DEVELOPMENT OF A NEW TEST METHOD AND RELATED INSTRUMENTATION TO MEASURE RELATIVE STABILITY OF MIDDLE DISTILLATE FUELS UNDER HIGH TEMPERATURE AGING CONDITIONS WITH LIMITED AIR EXPOSURE

In a snapshot the test method and instruments developed provide an indication of thermal oxidative stability of distillate fuels when heated to high temperature which in turn helps simulate the real world environment encountered, in certain types of recirculating engines, or burner fuel delivery systems . In general, the test is used to monitor manufacture or storage of fuels and for doing so, changes in filter rating values help indicate relative change of inherent stability. But let us start at the beginning as the heart of the instrumentation is an automatic reflection meter and the automation of perception of color.

A 2010 study done by Nidhi Jaint et al., revealed a disparity between male and female color perception [1]. When given the task of matching 22 test color strips with 2 shade charts of different colors, female participants gave more correct responses, particularly for the red and green color [1]. Since then, multiple studies have surfaced supporting the same claim; women have better color perception capabilities than men. Importantly, this proves that different people experience drastically different color perceptions which can result in inconsistent laboratory analyses.

The connection of color perception disparity and middle distillate fuel stability is quite surprising. Fuel stability is integral to the performance and longevity of recirculating engines, specifically diesel engines. Old diesel fuels develop gunk and sludge that will not burn properly, causing production of black smoke [2].

Gunk and sludge, shown in Figure 1, will severely damage the fuel injection system of the engine and will likely cause failure [2]. With 70.5 % of food transportation in the US being done by truck, keeping diesel engines running efficiently is integral to the economy [3]. Having a system to test the stability of stored, aged fuels is thereby helpful. ASTM D6468 is utilized for monitoring the manufacture and storage of fuels using a grading scale dependent on the color changes in a pad filter after high temperature aging [4]. Stored fuel is filtered, aged in a high temperature bath, then vacuum filtrated through a funnel and filter system with nominal porosity of 11 μm and analyzed [4]. If the gunk/debris left on the filter is not consistently distributed across the filter, the test must be run again, for the light passing through the filter unevenly will skew results and introduce sources of error [4]. Since men and women perceive colors differently, the grading scheme may be interpreted differently among researchers, causing different numerical gradings across the same harvested filters. This subjectivity must be replaced by objectivity, where a pre-determined rating standard is independent of human color perception. This is done by using the Koehler Instrument Company's K30700 Reflectometer, shown in Figure 3 below.

Figure 1. Color and Integrity Disparity Among Stored Diesel Fuels [6]

In ASTM D6468, high temperature stability for middle distillate fuels such as diesel and heating oil is investigated. This test method not only applies to the storage and manufacture of middle distillate fuels, but also provides an indication of thermal oxidative stability of middle distillate fuels heated to high temps [4]. The test method can be applied to the investigation of operational problems related to fuel thermal stability [4]. The middle distillate fuels, such as diesel, are then aged in a high temp (150 ± 1.5℃) bath, for example Koehler's precision bath showed in Figure 2, allowed to cool, and filtered via vacuum filtration [4].

The pad filters used in the vacuum filtration system are then analyzed using the Koehler Instrument Co. K30700 Reflectometer. The system requires a swift, basic 2 step calibration where a black cavity standard and a standard plaque with a known, calibrated reflectance value are used. The black cavity calibrates the zero offset for dark current correction and gives the designation ZERO. The standard plaque with the known reflectance value usually is the highest reflectance value and given the denotation of STD on the reflectometer unit. The reflectance of the tested material is then plotted linearly, using the linear relation of the photosensor output to make sample voltage and reflectance directly proportional. It is recommended that the reflectance value of the sample lies between the 2 calibrated points for the most accurate, reliable results. Alternatively, for ASTM D6468 an additional option for calibration that yields more applicable results is the replacement of the standard plaque with unused, fresh pad filters identical to the ones used for the vacuum filtration. After calibration, the used filters are placed atop the ¼ inch aperture of the y search unit of the reflectometer and the percent reflectance, based linearly upon the two calibration points, is displayed. A grading system has been created for grading the percent reflectance of a test filter and is shown below in Table 1.

