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Limitations of the use of cetane index for alternative compression ignition engine fuels

Noel Bezaire, Kapila Wadumesthrige, K.Y. Simon Ng, Steven O. Salley *

Department of Chemical Engineering, Wayne State University, 5050 Anthony Wayne Drive, Detroit, MI 48202, USA

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ABSTRACT

The cetane number of a fuel is an important factor in determining the quality of ignition in compression ignition (CI) engines. The significance of accurate measurement of cetane number has become even greater since the use of alternative fuels and modern CI engines. In this work, the comparison of different methods of cetane value measurement for fuels with different chemical composition such as ultra low sulfur diesel (ULSD), synthetic jet fuel (S-8) and military grade jet fuel (JP-8), trace amounts of additives and biodiesel blends under different conditions is reported. The cetane index was calculated by ASTM D4737 and ASTM D976 and the derived cetane number (DCN) was measured using an Ignition Quality Tester (IQT) as a basis of comparison with the cetane index. The best agreement among three methods was observed for ULSD, while S-8 showed the largest discrepancy. The cetane indices for S-8 were 70.2 and 67.3 calculated using D4737 and D976 respectively, while the DCN was 52.8. The addition of biodiesel to ultra low sulfur diesel (ULSD) fuel alters the chemical properties of the fuel. The derived cetane number reflected the increase in ignition quality with the addition of biodiesel while calculations for cetane index did not. The cetane indices for a commercial B20 were 45.30 and 46.70 while the DCN showed a significantly higher value of 48.50. Blending 5% oxidized biodiesel with ULSD caused an 8% increase in the derived cetane number of the blend. The cetane index of the 5% biodiesel was not significantly affected by oxidation. The effects of fuel additives on cetane measurements were reflected in the DCN measurements, but not with cetane indices.

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1. Introduction

The cetane number is a measure of the ignition quality or the auto ignition tendency of a fuel under the compression ignition process [1–7]. Ignition quality is quantified by measuring the ignition delay, which is the time period between the injection of the fuel into the combustion chamber and the start of combustion [1–7]. Fuels with shorter ignition delay (high cetane number) start to ignite shortly after injection into the cylinder, thereby having enough time for complete combustion of fuel during the power stroke. Fuels with a lower cetane number can be accumulated before the start of combustion. This leads to a sudden pressure rise followed by pressure pulses and subsequent vibrations causing diesel knock, which leads to poor thermal efficiency, excessive noise and reduced life of engine components. Lower cetane numbers result in poor combustion characteristics and lead to excessive emissions of smoke and particulates. Improving the cetane number in diesel fuel has several beneficial effects on the engine. Higher cetane numbers improve cold starting of the engine and will also reduce the smoke during start up. Higher cetane numbers will also increase fuel economy, reduce exhaust emissions, decrease the knocking and noise of the engine, and improve the overall durability of the engine [3–7]. The problematic long-term supplies of oil and, also the regulatory actions taken by the Environmental Protection Agency (EPA) and the Energy Policy Act (EPAct) have increased the use of alternative fuel percentages in CI engines. Also the use of alternative fuels such as JP-8 and synthetic aviation fuels in the nontactical military ground fleet under the directive of the Single Fuel Forward (SFF) policy [8,9] is under active evaluation. With these factors and with modern CI engine technologies, the cetane number has become a more important parameter for fuel combustion now than a decade ago.

The cetane number has been included as a fuel quality specification in the petroleum diesel standard, with a minimum of 40 in the American Society for Testing and Materials (ASTM) D975-09a [10] as well as biodiesel standards, with a minimum of 47 prescribed for neat biodiesel in ASTM D6751-09 [11], and a minimum of 51 in some European countries (e.g., German standard E DIN 51606). However, engine manufacturers specify their own cetane requirements depending on the engine design and operating condition. Depending on the molecular composition of the fuel, a wide

* Corresponding author. Tel.: +1 313 5775216; fax: +1 313 5773810.
E-mail address: ssalley@wayne.edu (S.O. Salley).

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range of cetane numbers ranging from 35 to 55 is observed. Some special compounds, called cetane improvers, are frequently added to diesel fuel to increase the cetane number.

The CN of a diesel fuel is defined as the percentage by volume of normal hexadecane (cetane, $C_{16}H_{34}$), in a blend with 2,2,4,4,6,8,8-heptamethylnonane (iso-cetane), which matches the ignition quality (ignition delay of 2.407 ms) of the diesel fuel being rated under the specified test conditions of ASTM D613-08 [12] test method. By definition and somewhat arbitrarily, normal cetane has been assigned a CN of 100 whereas iso-cetane has a CN of 15. This implies that CN = % (*n*-cetane) + 0.15(% iso-cetane).

The ASTM D613 method involves running the fuel in a special, expensive, single cylinder diesel engine called a Cooperative Fuel Research (CFR) engine with a continuously variable compression ratio under a fixed set of conditions. This test method suffers from many disadvantages, some of which include a relatively large fuel sample volume requirement, significant time consumption, and a high reproducibility error.

