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.

Experimental Setup

ASTM D130

ASTM D525

1. Test Bath Unit of ASTM D130
2. Pressure Vessel
3. Copper Test Strips 12.5x1.5-3.0mm x 75mm
4. ASTM Copper Strip Corrosion Standards
5. Test Bath Unit of ASTM D525
6. Oxidation Pressure Vessel

Materials

1. Gasoline 87
2. Fuel Additive (Petroleum Distillate Aliphatic 80-90%, Kerosene Hydrodesulfurized 3-5%, Naphthalene < 0.3%)
3. Wash Solvent (Isooctane 99.75% purity)
4. Distilled Water
5. Hydrogen Sulfide Water Solution (Water 99.6%, Hydrogen Sulfide 0.4%)
6. Oxygen (99.6% Purity)

Test Methods:

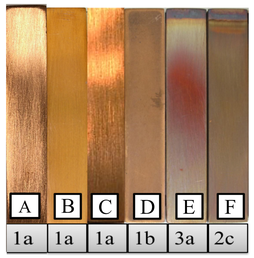
1. ASTM D130: Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test
2. ASTM D525: Standard Test Method for Oxidation Stability of Gasoline (Induction Period Method)

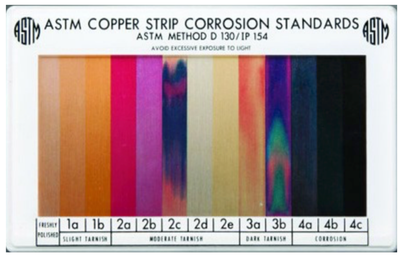
Samples Used:

Samples	Contents
Sample A	Gasoline 87
Sample B	Gasoline 87 + Fuel Additive
Sample C	Gasoline 87 + Distilled Water
Sample D	Gasoline 87 (Aged for 6 months)
Sample E	Gasoline 87 + Hydrogen Sulfide Water Solution
Sample F	Gasoline 87 + Hydrogen Sulfide Water Solution + Fuel Additive

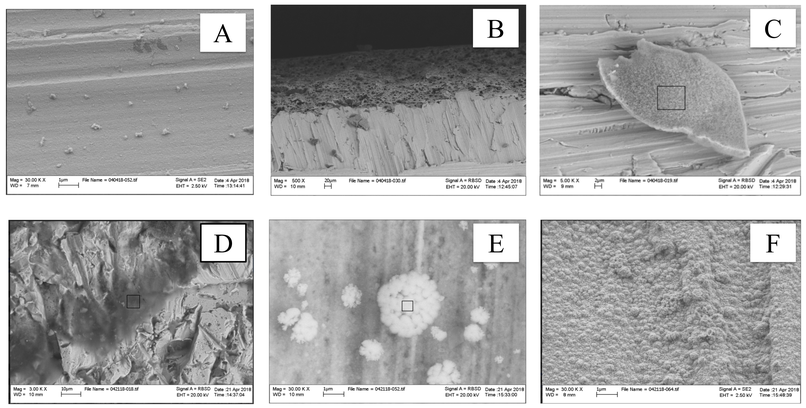
Experimental Results

a. Cu Strip Categorization:

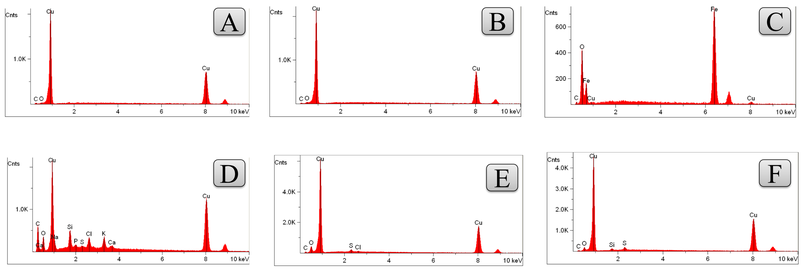




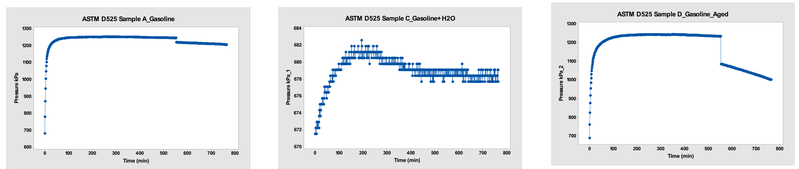
b. Scanning Electron Microscopy:



c. Energy Dissipative X-ray (XRD):



d. Gum Formation in Gasoline



Result Analysis:

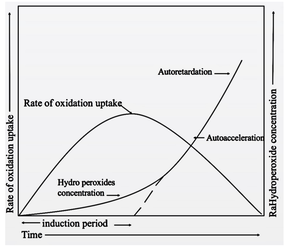
Copper Corrosion (D130):

- Sample B reacts with the Hydrodesulfurization product in the sample mixture creating a “foam-like” protective layer on the surface of the strip preventing further oxidation of the Cu-strips
- In most cases the additives in sample D & E creates salt deposits on the cathodic Cu-strips metal surface. The salt ring formed in E is due to flow of the H_2S solution over the metal surface that assists on the nucleation of salt ions.
- Oxidation reactions can result in the Cu-alloys used in automobiles due to gasolines having traces of sulfur or oxidative molecules resulting in further damage of the parts in the engine.

Therefore, Cu-Strip in the 1a category passes the ASTM D130 fuel specification

Gum Formation (D525):

- Following the Ideal gas law Ideal gas law: PV=nRT, the induction period method of ASTM D525 was applied.
- 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.



Effect of Hydroperoxide Concentration on the Rate of Oxidation

- In sample A and B, the induction period lasts up to 500 minutes
- In sample B the presence of a polar solvent accelerates the oxidation process creating continuous peroxide formation reaction in the system.

✓ Combination of D130 and D525 shows oxidative behavior of gasoline in different condition

✓ A basis to modify the D130 method since the current method creates visual error.

Future Work:

✓ Conducting FT-IR analysis of the Cu-strips to further demonstrate the reaction chemistry of the surface

✓ Improve the D130 test method to reduce human errors