaction that results in corrosion, gum formation in the heat-engines. These oxidation reactions can be caused by the sulfur, oxygen and other hydrocarbon molecules present in the petroleum oil. The sulfur compounds remaining in the petroleum products, some can have a corroding action on various metals [1]. The effect varies according to the presence of sulfur compounds present in the petroleum products. The Cu-strip corrosion test [1] is designed to test the relative degree of corrosivity of a petroleum product.

Petroleum products such as gasolines are unstable as they form gum upon aging in the presence of air, which is directly related to oxidation of gasoline. In previous studies [3], it was shown that the gum content correlates with the peroxide number of aged gasolines, indicating that gum formation takes place mainly by polymerization of peroxides. Oils that are used to lubricate equipment in the petroleum industry are hydrocarbon based which makes them susceptible to degradation in the presence of water. Oxidation results in the formation of polar compounds namely aldehydes, ketones, carboxylic acids and oxygenated polymers. The products after oxidation reaction are highly corrosive and results in formation of resin,

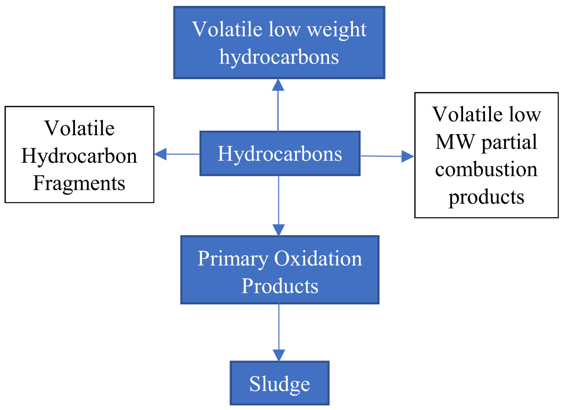

Figure 1: High temperature lubricant degradation model [2].

deposits, and sludge [2]. The presence of the by-products of degradation affects the proper functioning of the equipment. The deposits produced in the oxidation consists of materials of much higher molecular weight mixed with water, oil, and other contaminants [3, 4]. During the oxidation process, oxygen in the system readily reacts with labile hydrogens of the hydrocarbon structures that make up the lubricant. The oxidation of the hydrocarbons proceeds in three stages-initiation, propagation and termination. During the initiation stage, oxygen reacts with the fuel and lubricant forming alkyl radicals. During the propagation stage, these radicals react with oxygen and the lubricant to form peroxy radicals and hydroperoxides.

Hydroperoxides are mostly accumulated during the induction period after which autoacceleration of oxidation occurs (figure 2). The induction period in this case is used as an indication of the tendency of motor gasoline to form gum in storage [5].

This research focuses on applying ASTM test method ASTM D525 Standard Test Method for oxidation stability of gasoline (Induction Period Method) and ASTM D130 Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test to evaluate the oxidative properties of automotive gasoline. ASTM D130 consists of immersing the Cu-strips in gasoline, maintaining the strip at 50°C in a bath. However, in this experiment we have used 100°C in the test bath and water as the heating media to see if the increase in temperature affects the oxidation process profoundly. The test was run for 5 hours instead of 3 hours for further investigation.

ASTM D525 was also applied to determine the oxidation stability of petroleum products specifically gasoline and improving the oxidation stability of gasoline by improving the additive levels, varying temperature and pressure, and applying catalysts. Following the Ideal gas law:

$$PV = nRT$$

for the reaction system, the induction period method of ASTM D525 was applied. Initially the system has free oxygen and this amount is fixed. As the oxidation occurs in the system the moles of oxygen decrease that results in the pressure drop. The system has excess amount of stoichiometric amount of oxygen (not equimolar) that continuous the free radical reaction of hydrocarbons forming different kinds of hydrocarbon products in the system.

