

## Expanding the Experimental Capabilities of the Ignition Quality Tester for Autoigniting Fuels

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### ABSTRACT

This paper reports the development of new fuel ignition quality and combustion experiments performed using the Ignition Quality Tester (IQT). Prior SAE papers (961182, 971636, 1999-01-3591, and 2001-01-3527) documented the development of the IQT constant volume combustion chamber experimental apparatus to measure ignition qualities of diesel-type fuels. The ASTM International test method D6890 was developed around the IQT device to allow the rapid determination of derived cetane number (DCN).

Interest in chemical kinetic models for the ignition of diesel and biodiesel model compounds is increasing to support the development of advanced engines and fuels. However, rigorous experimental validation of these kinetic models has been limited for a variety of reasons. Shock tubes and rapid compression machines are typically limited to premixed gas-phase studies, for example. Since the IQT is a constant volume spray combustion system that allows ignition and combustion studies of low-volatility fuels, the IQT has potential to generate experimental data relevant to validating kinetic ignition models by virtue of its well-controlled temperature, pressure, and start of fuel injection. IQT-based DCN measurements have been shown to be reliable over a range of cetane numbers for middle distillate and some non-conventional diesel fuels. However, significantly improved understanding of the IQT's injection, ignition and combustion processes are necessary to facilitate expanded use of this device for fuels research. This paper reports on the development of the IQT as a heterogeneous combustion research device enabling the study of fuel ignition and combustion in terms of fuel chemistry and physical properties.

This development includes fuel injection process improvements based on detailed injection spray characterization and on-line measurement of NO<sub>x</sub> as an indicator of combustion quality. The results illustrate the potential of the IQT as a research device, filling an experimental void for low-volatility fuels and enabling ignition studies of research fuels, which may only be available in small quantities.

### INTRODUCTION

Enhanced understanding of kinetic pathways to combustion autoignition has become increasingly important to the development of advanced combustion engines and fuels. Homogeneous charge compression ignition (HCCI) and other forms of low-temperature combustion (LTC) strategies rely on fuel autoignition kinetics to control combustion timing [1, 2]. Additionally, the autoignition characteristics of new generation biofuels are currently of great interest [3, 4]. Development of accurate chemical kinetic models for the ignition of diesel and biodiesel model compounds relies on well-characterized experiments [5]. However, rigorous experimental validation of these kinetic models has been limited for a variety of reasons. Shock tubes and rapid compression machines are typically limited to premixed gas-phase studies, for example [6, 7]. Although some progress in studying lower vapor pressure fuels has been made with these devices [8, 9], other research platforms may complement this work and extend ignition kinetics studies.

The Ignition Quality Tester, or IQT, is a bench-scale, constant volume combustion device (see Fig. 1) with a spray injection system designed for the direct measurement of the ignition delay of diesel type fuels [10,11,12,13,14,15,16]. The IQT conveniently quantifies autoignition for traditional

hydrocarbon fuels through a semi-empirical correlation between measured ignition delay (ID) and engine-based cetane number [14]. The ASTM International method D6890-08 was developed around the IQT device to allow rapid determination of derived cetane number, or DCN. DCN is calculated for a fuel based on correlation of averaged ignition delay times from a series of IQT injection events to reference fuel test results from the ASTM D613 engine-based cetane number (CN) method [17, 18]. IQT-based DCN measurements have been shown to be reliable over the limited range of 34-61CN for middle distillate and some nonconventional diesel fuels [19, 20, 21]. The DCN-CN correlation degrades outside this range and may be invalid for new fuels with chemistries different from petroleum, such as fuels derived from triglycerides and oil sands. The latter is indicated by the work of Yates et al. [16], who showed why the correlation equation in ASTM D6890-08 cannot accommodate the variations in the pressure and temperature sensitivities of secondary reference fuels and n-heptane. They then developed global ignition models based on the Arrhenius equation that significantly improved the DCN-CN correlation.

The IQT is a successful device for its designed purpose, measuring the ignition delay of liquid fuels. However, the IQT has the potential of becoming a research platform to further characterize ignition of low-volatility fuels and validate ignition kinetic models. The IQT may generate experimental data relevant to validating kinetic ignition models by virtue of its well-controlled temperature, pressure, and start of fuel injection. Better understanding and refinement of the IQT combustion process may lead to its use as a development and validation platform for kinetic models of novel fuels, as the device provides a well-controlled environment for such tests in comparison to a traditional engine. Experimental parameters such as charge pressure and temperature, chamber wall temperature oxygen concentration, and mass of fuel injected are easily quantifiable for model implementation. The IQT offers the additional benefit of a low fuel quantity requirement (capable of testing with approximately 50 mL), increasing its desirability for testing experimental biofuels that may be produced on research scale in small amounts.

