

Reference and Pure Component Fuel Characterization in an Ignition Quality Tester Derived Cetane Rating Unit

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ABSTRACT

Primary diesel and gasoline reference fuels, along with secondary reference diesel fuels across a very broad cetane range were tested in an Ignition Quality Tester (IQT) unit using the ASTM D6890 protocol. Additionally, numerous pure component fuels across a range of hydrocarbon size and structure were evaluated. The reference fuels' ignition delay (IGD) followed expected trends, however, the diesel PRF fuels in the low cetane range produced DCNs (derived cetane numbers) that were moderately higher (shorter IGDs) than their cetane reference values. From the perspective of fuel size, IGD shows a significant 'shortening' - faster nature with increased fuel carbon number. For a given carbon number fuel molecule, normal alkanes showed the 'fastest' IGD, with alkenes and branched alkyl aromatics leading to moderately longer IGDs. Cyclo-paraffins had the 'slowest' - longest IGDs. Various methods were used to determine the IGD of the various fuels. The pressure recovery start of combustion IQT criterion is quite comparable to the 5% energy release criterion often used in diesel engine combustion analysis. Companion modeling was also pursued in this study in order to further understand these experimental results.

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INTRODUCTION AND BACKGROUND

Since 2010 the US Navy has been testing and certifying renewable alternative fuels for drop-in replacement of jet and diesel fuels as part of the Great Green Fleet Initiative. The US Navy has already certified 50-50 blends of conventional petroleum diesel with a Hydroprocessed Renewable Diesel fuel (HRD) as well as a Hydroprocessed Renewable Jet (HRJ) fuel. Other renewable fuels at lower blend fractions have also been more recently certified.

Some of the renewable fuels that have been studied possess higher than normal (as compared to conventional petroleum) cetane numbers, and thus are more easily ignitable. References [1] and [2] discuss some testing of the HRD and HRJ fuels. These fuels are principally paraffinic in nature, lacking the less reactive aromatic type hydrocarbon components. Some of the newer renewable fuels tested have lower ignitability. These fuels are derived from biomass and plant products that possess significant percentages of aromatic, cyclo-paraffinic and/or highly branched alkane hydrocarbon compounds.

One newer renewable alternative fuel, a Hydrotreated Depolymerized Cellulosic Diesel (HDCD) fuel from biomass sources was seen to have roughly equal fractions of aromatic and cyclo-paraffinic compounds [3]. This less reactive alternative fuel could only be

added in minority fractions to base petroleum fuels due to cold start diesel concerns [4]. Additionally, a highly branched alcohol processed to jet fuel (ATJ) could only be added to conventional jet fuel in minority fraction also due to cold start engine concerns [5]. In cases where fuels are used for emergency diesel backup generators, engine cold start is of paramount importance. For these applications, lower cetane renewable fuels (e.g. HDCD and ATJ) may have starting issues and thus their properties need to be fully understood to avert degradation in performance.

The standard (D613) cetane rating engine is the Waukesha Diesel Cooperative Fuel Research (DCFR) F-5 single cylinder engine. When rating fuels, this engine's (variable) compression ratio is adjusted such that ignition delay (IGD) is 13 crank angle degrees which results in start of combustion (SOC) occurring at TDC since start of injection (SOI) is at 13 °BTC). The inlet air temperature is elevated (65 °C) and the fuel flow rate adjusted to 13 cc/min. The fuel of interest then needs to be bracketed by engine testing with moderately higher and lower reactivity reference fuels. While still the 'gold standard', the application of this DCFR engine is costly. Lower ignitability fuels can also be challenging to test due to the inherently greater cycle-to-cycle variability with low reactivity fuels.

In recent years, alternative cetane rating units have been developed that seek to provide fuel ignitability measurements (e.g. cetane like measurements) at lower cost and in shorter test times. These generally fall into the constant volume combustion chamber (CVCC) type of combustion testing rig. This type of fuel evaluation testing has a rich heritage [6, 7]. Two papers from the early 1950's discuss electrically heated CVCC operation with mechanical single shot fuel injection using various fuels and operating conditions (e.g. chamber pressure and temperature). IGD was the primary measured metric for fuel characterization. Measuring a fuel's ignition characteristics in a CVCC can be useful in predicting resulting combustion behavior at other operational conditions.