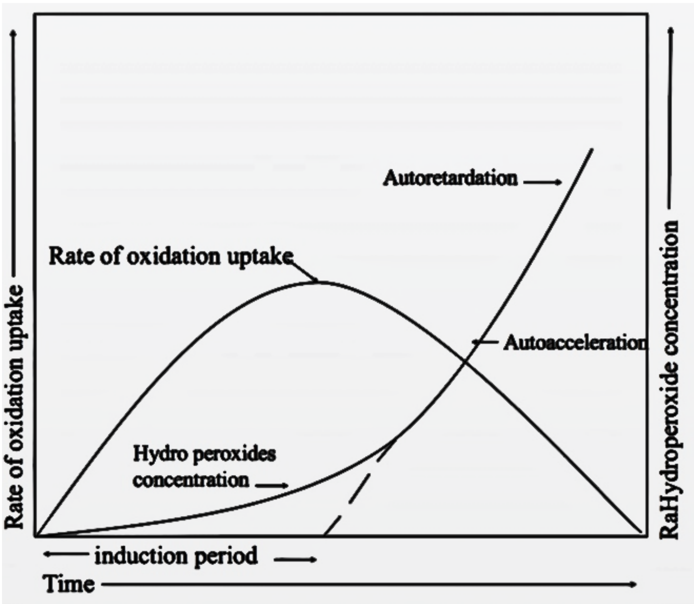

Figure 2: Effect of hydroperoxide concentration on the rate of oxidation [2].

One of the major problem that arises using ASTM D130 method is visual errors as the test results entirely depends on the testers subjectivity and high experience. Since Cu-strip corrosion originated by sulfur compounds in the petroleum gasoline causes very thin oxidation layers, often only a few micrometers (µm) thick, it is important to analyze the surface of the Cu-strips using surface analysis and micro-analysis methods. In this study, electron microscopy (SEM) technique was used to test the corrosion level on the strips.

2. Experimental

2.1. Materials

2.1.1. Gasoline

Briggs @ Stratton gasoline fuel can
Octane rate 87

2.1.2. Fuel Additive

Motor Medic Lead Substitute which was manufactured by RSC Chemical Solutions (part No. M5012) [6].

Table 1: Composition of Fuel Additive

Chemical Name	CAS Number	%
Petroleum Distillate Aliphatic	68476-34-6	80-90
Kerosene Hydrodesulfurized	64742-81-0	3-5
Naphthalene	91-20-3	<0.3
Other components below reportable level		10-20

2.1.3. Copper Strips Specification

Use strips that are 12.5 6 2-mm (1/2-in.) wide, 1.5 to 3.2-mm (1/16 to 1/8-in) thick and cut 75 6 5-mm (3-in) long from smooth-surfaced, hard-temper, cold-finished copper of 99.9%+ purity; electrical bus bar stock is generally suitable (see Annex A1). The strips may be used repeatedly but shall be discarded when the strips surface shows pitting or deep scratches that cannot be removed by the specified polishing procedure, or when the surface becomes deformed, or the dimensions for the copper strip fall outside the specified limits [1].

Figure 3: Copper Strip (Dimension 12.5mm X 1.5mm X 75.6mm)

Table 2: Copper Strip Classifications

Classification	Designation	Description
1	slight tarnish	a. Light orange, almost same as freshly polished strip b. Dark orange
2	moderate tarnish	a. Claret red b. Lavender c. Multicolored with lavender blue or silver, or both, overlaid on claret red d. Silvery e. Brassy or gold
3	dark tarnish	a. Magenta overcast on brassy strip b. Multicolored with red and green showing, but no gray
4	corrosion	a. Transparent black, dark gray or brown with peacock green barely showing b. Graphite or lustless black c. Glossy or jet black

2.1.4. Wash Solvent

Trimethylpentane (isooctane) of minimum 99.75% purity from Fisher Chemical. LOT 173733 [1].

2.1.5. Distilled Water

Laboratory reagent grade distilled water from Research Products International. LOT 48366-48873.

2.1.6. Surface preparation/Polishing Materials

Silicon carbide paper 220 grit FEPA grade Koehler Instrument Inc. 380-220-001.

Silicon carbide grain 150 grit FEPA grade Koehler Instrument Inc. 380-150-003 [1].

2.1.7. Oxygen

Commercially-available extra-dry oxygen of not less than 99.6% purity [5].

2.1.8. Hydrogen Sulfide Water Solution

LabChem LC154701 Water 99.6%, Hydrogen Sulfide 0.4% [7].

