RECENT ADVANCES IN TEST METHOD DEVELOPMENT, AND INSTRUMENTATION USED FOR TESTING DIESEL FUEL

Diesel fuel is an important contributor in powering the U.S. economy, moving more than 80 percent of all cargo in the U.S and more than 90 percent throughout the world [1]. Most of the diesel fuel produced and consumed in the United States is refined from crude oil at petroleum refineries. U.S. petroleum refineries produce an average of 11 to 12 gallons of diesel fuel from each 42-gallon barrel of crude oil [2]. In 2020 distillate fuel consumption by the U.S. transportation sector was about 44.61 billion gallons, an average of about 122 million gallons per day. This amount accounted for 77% of total U.S. distillate consumption, 16% of total U.S. petroleum consumption, and on an energy content basis, about 27% of total energy consumption by the U.S. transportation sector [3]. Due to commercial, environmental, quality, processing, and safety regulations, there is an immense number of specifications and related test methods that must be performed for verifying the quality of diesel fuel. These testing methods range from testing for the cetane rating, flashpoint, suspended water, and particulate contaminate value, distillation temperature, oxidation, and storage stability, etc. In recent years new equipment and instrumentation now allow for easy to use and cost-efficient ways to test for important performance and safety properties of diesel fuel.

Every diesel fuel has a cetane rating that represents the quality and performance of that specific fuel. Cetane is a chemical compound found naturally in diesel, and it ignites easily under compression with heated air. Due to its high combustibility, the diesel cetane rating serves as the industry-standard measure for evaluating fuel combustion quality [4]. As the displacement of petroleum-based ultra-low-sulfur diesel (ULSD) with low-net-carbon biofuels becomes necessary to help mitigate potential effects on global climate change, problems may arise if these new blends cause significant changes to the combustion phasing of the conventional diesel combustion process, particularly the ignition delay [5]. Cetane number (CN) is the most conventional and universally accepted ignition quality measurement that helps evaluate the expected ignition delay of a fuel. Alternatively, several other constant-volume combustion chamber-based cetane rating devices have been developed to rate fuels with an equivalent derived cetane number (DCN) or indicated cetane number (ICN) [6]. The ASTM D6890 test method [7] defines and determines the measurement produced for the DCN. The ignition delay, which is the pressure recovery time after the injection of liquid fuel at around 21 atm and 830 K, is measured in an ignition quality tester and then transformed to the DCN. This measurement method requires less fuel to operate than does the CN test method D613 [8]. The ASTM D8183 [9] test method covers the quantitative determination of the ICN of different diesel fuels containing CN improver additives by utilizing a constant volume combustion chamber with direct fuel injection into heated compressed air. ICN is determined directly from ignition delay using an instrument-specific reference fuel calibration curve. The ADA5000 Automatic Distillation Analyzer by Koehler Instruments (Figure 1) calculates the cetane index for estimating ASTM D4737 cetane number where a test engine is not available for determining this properly [10,11]. Higher cetane number fuels tend to lessen combustion noise, increase engine efficiency, increase power output, start more easily, reduce exhaust smoke, and reduce exhaust odor.

Figure 1: ADA5000 Automatic Distillation Analyzer by Koehler Instruments [10].

The flashpoint of fuel often has no significant relation to its performance. Auto-ignition temperature is not influenced by variations in the flashpoint, but flashpoint is specified primarily for safety during transport, storage, and handling. A low-flash-point fuel can be a fire hazard, subject to flashing, and possible continued ignition and explosion [12]. The Automatic Pensky-Martens Closed Cup Flash Point Tester by Koehler Instruments (Figure 2) represents a perfect union of next-generation technology with traditional robust quality [13]. The analyzer conforms to ASTM D93 and related specifications for flash point determination of different petroleum products such as diesel [14]. One experiment revealed the dependence of flashpoints on reduced pressures at high altitudes, by performing a series of field flash point determinations at six different altitudes on the Qinghai-Tibet Plateau [15]. The ASTM D93 standard followed in this work, which is the close cup method, was used due to the close cup method giving lower values than the open cup method. Liquid fuel samples were heated at a specified rate in a copper cup and an ignition source with specified strength was equipped 10-14 mm above the sample surface to ignite the vapor-air mixture. The temperature at which flashover occurs and propagates through the vapor-air mixture to the liquid surface was taken as the flashpoint of this sample. In the closed cup method, there is a cover on the copper cup, with a shutter on the cover as well where the fuel vapor accumulates in the cup until the shutter opens for ignition, so the fuel vapor in the cup is easier to reach its lower flammability limit than an open cup method. The results of the field determinations indicate that flashpoints of liquid fuels decrease nonlinearly with the reduced pressure at high altitudes, and the influence of atmospheric pressure on flashpoints is strengthened with the increasing of altitudes. Compared with the field-determined flashpoint temperatures, the predictive accuracy of the two methods is similar, and both methods give more accurate predictive flashpoints than the linear relationship. The higher the flashpoint, the safer the material is to handle [16], noting the dependence upon the pressure in the air which can change the flashpoint.

