RECENT ADVANCES IN VARIOUS BENCH SCALE ACCELERATED OXIDATIVE TESTING METHODS FOR FUELS

Introduction

Petroleum-based fuel products are an integral part of modern transportation methods, industrial and residential heating, and electricity generation. 71% of daily consumed petroleum products are gasoline, diesel, fuel oil, and kerosene (aviation fuel) [1]. These petroleum products can be derived by distilling crude oil, breaking the crude into various components that will be selectively remolded into new products [1]. After the distillation process, heavier hydrocarbons are broken down into lighter ones allowing for the creation of gasoline, diesel, and aviation fuels through a process known as cracking [1,2]. An unforeseen side effect, however, is that the cracking process forms unsaturated hydrocarbons, often leading to low oxidation stability—also known as storage stability [2]. These unsaturated hydrocarbons, olefins, and dienes have the tendency to react with oxygen and degrade, resulting in fuel quality and performance decline. This paper serves to highlight the importance of developing oxidative stability tests, discuss the newest accelerated oxidative testing standards and equipment, and give an overview of the limitations of current testing methods.

Importance of Testing Oxidative Stability

Unsaturated hydrocarbons—olefins and dienes—are unstable species that are highly reactive with oxygen to form free radicals [3,4]. As shown in Figure 1, these free radicals cause a chain reaction with more oxygen atoms and olefins to polymerize and produce gum [3]. Gums are deposits that can clog fuel lines, injectors, and filters, as shown in Figure 2, resulting in issues with fuel quality and performance preventing combustion [5, 6]. Thus, additives such as antioxidants, which can neutralize the free radicals, must be incorporated to extend shelf-life [5].

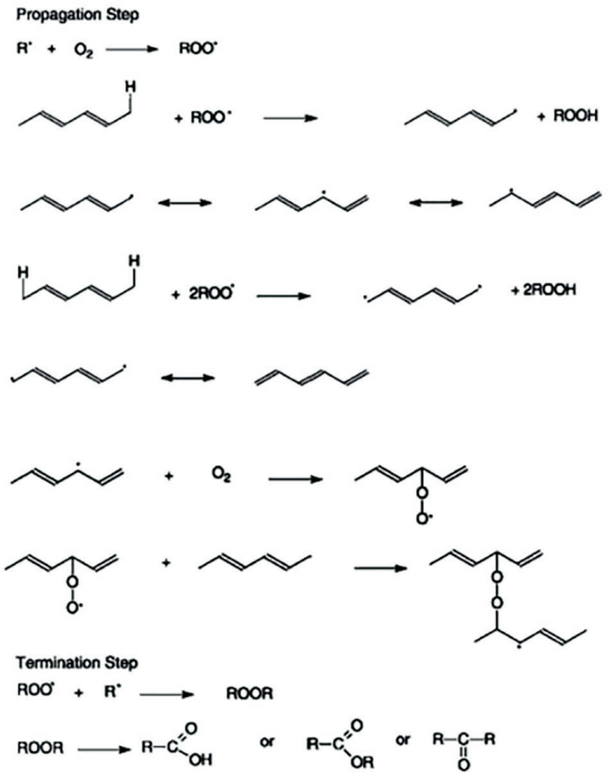

Figure 1. The possible propagation process of 2,4-hexadiene is unknown, it can be caused by a wide variety of radicals [4].

Figure 2. Gummed up fuel pump from a car [7].

Antioxidants stop the chain reaction that continuously forms gums [3]. However, antioxidants are not solutions to stop the oxidation process; rather they are used sacrificially to prolong the shelf-life of hydrocarbon-based fuels [8]. Once consumed, the fuel will continue to oxidize. The sacrificial nature of antioxidants, in addition to the varying compositions and additives of fuels, complicates predicting fuel shelf-life. The exact chemical process of fuel degradation is not well understood, with extra traces of oxygen, sulfur, nitrogen, or even metal ions able to catalyze the oxidation process, reducing fuel stability in storage [9]. This contributes further to the complications regarding predicting fuel shelf-life as it is unknown how great an effect each catalyst may have on the oxidation rate.

Fuel additives vary for each company and can even differ from within as fuel blends may change each season [6]. In the summer, fuels tend to evaporate faster due to high heat. Therefore, summer fuel blends need to have a lower Reid vapor pressure (RVP), also known as volatility, to prevent evaporation which creates smog and pollution [10]. Fuel regulations vary from state to state with the typical RVP being between 7.9-9 psi per gallon during summer months [10]. Different states have different reformulation regulations based on local climate and pollution concerns which leads to the production of over 14 different blends of gasoline during the March-April transition to summer blends [11].

In the winter, fuel blends tend to be more volatile, at 12 psi, to allow for easier combustion. The addition of butane typically increases volatility as it has a boiling point of 32°C, however this also makes butane especially susceptible to evaporation in temperatures above freezing [12]. Summer blends are typically composed of 2% butane while winter blends can contain 10% [10]. Butane is also used as a cheap filler to increase octane ratings for less refined fuels which contain more unsaturated hydrocarbons, leading to lesser oxidation stability. All the varying fuel blends and contributors further complicate predicting shelf-life, thus needing standardized test methods working across the board to gain a general idea.