As the IQT is a heterogeneous spray combustion system, the measured ignition delay comprises both physical processes (e.g., spray breakup, vaporization, mixing) and the chemical kinetics of ignition [10]. Each of these processes must be characterized, so that physical effects may be separated from chemical effects. This paper covers three areas of IQT development:

- Expanding the operating parameter space beyond the DCN measurement conditions to determine Arrhenius ignition parameters.
- Instrumentation to measure combustion products for study of the combustion chemistry.

- Characterizing the physical and chemical processes within the combustion chamber, including detailed studies of the physical characteristics of the spray.

This last effort led to the development of a three-dimensional KIVA-3V numerical model [22]. This model enables simulation with reduced chemical kinetic mechanisms, providing the link for the IQT to validate kinetic models. Through this improved understanding of the spray and combustion processes in the IQT, in concert with the determination of global kinetic parameters, the IQT is being developed into a research platform that may fill the experimental void for low-volatility fuels and complement other research platforms.

## BACKGROUND AND EXPERIMENTAL DETAILS

### IQT OVERVIEW

A piezo-electric pressure transducer installed in the IQT combustion chamber measures the pressure rise during the combustion event. The time delay between start of injection (SOI) and the rise in combustion pressure to the “combustion pressure recovery point” determines the ignition [10], as shown in Fig. 2. The ignition delay involves both physical processes (e.g., spray breakup, vaporization, air entrainment) and the chemical kinetics of ignition [10].

A pneumatically driven mechanical fuel pump is used for the injection of the fuel through a single-hole S-type delayed (inward opening) pintle nozzle, as seen in Fig. 3. The needle is held closed by a spring pressure of approximately 17.9 MPa; thus, a rise in fuel pressure to above that holding the needle closed lifts it open. The injection actuator air pressure is 1.21 MPa. The fuel injection pressure is approximately 22.5 MPa during the main injection period. Fuel is delivered using a 1.5 mm (inner diameter) fuel line. The mass of fuel injected (avg: 72 mg, range:  $\pm 7$  mg) is measured ex situ, by collection in a closed tube fitted on the injector nozzle, which is weighed after each injection to quantify injection variability.

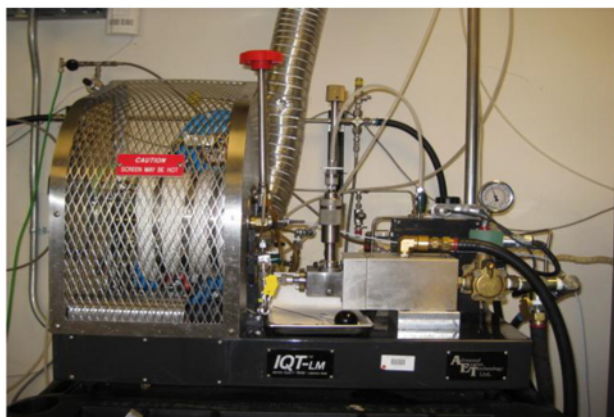


**Fig. 1. The Ignition Quality Tester (IQT)**

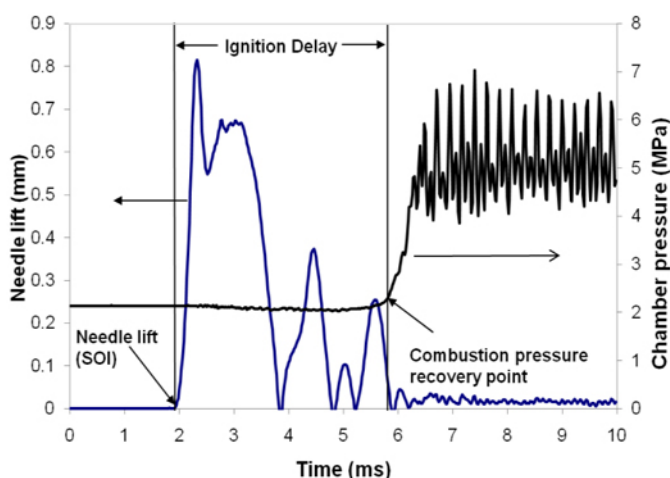


**Fig. 2. Combustion pressure and needle-lift traces used to determine ignition delay; n-heptane,  $m \approx 72$  mg/inj.**