2.2. Experimental Methods

2.2.1. Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test (ASTM D130)

This test method covers the determination of the corrosiveness to copper of automotive gasoline. A polished copper strip is immersed in a specific volume of the sample being tested and heated under conditions of temperature and time that are specific to the class of material being tested. At the end of the heating period, the copper strip is removed, washed, weighed and the color and tarnish level assessed against the ASTM Copper Strip Corrosion Standard.

Remove all surface blemishes from all six sides of the strip, with the 65-m (220-grit CAMI-grade or P220 FEPA-grade) silicon carbide paper or cloth, removing all marks. Polish with the 105-m (120-grit to 150-grit CAMI-grade or P120 to P150 FEPA grade) silicon carbide grains.

Place 30 mL of sample in dry test tube and slide in the copper strip into the sample tube. Place the sample tube into the pressure vessel and screw the lid on tightly. Put in the pressure vessel in 100 ± 1 °C and for 5h ± 5 min.

Empty the contents of the test tube and withdraw the strip with forceps and immerse in wash solvent, trimethylpentane (isooctane) of minimum 99.75% purity. Dry and inspect for evidence of tarnishing or corrosion by comparison with the Copper Strip Corrosion Standards.

Figure 4: Test Bath Unit for ASTM D130.

2.2.2. Standard Test Method for oxidation stability of gasoline (Induction Period Method, ASTM D525)

This test method covers the determination of the stability of gasoline under accelerated oxidation conditions.

The sample is oxidized in a pressure vessel initially filled at 15 to 25°C with oxygen pressure to 690 to 705 kPa and heated at a temperature between 98 to 102°C. The pressure is recorded at stated intervals until the breakpoint is reached. The time required for the sample to reach this point is the observed induction period at the temperature of test, from which the induction period at 100°C can be calculated.

Figure 5: Test Bath Unit and Pressure Vessel for ASTM D525.

2.3. Analytical Methods

2.3.1. Scanning Electron Microscope (SEM)

Scanning Electron Microscopy was carried out using a LEO-1550 Gemini microscope.

3. Results and Discussion

3.1. Analysis of the test strips

3.1.1. Cu-Strip Characterization

Table 3: List of Samples

Sample ID	Contents
A	Gasoline 87
B	Gasoline 87 + 0.1% of Fuel Additive
C	Gasoline 87 + 0.1% of Water
D	Gasoline 87 (Aged for 6 months)
E	Gasoline 87 + Hydrogen Sulfide Water Solution
F	Gasoline 87 + Hydrogen Sulfide Water Solution + Fuel Additive

The results of the ASTM D130 copper strip test are shown in Figure 7. Specimen A, which is pure gasoline, is light orange in color, similar to a freshly polished strip

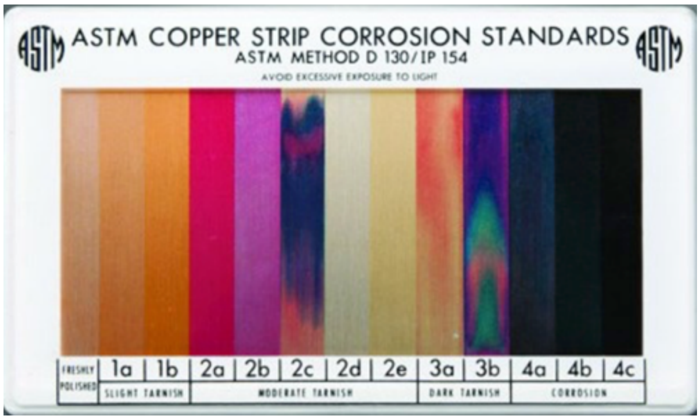

Figure 6: ASTM D130 Corrosion standard for Copper strip.