Therefore, there have been many attempts to develop alternate tests to replace the ASTM D613 method. These include devising better engine tests and developing correlative models to predict CN from bulk properties of the fuel that may be measured more quickly and reliably. A common method for measuring cetane number is ASTM D-6890-08 [13]. ASTM D6890 measures the ignition delay of the fuel with an Ignition Quality Tester (IQT). The ignition delay is used to calculate the derived cetane number (DCN) and the results are accurate with a repeatability of 0.7 for cetane numbers between 33 and 60 [13,14]. The test is feasible because of the small sample volume and relatively lower cost. It has been shown that the DCN corresponds well with the cetane number measured by engine ASTM D613 [14]. The ASTM D2 committee approved ASTM D6890 for inclusion within the US Diesel Specification ASTM D975 and biodiesel specification (B100) ASTM D6751 as an alternative to the established ASTM D613 test method, which for the short term will remain the referee test procedure. There are numerous reports available on the use of IQT™ for the measurement of DCN [6,7,15–20]. Some of these reports use IQT™ as a reliable experimental tool to compare the predicted cetane numbers using different mathematical models [19,20].

Cetane index may also be used to estimate the cetane number of a fuel. ASTM D4737 [21] uses a four variable equation for estimation and is based on the bulk physical properties of the fuel such as density and boiling temperature. ASTM D4737 was originally released in 1996 as ASTM D 4737-96a, and the active current version is ASTM D 4737-04. ASTM D4737 is only to be used when ASTM D613 is not available. The estimation by this method is not to be used when cetane improvers are added and is only valid when the boiling temperature at 90% recovery is less than 382 °C. ASTM D976-06 [22] is a supplementary estimation for cetane index that is based upon American Petroleum Institute (API) gravity and boiling temperatures in the middle range. It is stated in ASTM D976-06, that this test method is one tool available for estimating Calculated Cetane Index where a test engine is not available for determining Cetane number. It may be employed for approximating cetane number where the quantity of sample is too small for an engine rating. In cases where the cetane number of a fuel has been initially established, the index is useful as a cetane number check on subsequent samples of that fuel, provided its source and mode of manufacture remain unchanged [22], indicating that this method is suitable as a cross check of cetane number of fuels with identical fuel compositions.

Because of the simplicity and availability of the instruments to measure bulk physical properties, the above two cetane indices are widely used to represent ignition quality both in industrial and academic environments, regardless of the types of fuels, such as petroleum diesel [23,24], Synthetic F-T fuels [25–27], petroleum Jet fuels [27–29] and biodiesel blends [30,31]. In some reports, the cetane index calculated using ASTM D976 is reported as cetane number. There are discrepancies, however, among the cetane values calculated using the different methods. Cetane number calculated by ignition delay heavily depends on the chemical properties of the fuel. Chemical compounds even at trace amounts, such as cetane improvers present in fuel and biodiesel components and oxidative products in biodiesel which affects the initiation of combustion may not affect the physical properties such as boiling temperature and density. Cetane index, however, is influenced by physical properties. As a result, cetane index may not be a suitable method for the approximation of the cetane number for biodiesel blends. It is known that the oxidation of biodiesel blends changes the chemical properties of the fuel, however it is assumed that the physical properties of the fuel would not change significantly enough to accurately predict a cetane number.

The objective of this study is to analyze the differences between derived cetane number as measured by the IQT™ with the cetane index by ASTM D4737 and ASTM D976 for fuels with different chemical compositions and fuels with trace amounts of additives. The study also investigates how the conditions of biodiesel blends affect cetane measurements. The data presented here will help both the academic and industrial communities to identify the proper use of cetane measurement techniques appropriate for the type of fuel. With the increasing demand of alternative fuels such as synthetic F-T fuels and biodiesels and modern high speed CI engines, the accurate measurement of ignition delay (cetane number) is important.

2. Materials and methods

2.1. Materials

2.1.1. Fuels

Biodiesel produced from soybean oil (SBO), was obtained from NextDiesel, (Adrian, Michigan). Certification #2 ultra low sulfur diesel (ULSD) was obtained from Haltermann Products (Channelview, Texas). A sample of synthetic aviation fuel (S-8) produced by Syntroleum Corporation, (Tulsa, Oklahoma) and military grade jet fuel (JP-8) were provided by National Automotive Center, US Army, Warren, Michigan. The commercial ULSD and B20 were purchased from RKA Petroleum Corporation (Romulus, MI). A sample of cold flow additive, Cold Flo 6300 RK (Midcontinent Chemical Company, Overland Park, KS) (CFA) was kindly provided by RKA Petroleum Corporation.

2.1.2. Distillation of biodiesel

Five hundred millilitres of SBO biodiesel were distilled under reduced pressure (3×10^{-3} Torr) at about 130–150 °C. The distillation was performed to remove natural antioxidants present in the biodiesel. Analysis of the distillates using a Perkin–Elmer (Shelton, CT) Clarus 500 gas chromatograph equipped with a flame ionization detector (GC-FID) indicated that they contained only FAMEs [17]. Once distilled, they were stored at 4 °C. Portion of this distilled biodiesel was kept in a glass bottle in ambient conditions for 1 year. This oxidation resulted in a derived cetane number of 120.

2.1.3. Biodiesel blend preparation

The blends of regular, distilled and oxidized biodiesel in ULSD on a 1%, 2%, 5%, 10%, 15% and 20% volume basis were prepared and stored in dark glass bottles at room temperature. A blend of 20% biodiesel with 80% ULSD, by volume, is termed: “B20”. Both cetane indices and DCN measurements for given blends were carried out within the same day.