In 1985, Siebers at Sandia National Lab tested various fuels in a CVCC with conditions representative of diesel engines [8]. He showed that while CVCC provide directly correct fuel ignitability indication, specifically, cetane number (CN) cannot provide a consistent and accurate measure of IGD of fuels whose ignition characteristics depend on temperature (e.g. compression ratio) in a manner different than reference fuels. Siebers showed that some alternative fuels have different IGD v. chamber temperature characteristics, and thus variations in both cold and hot (high load) performance may result. Thus, similar CVCC-based IGDs may lead to differences in performance at engine cold starting or high load limits.

Around this time at the Southwest Research Institute (SWRI), CVCC developments were pursued as an alternative method to evaluate the ignition quality of fuels. This work would later develop into the IQT. Ryan and co-workers [9, 10] used a CVCC with conventional, alternative and reference fuels. They noted that the IGD of conventional fuels in the CVCC was highly correlated to the actual engine based cetane numbers. Alternative fuels were less strongly correlated to cetane, and the primary reference fuels tested were slightly shifted in IGD character as compared to the conventional fuels.

The SWRI work was further advanced for diesel fuel ignition quality evaluation by Advanced Engine Technologies (AET). AET automated the derived cetane rating (DCN) procedure into what is now called the IQT (Ignition Quality Tester). From 1996 to 2001 four technical papers [11, 12, 13, 14] mapped out the IQT developments. The principle focus of this work was on fuels in the commonly available 40 to 55 cetane range. The IQT calibration development work also used HMN (Heptamethylnonane also called isocetane) as the CN15 reference, as well as n-hexadecane as the CN100 reference. While a few reference fuels in the very low cetane range were tested, a detailed study of these low cetane reference fuels was not presented. Secondary reference fuels were also evaluated as part of the IQT developments. These papers discuss some modest differences that exist between the reference fuels and petroleum fuels.

IQT testing that follows the ASTM testing protocol nominally operates at 21.4 bar chamber air pressure and 825 K. The ASTM D6890-13b standard focuses on the IGD range from 3.1 to 6.5 msec (64 to 33 DCN), and 'There is no information about how DCNs outside the 33 to 64 range compare to Test Method D613 cetane numbers'. Thus, very low and very high cetane fuels may not be

accurately represented by the standard ASTM protocol. IQT repeatability (the difference between successive results by same operator/rig) at DCN 60 is nominally 1 unit, while reproducibility (difference between two single and independent results) is nominally 3 DCN units.

While CVCCs can produce similar trends as compared to an engine, engines can operate at higher temperatures and pressures (as well as shorter time scales), thus, some differences in combustion characteristics are expected to exist. The current NIST Cetane Compendium also mentions that comparisons between the cetane rating engine and CVCC approach are not perfect for many compounds.

A 2004 work by Yates and co-workers studied the connection between the different operating conditions between the IQT and cetane test rating engine, including studying some diesel primary reference fuels (PRFs) in the conventional diesel fuel and higher cetane range (CN 40 and greater) [15]. They used a global reaction model to characterize reference fuels in the IQT, then with an engine model predicted the engine-based compression ratio necessary to achieve a 13 crank angle degree ignition delay. They showed a good correlation between predicted CN and DCN, although some deviation occurred with actual data in the very high cetane range, as well as differences between diesel PRF and SRF reference fuels.

Some nice fuel characterization research work has been performed using an IQT by Bogin and co-workers [16]. An IQT was used 'off-ASTM' characterization of the IGD of numerous fuels across a broad range of chamber temperatures and pressures. Bogin also performed detailed 3-dimensional modeling of the spray and combustion characteristics inside an IQT. Zheng and co-workers at Wayne State Univ. also looked at IGD behavior at various IQT temperatures, along with additional detailed analysis of physical and chemical delay fractions [17]. They evaluated different military fuels in the IQT with nice companion analysis for enhanced understanding of these fuels.