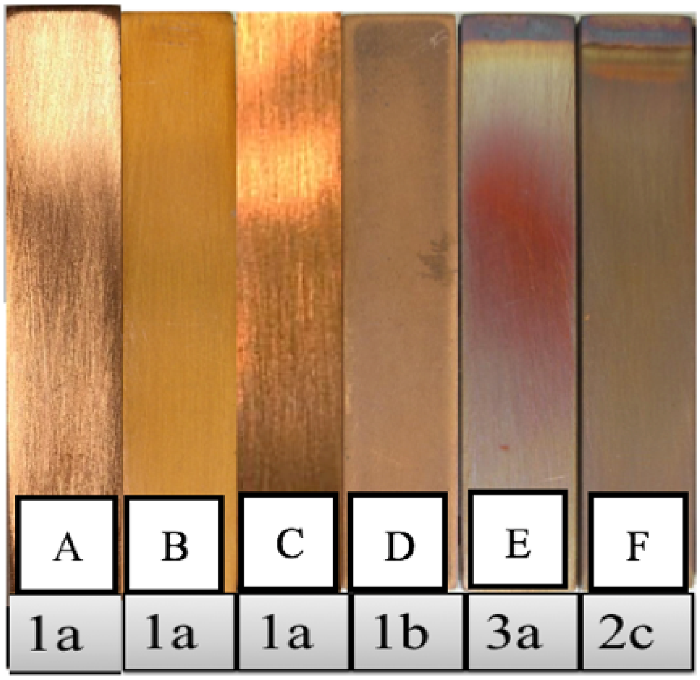

Figure 7: Cu strip after D130 test in modified condition.

(Table 2). Following figure 6, Sample A it can be categorized into 1a group. Similarly, Sample B & C falls on to the same group 1a category as well. According ASTM D130 when a strip is in the obvious transition state between that indicated by any two adjacent strips, the strips should be rated into more tarnished category. Thus, Sample D can be identified as 1b (Table 2). Sample E shows magenta overcast on brassy strip making it fall under 3a category. In order to distinguish between group 3a and 2a, the strip was immersed into iso-octane solvent as mentioned in section 12.1.1 in ASTM D130 method. The strip didnt change its appearance; therefore, it falls into 3a category. The results can be interpreted using the following formula mentioned in ASTM D130:

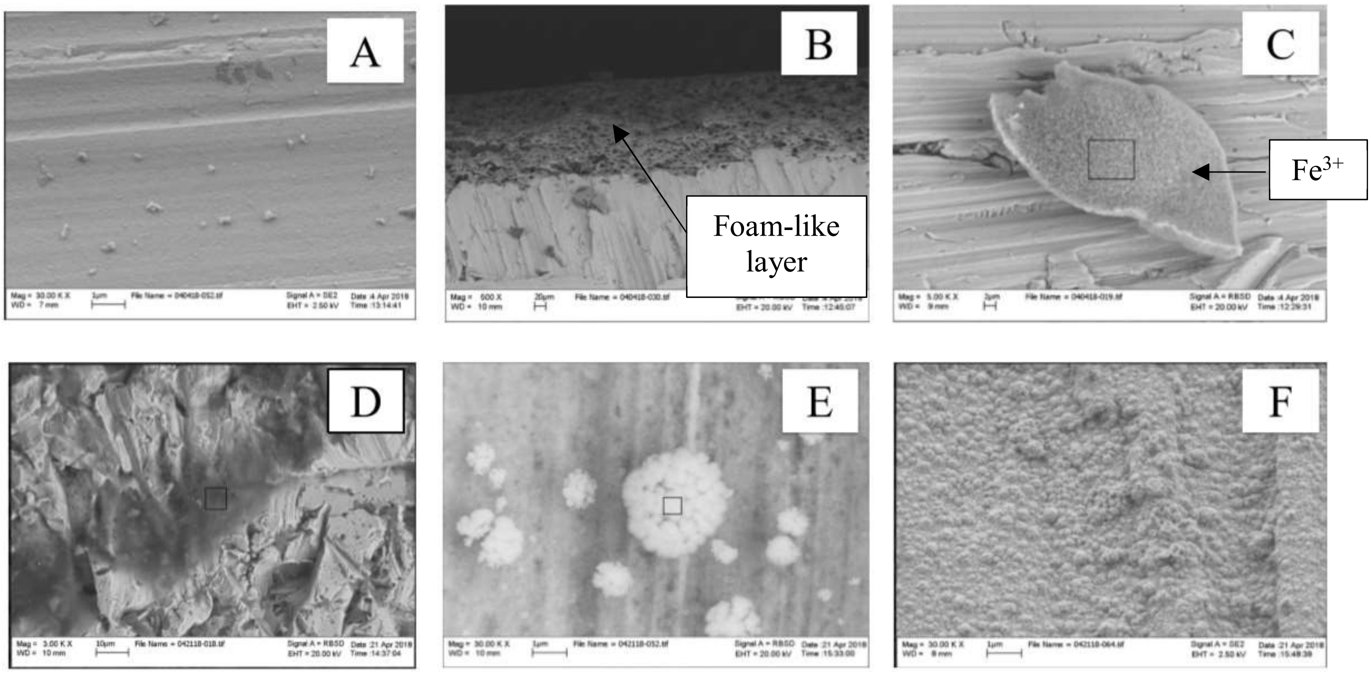

Figure 8: Scanning Electron Microscopy Images of Samples; (A) Surface of Cu-strip sample immersed in gasoline; (B) Cu-strip surface immersed in gasoline + fuel additive builds up passivation layer; (C) Traces of Fe^{3+} on the surface of Cu-strip after being exposed in gasoline and water mixture; (D) Cu-strip surface immersed in aged gasoline shows formation of salt rings; (E) Formation of salt particles on the Cu-strip surface as result of oxidation reaction in the gasoline + H_2S solution; (F) Accumulation of salt particles on the Cu-strip surface as result of oxidation reaction in the gasoline + H_2S solution + fuel additive.

$$Corrosion\ copper\ strip\left(\frac{Xh}{Y^\circ C}\right),\ Classification\ Zp \quad (1)$$

Where,

$$X = test\ duration,\ in\ hours$$
$$Y = test\ temperature,\ ^\circ C$$
$$Z = classification\ category\ (i.e.\ 1,\ 2,\ 3,\ 4)$$
$$p = classification\ description\ for\ the\ corresponding\ Z\ (i.e.\ a,\ b)$$

Following the same format, the results are following:

i Corrosion Sample A (5h/100°C), Classification 1a
ii Corrosion Sample B (5h/100°C), Classification 1a
iii Corrosion Sample C (5h/100°C), Classification 1a
iv Corrosion Sample D (5h/100°C), Classification 1b
v Corrosion Sample A (5h/100°C), Classification 3a
vi Corrosion Sample A (5h/100°C), Classification 2c

3.1.2. Scanning Electron Microscope (SEM)

In order to examine the surface of the Cu-strips, SEM imaging were taken. The SEM imaging shows variance in surface behavior.

The Images from Figure 8 are SEM images of Samples. Figure 8A shows smooth copper surface after the heating period. There were not any traces of significant oxidation reaction on the surface. Figure 8B shows accumulation of foam-like passivation layer. The foam-like passivation layer is further example of etching. Etching is a major problem since it can weaken the metal and accelerate wear. This type of additive can be worse than corrosion since it causes surface loss. The active ingredient in the fuel additive are proprietary secrets and their composition is unknown. However, this suggests that the use of this type of additive is not recommended with metals. Figure 8C demonstrates the effect of oxidation reaction in the presence of polar protic solvents such as water (H_2O). Water plays a vital role in the corrosion of metal alloys. The EDS spectra in Figure 9C shows traces of Iron (Fe) on the surface. In the case of aged gasoline Sample D the SEM image Figure 8D shows formation of salt-ring on the surface of the metal. The EDS data in Figure 9D also shows traces of metallic salt particles. This degradation is caused due to the presence of sulfur in the aged gasoline. As the gasoline was about 6+ months old, the sulfur in the gasoline started to initiate oxidation reaction under high temperature condition used in D130 method.

Figure 8E shows sample immersed in H_2S solution (10% H_2S). Theoretically, the presence of H_2S is highly corrosive for petroleum products such as gasoline [8]. It reacts with the Cu surface in the following way:

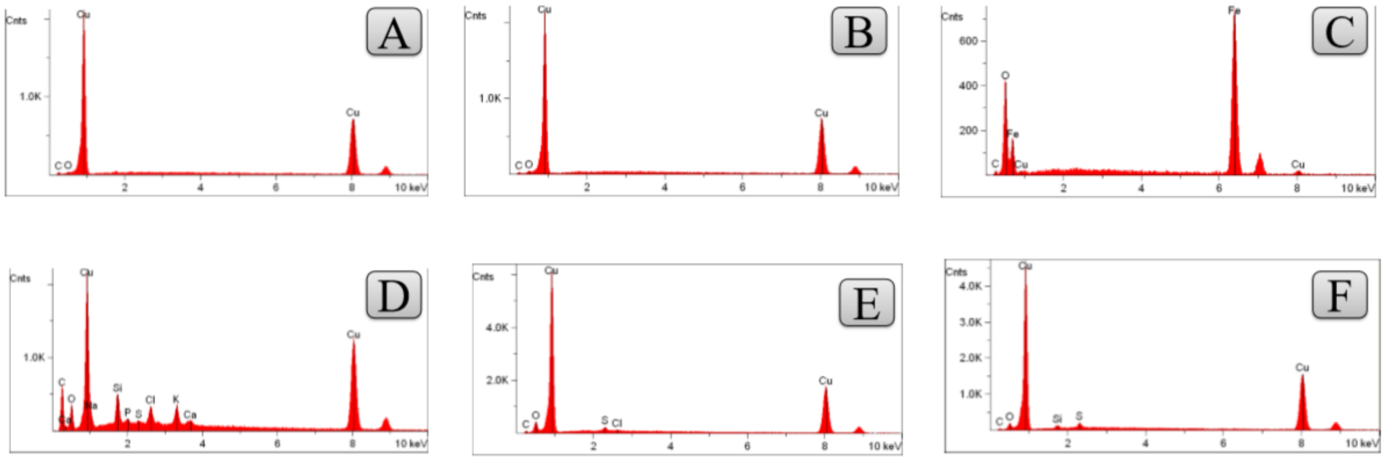

Figure 9: Energy Dissipative X-ray Spectroscopy (EDS) of Samples; (A) Cu-strip surface immersed in gasoline; (B) EDS of Cu-strip immersed in gasoline + fuel additive doesnt show any molecules other than Cu itself; (C) Presence of FeO formation on the Cu-strip surface; (D) Traces of several salt is detected due to contamination; (E) & (F) EDS do not show any salt traces, this could be related to Sulfurs small cross section area which is not detectable by EDS.

$$Cu_{(s)} + H_2S + \frac{1}{2}O_{2_{(g)}} = CuS_s + H_2O_{(l)} \qquad (2)$$

The equation (2) reaction [8] creates accumulation of metallic salt on the surface of Cu strip. Such precipitation can lead to the degradation of metals in automotive engine parts. For Sample 8F, gasoline was mixed with H_2S and fuel additive (Section 2.1.2) to demonstrate if addition of corrosion inhibitor would decelerate the oxidation process in gasoline. Even though the SEM image shows salt precipitates on the surface of Cu-strips, the EDS images could not identify the layer since sulfur has small very small cross section area which is harder to detect using EDS. Further testing is needed to demonstrate the theory.

3.2. Analysis of the Gum Formation

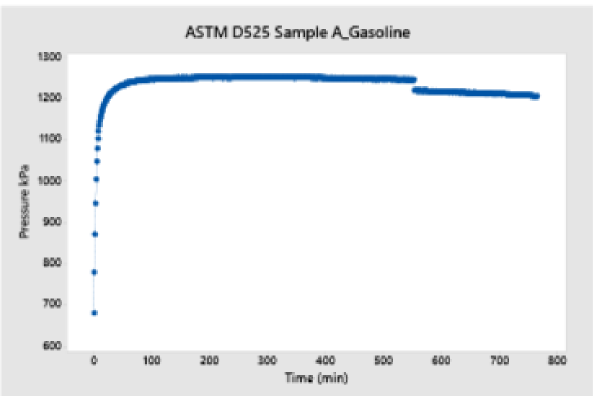

Figure 10: ASTM D525 pressure vs time graph demonstrating the induction period of Sample C.

In order to test the oxidation condition of gasoline, ASTM D525 was applied in the same batch of gasoline

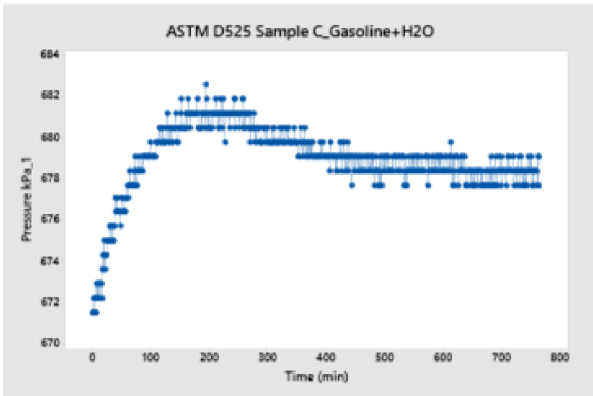

Figure 11: ASTM D525 pressure vs time graph demonstrating the induction period of Sample C.