Figure 2: Automatic Pensky-Martens Closed Cup Flash Point Tester by Koehler Instruments [13].

Particle counting is a newer test method for fuel cleanliness, where particle measuring technology is used to control the cleanliness of liquids and to identify quality deficiencies and potential excessive wear to avoid eventual costly machine failures [17]. Poor performance and component failure are more likely related to the condition of the fuel than to mechanical fatigue. Particle counters are simple to operate and provide immediate results. They measure and count particles, presenting the results in size bands, giving a snapshot of the particle distribution in terms of particles/ml and ISO 4406 cleanliness code [18]. The cleanliness specification mentioned in the ASTM D975 Standard Specification for Diesel Fuel [19] highlights using particle counting as a method of testing the degradation of diesel fuel that has been in storage for an extended period. ASTM test method D7619 is a method that can be used for particle counting in middle distillate fuels which includes diesel and biodiesel in its scope [20]. A research study presents the results of diesel fuel contamination with abrasive particles in various size ranges, determined following ASTM D7619 [21]. The purity of diesel fuel is a critical issue, in the face of modern injection systems operating under very high pressures with very precisely fitted mating parts. At these high pressures and temperatures, injectors are exposed to abrasive wear due to the presence of fine, hard abrasive particles in diesel fuel. Based on the results of the tests carried out, it can be concluded that exceeded number of particles in individual size ranges are not always related to the content of impurities in a form of metallic pulp, nevertheless, they may be one of the factors contributing to damage to precision fuel injection systems.

As the use of synthetic and bio-derived fuels increases with the introduction of modern engines utilizing high-pressure fuel injectors the measurements of haze and freedom from particulate materials are becoming an increasingly important product specification that must be measured within stringent standards [22]. The ASTM D8148 Standard Test method covers a spectroscopic method procedure for determining the level of suspended water and particulate contaminate, known as the haze, in liquid middle distillate fuels including those blended with synthesized hydrocarbons or biofuels [23,24]. This method generates an ordinal, whole-number, Instrument Haze Rating (IHR) from 1 to 6 and a Haze Clarity Index (HCl) from 50.0 to 100.0. HCl can be used to evaluate Haze intensity changes to a much finer degree than could ever be achieved with visual inspection procedures. The new ASTM test method D8148 delivers the rapid, precise, and reliable Haze and Clarity determination measurement capabilities needed for today's demanding petroleum-based process control and product quality assurance applications [25]. The Clarity Choice hz (Figure 3), developed by Choice Analytical, is a compact and lightweight analyzer that can readily measure Haze and Clarity in petroleum products within 105 seconds, as per ASTM D8148. The achievement of obtaining the ASTM method is a significant step in the continued growth of new technologies and equipment for measuring Haze and Color.