Evaluating new fuels is costly and time consuming, often requiring significant engine testing. In the future it is hoped that as a more fundamental understanding develops, first principles analysis of new fuel structure might lead to accurate engine performance predictions with less cost. Fuel certification of new future fuels would thus proceed more efficiently.

Thus, the objective of this paper is to look at primary and secondary reference fuels at the limits of the cetane scale (very low and very high). Further, with some new alternative fuels being developed with a near single component nature, various pure components are tested in the IQT such that HC size and structure effects can be observed. As part of this study various start of combustion (SOC) criteria are examined such that correlation to engine heat release may be more evident. Lastly, an examination of the relative physical and chemical delay effects are analyzed.

EXPERIMENTAL SETUP AND PROCEDURE

The IQT was operated in standard ASTM D6890 automatic mode. After a new fuel was added (and lines purged), the automated test procedure performed 15 single combustion event runs to stabilize the unit and purge out any old fuel. Then 32 combustion event runs were completed and several operational variables were monitored and saved. Key control variables include 21.4 bar air charge pressure and an air charge temperature of 560 °C.

Normal heptane was regularly run to ensure that it was correctly providing nominally 54 +/- 1 DCN (3.78 msec IGD). Fuels were tested at least twice to ensure that the results were consistent. Summary and individual detailed pressure and injection data were downloaded after testing for post-processing analysis in MATLAB.

Primary reference diesel (PRF) fuels were blended from 99+% pure HMN (Heptamethylnonane or isocetane: CN = 15) and 99+% pure normal hexadecane (CN = 100). Secondary reference fuel (SRF) was procured from Chevron-Phillips. In this study T-28 and U-21 were used and blended according the Chevron-Phillips guidelines. PRF gasoline isooctane with n-heptane blends were also used in this study.

PRIMARY AND SECONDARY FUELS PROPERTIES

The viscosity of the fuels was measured using an Anton Paar SVM 3000 Stabinger Viscometer, while the density and speed of sound were measured using an Anton Paar DSA 5000 Density and Sound Analyzer from. Certified reference standards for viscosity (Standard S3, Cannon Instrument Company) and density (NIST toluene standard) were used to test the accuracy of these instruments, which were recalibrated if they failed testing. Duplicate samples of each liquid were measured using each instrument, and these duplicates were used to determine the precision of the measurement.

Surface tension was measured using a Kruss USA™ DS100 drop shape analyzer. In this analyzer, a droplet of the fuel formed on the tip of a needle is magnified and its shape is analyzed using the Young-LaPlace equation with inputted values of needle diameter, fuel density, and air density. The flash point was measured using a Setaflash Series 8 closed cup flash point tester Models 82000-0 (Stanhope-Seta) under temperature ramping and No Flash/Flash settings. Per the manufacturer's literature, this flash point model conforms to ASTM D3278, ASTM D7236, and ASTM E502.

The distillation values were determined using a Grabner MiniDis ADXpert™ automatic Distillation Unit. Per the manufacturer's literature, this unit conforms to ASTM D7344, Min-method for the Distillation of Petroleum Products at Atmospheric Pressures. This instrument was tested using a Group 4 distillation standard (AccuStandard, Inc) and Jet fuel standard (Fluka Analytical) that were ASTM certified.

Detailed results are located in [Table 1](#) below as well as in the [appendix](#).