ASTM Testing Methods

The most obvious method of testing would be to store the fuel in a sealed container located in cool, dry, dark conditions and then wait for the fuel to oxidize. However, this inefficient method demands for accelerated tests to characterize oxidative changes of a particular gasoline. Currently, numerous accelerated methods have been developed to predict the stability, oxidation, and gum formation of fuels, most notably being the standardized American Society for Testing and

Materials (ASTM) procedures that are revised frequently. ASTM standards are created through many voluntary subcommittees that have identified a need in the industry and devised an activity to resolve the need [13]. In the case of fuel oxidation, it was discovered gum formation and thus stability of fuels, varied greatly depending on blends and additives in the fuels, leading to the formation of many standards, including D525, D873, and D3241.

ASTM D525 is a standard test method for the oxidation stability of gasoline used to predict the tendency of gasoline forming gum in storage through an induction period [14]. Induction periods measure the length of time it takes to reach the break point, which is defined as "the point in pressure-time curve that is preceded by a pressure drop of exactly 14kPa within 15 min and succeeded by a drop of not less than 14kPa in 15 min" [14]. According to ASTM, the induction period obtained "may be used as an indication of the tendency of motor gasoline to form gum in storage" [14]. In the special cases where the induction period exceeds a product's specifications, the results are reported as being greater than the maximum minutes the product is capable of measuring. Exceeding the induction period refers to pressure increases exceeding the vessel's maximum build-up prior to reaching the break point [14]. In another special case where no break point is observed but a pressure drop greater than 14 kPa is observed, the sample should be reported as a slow oxidizing fuel also indicating the total time of the test and overall pressure drop from the start of the test [14]. The purpose of measuring the pressure drop is to correlate when a chemical reaction has occurred [9, 15]. The air inside the pressure vessel prior to the start of inducing oxidation is replaced with minimum 99.6% pure oxygen [14]. As oxidation occurs, the oxygen molecules in the vessel react with the unsaturated hydrocarbons reducing the moles of oxygen present which causes a pressure drop.

Gasoline fuel samples are tested in a glass sample container which is placed in a stainless-steel pressure vessel with a safety burst-disc as shown in Figure 3. Oxygen is pumped in to flush out the air and oxygen is continually added until the pressure reaches 690-705 kPa [14]. Tests to check for leakage are performed before placing the pressure vessel in boiling water bath or liquid bath. If using a dry block bath, the sample must be temperature calibrated inside the pressure vessel by equilibrating for one hour inside the dry block. If a temperature difference is found, the dry block temperature is adjusted until the sample equilibrates with the dry block [14].

In addition, ASTM D873 is a potential residue method for testing the oxidation stability of aviation fuels through gum and deposit formation [16]. This test functions similarly to D525 except the test does not stop at the break point. ASTM D873 is performed at 100±0.2°C in a liquid whose boiling point is between 99.5 to 100.5°C [16]. This liquid can be either water or a mixture of water and ethylene glycol; any liquid other than water requires a mechanical stirrer to maintain the uniformity of the liquid bath [16]. The length of time the sample is subjected to oxidation is determined by the user. Once the test is completed, the sample is washed with gum solvent and filtered in a filtering crucible. The filtrate is saved and dried in an oven to find the weight of the precipitate [16].

There are also many other ASTM standards like D525 and D873 for other non-fuel hydrocarbon-based liquids such as lubricating oils, and D2272 for turbine oils. All hydrocarbon-based liquids are subject to the same issues of oxidative stability but require different standards due to varying compositions and needs based on the use of the liquid.

ASTM standards are subject to revision at any time in addition to mandatory reviews every 5 years. Subcommittees can place publicly viewable work items if errors or flaws are found. Currently ASTM D525 has an open work item for revising a sample vessel figure [17].

Limitations to Current Testing

While these ASTM procedures and apparatuses are extremely useful for gaining a general idea of gum formation tendency, they cannot accurately replicate storage conditions. Storage conditions are extremely variable and occur under ambient temperatures, which can have highly different results compared to the accelerated methods [9]. ASTM standards use far higher concentrations of oxygen and elevated temperatures and can include catalyzers compared to typical aging conditions which can skew data trends. The results from accelerated ASTM methods, such as induction period and gum formation are correlated to real changes occurring in non-accelerated conditions, but these correlations have not been proven to accurately predict field performance, which is disclosed in ASTM D525 and D873 [9, 14, 16, 18].

Koehler Oxidation Stability Apparatuses

ASTM standards are used and accepted worldwide, as many apparatuses streamline testing procedures. A series of instruments that stand out are the Oxidation Stability Apparatuses for Gasoline and Aviation Fuels from Koehler Instrument Company, also known as the K645 series units. Koehler has recently released an updated successor model K64404, for one of their units, as seen in Figure 4 [19].