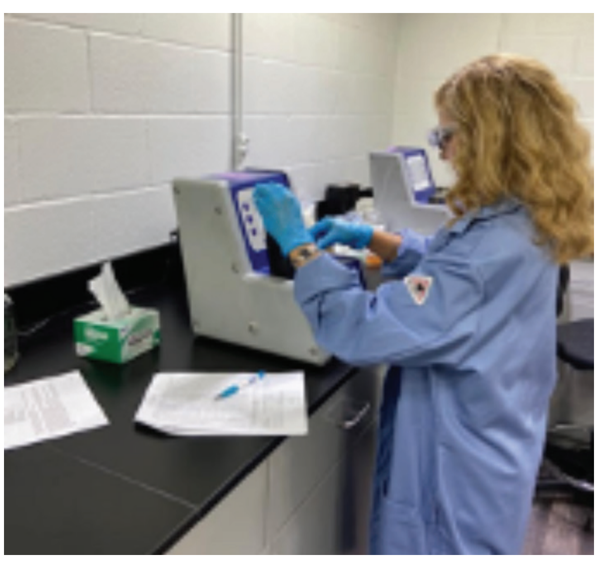

Figure 3: A lab technician taking part in the recent ILS to establish Reproducibility for Haze Clarity Index (HCl), as part of D8148, using the Clarity Choice hz [25].

It is well known that biodiesel in its pure, unblended form causes far less damage than petroleum diesel if spilled or released to the environment. With efforts to extend or replace mineral diesel and gas oil used to fuel on and off-road vehicles and static engines the production and usage of Fatty Acid Methyl Ester (FAME), the generic chemical term for biodiesel [26], has increased. The objective for bio-based lubricant manufacturers is to develop robust products with proven performance in key areas such as oxidation resistance and low-temperature performance. For many years Rancimat was the only standardized method for measuring the oxidation stability of FAME and FAME/diesel blends. However, this method does not apply to pure conventional petroleum products and so the effect of FAME on diesel fuel stability could not be evaluated directly. Rapid Small Scale Oxidation Test (RSSOT) : ASTM D7545 standard test method can be used for this purpose and it covers a quantitative determination of the stability of middle distillate fuels such as diesel fuels, with up to 100% biodiesel, [27, 28].

Diesel fuel is a distillate fuel obtained from petroleum compromised of a mixture of hydrocarbons, which determine its volatility, density, and viscosity. NMR spectroscopy is already widely used in the fuel industry for determining fuel properties and chemical composition; however, due to the expense and size of these spectrometers required, a more affordable, robust solution is advantageous. Detailed hydrocarbon analysis (DHA) applications are widely used in the petroleum industry to characterize light petroleum fractions with boiling points up to 225 [29]. These applications comply with ASTM methods D5134, D6729, D6730, and D6733 which use single-column gas chromatography to group the hydrocarbon components by structure [30,31,32,33]. DHA is applied to petroleum streams comprising naphtha, alkylate, reformer feed, reformate, isomerate, gasoline, and compressed liquids. DHA characterization of these streams is based on the Kovats Index and differentiates the composition and concentrations into five groups that are collectively called PIANO: Paraffins, Isoparaffins, Aromatics, Naphthenes, and Olefins [29]. PIANO analysis proves the identification and quantification of 500 to 1,00 different hydrocarbons in the fuel presented in either weight%, volume%, or molar concentration. The newest such method, ASTM D8368 Determination of Totals of Saturate, Aromatic, Polyaromatic and Fatty Acid Methyl Esters (FAME) Content of Diesel Fuel Using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV), has just had its test precision completed.

Many of these hydrocarbons would not be identified on traditional scans used for regulatory compliance. Several ratios of the hydrocarbons obtained from the PIANO scan can be found such as the refining ratio which can identify the grade of fuel. It is of great importance to understand the chemical composition of the fuel by utilizing this high-quality analytic standard to ensure the gas chromatography system is optimized for the proper performance of the DHA analyzer. These standards should be utilized to perform routine quality assurance checks which will reveal any need for maintenance, including when it is time to replace the equipment.

As the U.S. economy grows, so does the need for diesel fuel. Powering 15 key sectors of the U.S. economy, engines running on diesel show unmatched combinations of energy density, fuel efficiency, power, and performance compared to any other fuel. The use of proper techniques and methods for testing your diesel fuel can help avoid engine failure, minimize the number of expensive repairs performed, and ensure the quality of the fuel. As a result of EPA regulations, diesel engines manufactured today are cleaner than ever before however, it is still important to take into consideration the environmental impact of diesel fuel and the emissions it produces that contribute to the production of ground-level ozone. The future of diesel fuel is defined by reducing emissions even closer to zero and increasing the use of low carbon renewable biofuels at an affordable cost [34].

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