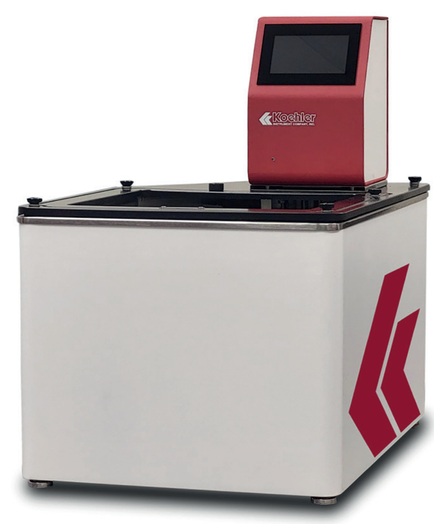


Figure 2. Koehler Precision Heating Bath

Table 1. Reflectance Grading Scale [5]

Visual Pad Rating	%Reflectance, W unit	%Reflectance, Y/Green filt. Unit	Relative Stability
1-2	85-100	90-100	Excellent
3-4	71-85	80-89	Good
5-7	62-70	70-79	Fair
8-10	53-61	60-69	Marginal
11-15	32-52	50-59	Poor
16-20	0-31	0-49	Very Poor

This grading system may be programmed into the reflectometer, which can immediately display both the reflectance value and the developed grading value for the test sample. Thereby, this instrument allows for independent, unbiased, objective examination of the reflectance of the used pad filter and yields a reliable grading based on a dependable rating scale. The Koehler Instrument Co. K30700 Reflectometer is shown below in Figure 3, which depicts both the reflectometer and Y search Unit.

Figure 3. K30700 Reflectometer

This instrument provides trustworthy results relating to the quality of not only middle distillate fuels, as reflectance values closer to the clean unused pad filter implies higher fuel stability, but most substances that contain color standards as a means of assessing quality.

One application where the reflectometer is utilized outside the realm of fuels is food quality control, specifically potato and coffee products. As stated previously, the K30700 Reflectometer can be integrated with a predetermined grading scale, such as the pad filter scale shown in Table 1 or, for coffee ground grading, the Specialty Coffee Association (SCA) industry scale. The SCA industry scale is an efficient way to gauge quality across batches of coffee grounds. This grading scale can be programmed into the reflectometer. The main difference in the utilization of the reflectometer in the pad filter ASTM method and the SCA scale is the search unit. While the Y search unit is primarily used for solids such as filters, the D-search unit is used for coffee grounds, potato chips and powders. The only main alteration from Y to D search units is that the aperture is larger on the D search unit and there is a sample cup that works in conjunction with the unit where the test material is placed. An image of the sample cup and the D search unit are included below in Figures 4 and 5, respectively.

Figure 4. D Search Unit Sample Cup [6]

An additional application that the Koehler Instrument Co. K30700 Reflectometer can possibly improve is ASTM 4048, or the Copper Corrosion test. This test method is used to detect the corrosiveness to copper of lubricating greases [8]. A prepared copper strip is completely immersed in a sample of grease then heated in an oven or liquid bath [8]. At the end of the heating period, the copper strip is removed and then visually compared to the Copper Strip Corrosion Standard [8]. Table 2 below shows the classification scale included in the Copper Corrosion Test, this table shows how based upon color, the strip is given a classification.

Because the classification necessitates color perception by the tester, the results of this test method are partially subjective, for the technician is responsible for the evaluation of the corrosion level on the strip. As previously stated, color is perceived differently among males and females, and this difference in acuity enables different designations on the same level of corrosion. Researchers are currently researching ways to create and implement a grading scale based on reflectance for this test method to make the test less subjective and independent of human color perception. This would take human color perception out of the grading completely and would eliminate discrepancies across research groups.

However, the non-uniform distribution of the corrosion experienced by the bearing is posing an issue. Therefore,

Table 2. Copper Corrosion Classification Scale [8]

Classification	Designation	Description
1	Slight Tarnish	Light Orange, almost the same as freshly polished strip
		Dark Orange
2	Moderate Tarnish	Claret red
		Lavender
		Multicolored with lavender, blue or silver, or both, overlaid on claret red
		Silvery
		Brassy or gold
3	Dark Tarnish	Magenta over case on brassy strip
		Multicolored with red and green showing (peacock) but no gray
4	Corrosion	Transparent black, dark gray, or brown with peacock green barely showing
		Graphite or lusterless black
		Glossy or jet black

Figure 5. D-Search Unit [7]

while this possible application is quite useful, especially in the petroleum-grease industry, it will take time to gain a foothold in widespread applications especially material that does not experience uniform distribution of color. Non-uniformity is just one of the few key challenges keeping the reflectometer from widespread outreach of application. Solving this issue opens the door to many avenues not yet traveled down.

In all, the Koehler Instrument Co. K30700 Reflectometer has a bright future in the petroleum-grease industry. Used for ASTM D6468, this instrument will prove vital to the scrutiny of both stored fuels and the investigation of failed engine systems, for by testing the thermal oxidative stability of fuels, possible causes of engine failure can be found. Along with its application in the food industry and possible integration into the Copper Corrosion Test (ASTM 4048), the Koehler Instrument Co. K30700 Reflectometer has a vast series of applications and provides a widespread, simple, user-friendly way to investigate quality control.