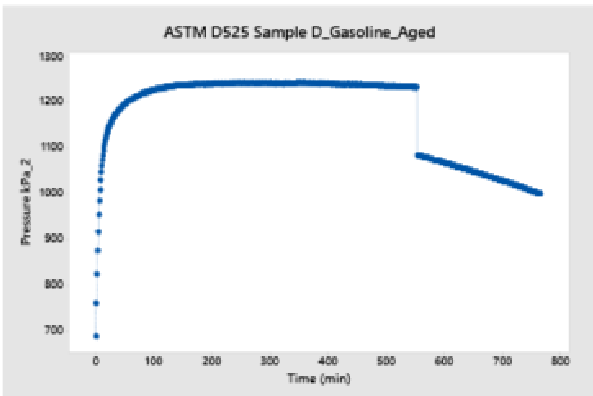

Figure 12: ASTM D525 pressure vs time graph demonstrating the induction period of Sample D.

used for copper corrosion. The induction period in this method is used to indicate the formation of gum by motor gasoline. Sample 8C (0.1% water + gasoline) and Sample 8B (aged gasoline) were also tested to examine the correlation between different condition of gasoline. For Sample A, Gasoline and Sample D, Gasoline aged, the induction period is almost in the same range. The break point in both samples occur at 1249 kPa. Since the motor gasoline that were tested in this case were from the same marketable source, they were expected to have similar and good oxidation stability in general. However, for Sample C_Gasoline+H_2O, the oxidation condition was highly unstable even before the heating period mentioned in ASTM D525 method. The presence of polar solvent accelerates the oxidation by forming hydroperoxides in the system. Therefore, the system has continuous pressure change. Since the system was already very unstable, the sample wasnt heated under accelerated condition as a safety measure in the lab.

4. Conclusion

The corrosiveness and oxidation stability of gasoline mixtures containing water and fuel additives was examined via ASTM D525 and D130 standard test methods. The effect was significant for the samples containing higher percentage of sulfur. In fact, sulfur corrosion has been a long existent problem in the petroleum industry. Addition of corrosion inhibitor in the presence of sulfur was not effective in the case of Sample F. Further test analysis is needed to observe the effect of corrosion inhibitor on Cu-strips. Addition of water as polar solvent accelerates the corrosion rate as seen in Sample C. Presence of water also initiates the hydro peroxide formation in the system in the case of D525 test. Therefore, traces of polar solvents and organic molecules in the motor gasoline can have negative effect on the fuel performance. Additionally, the current D130 method should be modified to avoid human error since the results completely depend on the observers judgment and experience.

5. Acknowledgements

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6. References

[1] ASTM D130-12. Standard test method for corrosiveness to copper from petroleum products by copper strip test. Technical report, ASTM International, 2012.

[2] George Totten, S Westbrook, and R Shah. Fuels and lubricants handbook: Technology, properties, performance, and testing. Jan 2003.

[3] V. Voorhees and John O. Eisinger. The effect of gum in gasoline. 1929.

[4] Florian Pradelle, Sergio L. Braga, Ana Rosa F. A. Martins, Franck Turkovics, and Renata N. C. Pradelle. Gum formation in gasoline and its blends: A review. *Energy & Fuels*, 29(12):77537770, 2015.

[5] ASTM D525-12a. Standard test method for oxidation stability of gasoline (induction period method). Technical report, ASTM International, 2012.

[6] Motor Medic Lead Substitute. *MSDS No. M5012*. RSC Chemical Solutions: Indian Trial, NC, Jun 2016. (Accessed 21 Apr 2018).

[7] Hydrogen Sulfide Water. *MSDS No. LC15470*. LabChem: Jackson Township, PA, Oct 2017. (Accessed 21 Apr 2018).

[8] William Henry Brown, Brent L. Iverson, Eric V. Anslyn, and Christopher S. Foote. *Organic chemistry*. Wadsworth Cengage Learning, 2014.