Table 1. Fuel Properties at 20 °C¹

	U-21	T-28	cetane	Iso-cetane *	Iso-octane **	n-heptane
Bulk Modulus (MPa)	1243	1347	1425	1297	842	907
Density (kg/m ³)	778.6	791.9	773.6	784.6	683.9	691.8
Viscosity (mm ² /s)	1.49	3.49	4.47	4.72	0.724	0.600
Surface Tension (mN/m)	23.8	26.8	27.3	24.1	18.7	20.3
T10 (distill) (°C)	159	236	287	240	99	98
T50 (°C)	176	261	287	240	99	98
T90 (°C)	213	291	287	240	99	98
Heat Evap(kJ/mol) ***			81.3	52.4	35.1	36

*2,2,4,4,6,8,8-heptamethylnonane = isocetane; n-hexadecane = cetane were taken from reference [18]

**2,2,4-trimethylpentane = isooctane; n-heptane from ref [20]

***V.K. Shen et al, NIST Standards Ref. No. Database 73

The general categories of components that are present in the U-21 and T-28 secondary reference fuels were determined using GC/MS analysis. An Agilent 5975 inert mass selective detector was used in conjunction with an Agilent 6890N Gas Chromatograph (GC) System under the same conditions utilized in previous studies [19]. The GC was equipped with a Zebron phase ZB-5ms® column (30 m, 0.25 mm, 0.25µm, 5% diphenyl-arylene/95% dimethyl polysiloxane) and operated at a helium flowrate of 1.5 mL/min. The compounds were separated using a temperature ramping program that started at 60.0 °C and climbed at a rate of 10 °C/min to 250 °C. An electron impact ionization (EI) method was used for the mass spectrometer with an m/z scan from 30 to 600. To prevent the detector from being saturated, all fuel samples were diluted in n-hexane (1/100 dilution), and the mass spectral analysis of the fuel sample was delayed until the solvent peak had passed. The fragmentation patterns of peaks found at several retention times were compared to those found in the NIST database to determine potential compounds present.

The chromatograms of the U-21 and T-28 are shown in [Figure 1](#). As can be seen, U-21 has components that boil at a lower temperature than do the components in T-28 fuel, as suggested by earlier retention times of less than 9 minutes for the U-21 fuel. Based on a NIST database search, the U-21 contained predominantly branched (~63%) and aromatic compounds (~26%) with smaller amounts of linear alkanes and polyaromatic compounds. The branched compounds ranged from eight to 13 carbons in length with a weighted average number of carbons to be 11, while the aromatic compounds ranged from 9 to 11 carbons in length with a weighted average number of

carbons to be a little greater than 9. In contrast, the T-28 contained mostly linear alkanes (~84%) and branched alkanes (8%), with smaller amounts of cycloalkanes, aromatic compounds, polycyclic compounds and tetralins. The 4 largest peaks are n-tetradecane, n-pentadecane, n-hexadecane (cetane), and n-octadecane. The linear alkanes ranged from 9 to 20 carbons in length with a weighted average number of carbons to be 15, while the branched alkanes ranged from 8 to 21 carbons in length with a weighted average number of carbons to also be 15.

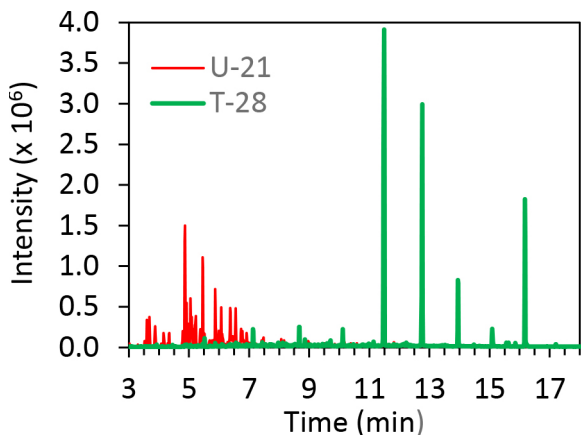


Figure 1. Chromatograms from the GC/MS of U-21 and T-28 Secondary Reference Fuels.