Works Cited

[1] Saint, N., Verma, P., Mittal, S., Mittal, S., Singh, A. K., & Munjal, S. (2010). Gender based alteration in color perception. Indian journal of physiology and pharmacology. Retrieved January 25, 2023, from https://pubmed.ncbi.nlm.nih.gov/21675035/

[2] Diesel, G. S. (2018, September 10). Does diesel fuel go bad? Gem State Diesel & Turbo Repair. Retrieved January 25, 2023, from https://gemstatediesel.com/does-diesel-fuel-go-bad/

[3] Tarlengco, J. (2022, August 8). Food transportation. SafetyCulture. Retrieved January 25, 2023, from https://safetyculture.com/topics/food-transportation/

[4] ASTM Standard D6468, 2022, "Standard Test Method for High Temperature Stability of Middle Distillate Fuels", ASTM International, West Conshohocken, PA, 2022, DOI: 10.1520/D6468-22

[5] Hagstrom, S., & Neci, J. (n.d.). Oil & Energy Testing Company - AMSPEC services. AmSpec Group. Retrieved January 25, 2023, from https://www.amspecgroup.com/wp-content/uploads/2017/09/amspec_techtalk_stability_5.pdf

[6] Sample cup for coffee ("D" search unit) 3671003. Photovolt. (2023, January 13). Retrieved January 26, 2023, from https://photovolt.com/products/reflectance/coffee-accessories/sample-cup-for-coffee-and-grind-d-search-unit/

[7] Homepage. Photovolt. (n.d.). Retrieved January 26, 2023, from https://photovolt.com/

[8] ASTM Standard D4048, 2022, "Standard Test Method for Detection of Copper Corrosion from Lubricating Grease", ASTM International, West Conshohocken, PA, 2022, DOI: 10.1520/D4048-22

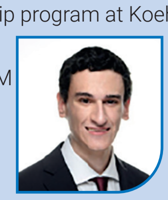
About the authors

Dr. Raj Shah is a Director at Koehler Instrument Company in New York, where he has worked for the last 27 years. He is an elected Fellow by his peers at IChemE, CMI, STLE, AIC, NLGI, INSTMC, Institute of Physics, The Energy Institute and The Royal Society of Chemistry. An ASTM Eagle award recipient, Dr. Shah recently coedited the bestseller, "Fuels and Lubricants handbook", details of which are available at https://bit.ly/3u2e6GY He earned his doctorate in Chemical Engineering from The Pennsylvania State University and is a Fellow from The Chartered Management Institute, London. Dr. Shah is also a Chartered Scientist with the Science Council, a Chartered Petroleum Engineer with the Energy Institute and a Chartered Engineer with the Engineering council, UK. Dr. Shah was recently granted the honorific of "Eminent engineer" with Tau beta Pi, the largest engineering society in the USA. He is on the Advisory board of directors at Farmingdale university (Mechanical Technology), Auburn Univ (Tribology) and Stony Brook University (Chemical engineering/ Material Science and engineering). An Adjunct Professor at the State University of New York, Stony Brook, in the Department of Material Science and Chemical engineering, Raj also has over 475 publications and has been active in the petroleum industry for over 3 decades

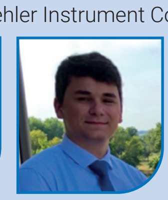
Anthony Schevon is a student of Chemical Engineering at SUNY Stony Brook University, where Dr. Raj Shah is the chair of the external advisory board of directors. Anthony works as Technical Applications Assistant at Koehler Instrument Company in Holtsville NY. Anthony is the founder of the newly established SBU Energy Club at Stony Brook University.

William Streiber is a student of Chemical Engineering at SUNY Stony Brook University, where Dr. Raj Shah is the chair of the external advisory board of directors. William is also part of a thriving internship program at Koehler Instrument Company.

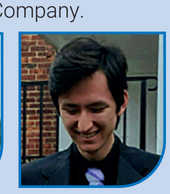
Stefan Lim is the Marketing & Sales Development Coordinator at Koehler Instrument Company in Holtsville NY. He has been an active member of ASTM International's D02 Committee on Petroleum Products since 2020 and was selected as an ASTM Emerging Professional in 2022. Stefan graduated from Stony Brook University in 2020 with a double major in Chemical Engineering and Mathematics and a minor in Business Management.



Anthony Schevon



William Streiber



Stefan Lim

Author Contact Details

Dr. Raj Shah, Koehler Instrument Company • Holtsvile, NY11742 USA • Email: rshah@koehlerinstrument.com

• Web: www.koehlerinstrument.com