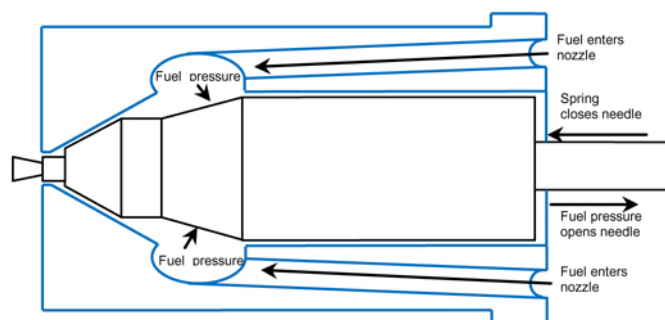


**Fig. 3. Schematic of the injector nozzle**

Several electric cartridge heaters are inserted into the outer wall of the stainless steel combustion chamber [12] to heat the charge air. For ASTM D6890 DCN measurements, the charge air temperature is approximately 550° C at the combustion chamber thermocouple near the nozzle tip (see Fig. 4). There is approximately a 40°C temperature gradient (increase) to the second thermocouple (down-range 7 cm)

along the axial direction of the combustion chamber. The lower charge air temperature near the injector is due to heat transfer to coolant around the injector body and chamber end-cap exposure to ambient air. All experiments were done using the ASTM D6890 [17], unless stated otherwise.

The chamber (volume  $\approx 0.21$  L) is pressurized to approximately 2.1 MPa prior to injection of fuel. The model fuel used in this study was n-heptane (>99.5%, Fluka). The IQT is normally programmed to run a total of 47 injections (15 pre-injections + 32 main injections). The 15 pre-injections are used to bring the system to steady state, while the 32 main injections are recorded and used to calculate the DCN based on the ignition delay [23].

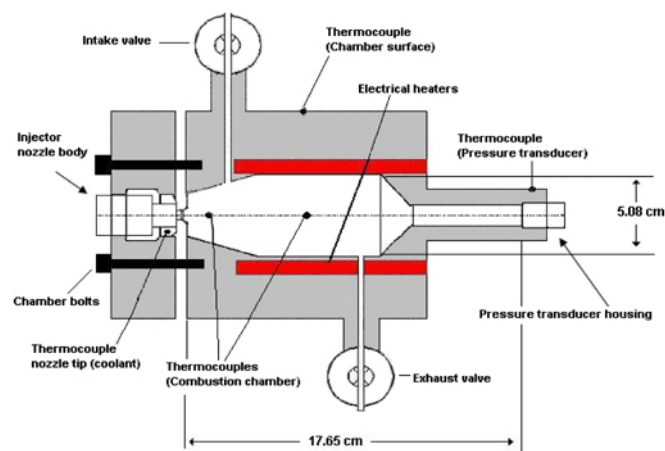


**Fig. 4. Schematic of the IQT combustion chamber**

## EXHAUST MEASUREMENT SYSTEM

Figure 5 shows a modified exhaust system connected to the IQT exhaust valve, which allows on-line analysis of  $\text{NO}_x$  emissions by an ECO PHYSICS CLd 700 EL ht  $\text{NO}/\text{NO}_2/\text{NO}_x$  analyzer. This capability combined with real-time combustion pressure measurement allows direct comparison of individual combustion event pressure variability with the variability in  $\text{NO}_x$  emissions. An inert gas purge port at the entrance to the exhaust system ensures the exhaust system is completely purged of combustion products prior to the next injection.

The exhaust system also allows trapping of exhaust gases into evacuated, fused-silica lined sampling canisters for off-line analysis by gas chromatography-mass spectrometry (GCMS). The canisters were filled by blocking the three-way valve, opening the canister valve and performing a single IQT combustion event. The gases were analyzed by an Agilent 6890/5975 GCMS coupled to an Entech 7100 preconcentrator system, the latter serving as the GC sample injector. The GCMS was equipped with a Restek Rxi-1ms column  $60 \text{ m} \times$

0.32 mm with a 1  $\mu\text{m}$  film. The GCMS is calibrated with a hydrocarbon standard known as CRC Mix No. 4 from Scott Gas. This allows many of the hydrocarbon species to be quantified, while other species are determined qualitatively.