RESULTS AND DISCUSSION

A characteristic single run (there are 32 runs per test) is shown in Figure 2. The injector pintle position signal (pink) is seen to rise rapidly just after 'zero' time. In this study, the start of injection (SOI) is defined to occur when the injection signal reaches 5% of its maximum value. The injection signal is nominally two milliseconds long and characteristically contains three dynamic open pintle 'waves' during the injection event. The measured in-chamber combustion pressure is shown in blue. Shortly after the SOI, the chamber pressure is seen to decline modestly below the initial starting 21.4 bar pressure, from approximately 1 to 3 milliseconds. This pressure decline is due to the evaporative cooling of the fuel in the IQT chamber. Then around 4 msec a rapid rise in chamber pressure is seen as the fuel is rapidly burning in the chamber. Pressure fluctuations are normally seen after the main combustion event (e.g. 4 to 5 msec) as a result of combustion chamber pressure resonance.

Exact definitions of the ASTM IQT SOI and start of combustion (SOC) metrics are not available. The ASTM 6890-13b standard describes SOI as 'initial movement or lift of the injector nozzle needle as measured by a motion sensor', and SOC 'is interpreted as that point in the combustion cycle when a significant and sustained increase in rate of change in pressure, as measured by a pressure sensor in the combustion chamber, ensures combustion is in progress'. Reference [16] mentions that the DCN SOC metric is 1.38 bar above the starting reference chamber pressure. In this study, 1.4 bar above the initial chamber pressure was used as the conventional SOC metric. Significant analysis and comparison to IQT system

software results has confirmed that this definition to be very close to the IQT software analysis (proprietary code). Ignition delay (IGD) is defined as the time difference from SOI to SOC.

An SOC metric based on pressure rise above the initial charge pressure does not necessarily have a fundamental meaning. In engine studies, a heat release analysis is most commonly used to define the SOC. Thus, in this study an engine based heat release analysis [21, 22] was also applied in order to determine how the fixed pressure SOC (pressure recovery + 1.4 bar) compares to a common engine based approach. A heat release analysis of CVCC pressure data is quite straightforward as the combustion chamber volume is fixed unlike in actual engines where the cylinder volume change needs to be considered. In this study, the specific heats as a function of temperature were based on the MIT heat release engine model approach.

The cumulative Heat Release (HR) results are shown as the red curve in Figure 2. This HR analysis follows the general pressure trend first falling due to evaporative cooling, followed then by strong and rapid combustion energy release. Similar to engine-based studies, a 5% and 10% of total heat release was used as a comparative metric to the ASTM IQT-based pressure recovery criterion. For this specific run of n-heptane, a quantitative summary of these three metrics is also shown in the figure. The pressure recovery plus 1.4 bar results in an IGD of 3.7 msec, the 5% cumulative HR result is 3.76 msec and the 10% cumulative HR shows a 3.84 msec IGD. In Bogin's reference [16] it was mentioned that a 276 kPa pressure rise (above initial chamber pressure) criterion was used in order to compensate for low temperature heat release, resulting in a more accurate start of combustion determination. In the following narrative, various SOC methods will be analyzed and discussed.

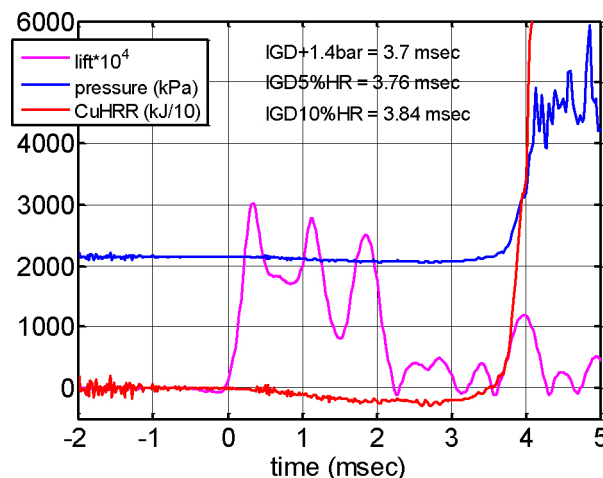


Figure 2. Single IQT run with n-Heptane. Injection position signal in pink, chamber pressure in blue and cumulative energy release in red.

A summary of three SOC methods is shown next in Figure 3 for the diesel PRF fuels. SOI is the same for all three methods. It can be seen that IGD (SOC-SOI) is very long for the lower cetane fuels.