Figure 3. K64404 Liquid Oxidation Precision Bath Model of Oxidation Stability Apparatus for Gasoline and Aviation Fuels from Koehler Instrument Company [19]

The K64404 Model can perform both ASTM D525 and D873 procedures. A sample is oxidized in a stainless-steel pressure vessel, as shown in Figure 5 and 6, and heated in a bath. Depending on the specific model, water, oil, or a solid aluminum block can be used as the medium for heat transfer.

Figure 4. K10500 Oxidation Pressure Vessel from Koehler Instrument Company [19].

The oxidative stability apparatus can test both gasoline and aviation fuels. When testing gasoline, the apparatus measures the time for a specific pressure drop according to the ASTM D525 standard. For aviation fuel, the apparatus measures the amount of gum and deposits formed in compliance with ASTM D873.

The pressure and temperature changes for the ASTM D525 and D873 tests performed can be tracked in real-time in Koehler's Oxidata® software [20]. In the software there are menu options to perform either ASTM D525 or D873 which will allow automatic detection when the sample reaches the break point or induction period. The software tracks the data in real-time and can detect the pressure drop or when a set time is reached according to the specifications listed in ASTM D525 or D873. Data can be displayed digitally using Koehler's Oxidata® pressure measurement system, as shown in Figure 5 which includes transducers to connect to the pressure vessel, a USB interface, RTD probe assembly, and connecting cables and other hardware. Results can be plotted directly to a graph or exported to various spreadsheet programs [20]. Oxidata® allows monitoring of twelve pressure channels and four temperature channels. A screen capture showing temperature monitoring of the Oxidation Stability Apparatus is also shown in Figure 5. Up to twelve pressure and four temperature channels can be monitored simultaneously, and each can be operated and configured separately for different start/stop times and ASTM methods [20].

Figure 5. K64404 Liquid Oxidation Bath Model of Oxidation Stability Apparatus with pressure vessel in place and connected to Oxidata software [21].

Conclusion

The field of oxidative stability testing is continually innovating and evolving to better predict accurate field performance. Although ASTM methods such as D525 and D873 currently do not correlate with real storage conditions, these methods are still currently the most promising industry method for gaining a general overview of gasoline behavior. Currently, Koehler Instrument Company is setting a high bar by producing high quality equipment to streamline ASTM procedures for industrial use. In addition to their Oxidation Stability Apparatus for Gasoline and Aviation Fuels, Koehler also produces a wide variety of equipment for oxidative stability testing of various other petroleum products. Some examples are the Oxidation Stability Bath for Mineral Insulating Oils, RPVOT Oxidation Test Apparatus, and Oxidation Stability Test Apparatus for Lubricating Greases. As further improvements and new methods for oxidative stability testing are developed, new devices will inevitably be produced and refined for efficient and accurate testing.

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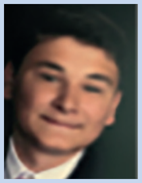
About the Authors

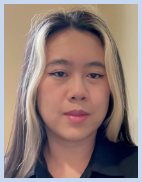
Dr. Raj Shah stands as the Director at Koehler Instrument Company in New York, showcasing an impressive 28-year tenure with the organization. Acknowledged as a Fellow by prestigious entities such as IChemE, CMI, STLE, AIC, NLGI, INSTMC, Institute of Physics, The Energy Institute, and The Royal Society of Chemistry, his contributions have earned him the esteemed ASTM Eagle award. A luminary in the field, Dr. Shah recently coedited the acclaimed “Fuels and Lubricants Handbook,” a bestseller that captivates readers with its insights into the industry. Delve into the details at ASTM’s Long-Awaited Fuels and Lubricants Handbook 2nd Edition Now Available (https://bit.ly/3u2e6GY).

Dr. Shah earned his doctorate in Chemical Engineering from The Pennsylvania State University and holds the distinguished title of Fellow from The Chartered Management Institute, London. He is also recognized as a Chartered Scientist by the Science Council, a Chartered Petroleum Engineer with the Energy Institute, and a Chartered Engineer with the Engineering Council, UK. Recently bestowed with the honorific of “Eminent Engineer” by Tau Beta Pi, the largest engineering society in the USA, Dr. Shah serves on the Advisory Board of Directors at Farmingdale University (Mechanical Technology), Auburn University (Tribology), SUNY Farmingdale (Engineering Management), and the State University of NY, Stony Brook (Chemical Engineering/Material Science and Engineering).

In addition to his role as an Adjunct Professor at the State University of New York, Stony Brook, within the Department of Material Science and Chemical Engineering, Dr. Shah has left an indelible mark on the energy industry, boasting a career spanning over three decades. His influence extends further through over 600 publications, solidifying his status as a thought leader in the field. **Discover more about Dr. Raj Shah at https://bit.ly/3QvfaLX. For further inquiries, please contact Dr. Shah at rshah@koehlerinstrument.com.**

In parallel, within the vibrant internship program at Koehler Instrument Company in Holtsville, **William Streiber,** and **Cindy Huang** shine as standout participants. These budding talents, all pursuing studies in Chemical Engineering at Stony Brook University, Long Island, NY, are under the guidance of Dr. Raj Shah, who currently holds the position of Chairman of the External Advisory Board of Directors at the university.


William Streiber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