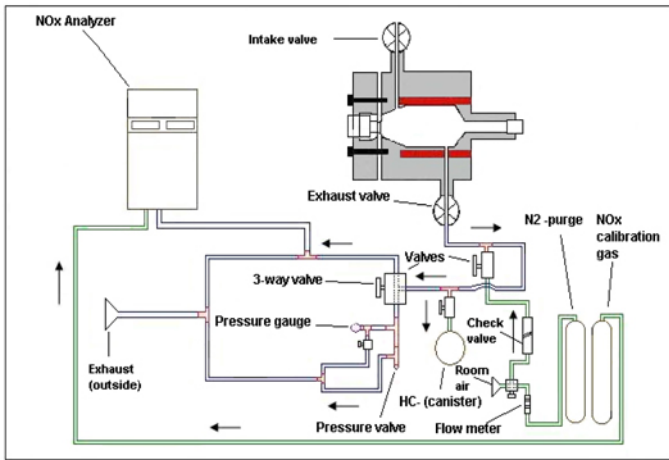


Fig. 5. Modified IQT exhaust system schematic.

## DISCUSSION AND RESULTS

### GLOBAL AUTOIGNITION MODELING

In addition to using the IQT to determine DCN according to ASTM D6890 for a given fuel, the IQT can also measure how ignition delay (ID) varies with temperature, pressure, and charge composition (e.g., oxygen fraction) [24,25,26]. Prior work at the National Renewable Energy Laboratory (NREL) studied ID over a range of temperatures (450-550°C), pressures (10-30 bar), and oxygen mole fractions (15-21%) [26, 27]. The oxygen compositions for these experiments effectively modeled exhaust gas recirculation (EGR) rates of 0-28% [27]. Because the IQT does not operate using compressive heating (unlike a shock tube or rapid compression facility, in which differing heat capacities affect the end-of-compression thermodynamic conditions), little thermodynamic effect results from substituting  $\text{N}_2$  for  $\text{CO}_2$  and  $\text{H}_2\text{O}$  present in exhaust gas. The chemical effect of substituting  $\text{N}_2$  for  $\text{CO}_2$  and  $\text{H}_2\text{O}$  present in exhaust gas is considered negligible, based on prior Rapid Compression Facility experiments with iso-octane [27]. A full factorial design of the conditions was developed, resulting in a 27-test-point matrix to complement the standard ASTM D6890 measurement. The experimental relationships of temperature, pressure, and oxygen concentration affecting ID time were calculated according to a simplified global rate model. The resulting Arrhenius relationships yield the apparent activation energy and oxygen order factor for a given fuel [27]. This allows for predictive calculations of ID time as a function of pressure, temperature, and oxygen mole fraction over the range studied, which provide more ignition behavior insight than DCN alone. Later developments at NREL resulted in a

reduced eight-test-point matrix that yields the same information; the reduced matrix requires a smaller quantity of test fuel, which is advantageous for experimental research fuels that may be available only in limited quantities.

As a demonstration, this eight-test-point matrix was applied in a Coordinating Research Council (CRC) characterization study of the nine Fuels for Advanced Combustion (FACE) diesel research fuels [28, 29]. The FACE diesel research fuels studied are identified as follows: FD1A = FACE Diesel - Fuel 1, Batch A. In that fuels study, the IQT spanned the following conditions.

- Combustion air charge temperatures of 450°C and 550°C
- Combustion air charge pressures of 15 and 30 bar (vs. 21.37 bar for ASTM D6890-08)
- Oxygen volume fractions of 15.0% and 20.9% (balance nitrogen).

### ARRHENIUS MODELING RESULTS

The parametric study ID data were plotted as a natural log of the ignition rate (inverse of ID) versus the inverse of temperature in Arrhenius form to determine how the ID rate varies with temperature, resulting in a slope indicating an apparent activation energy. Although the spray ignition in the IQT is not a single elementary reaction (instead involving spray, evaporation, mixing, and ignition chemistry), some justification exists for plotting IQT ID results in Arrhenius form [26]. A simplified global model may consider the IQT ignition event in reaction kinetic terms, including the time from initial fuel spray to the time the reaction has produced sufficient concentration of chain branching reactions with reactive intermediate species (such as OH), consuming sufficient fuel to register a threshold pressure rise. In terms of this lumped ID, incorporating both physical delay (with spray droplet breakup, evaporation, and mixing) and chemical delay, the slope of the Arrhenius plot is analogous to an “apparent” activation energy for ignition [26].

This simplified global rate model was fit to the parametric study data to deconvolute the effects of temperature, pressure, and oxygen mole fraction on the measured ID. The ID expression is shown in Eq. (1):

$$\text{ID} = A * P^b * \chi_{\text{O}_2}^c * \exp\{E_a / R T\} \quad (1)$$

where ID is ignition delay (ms), A is the pre-exponential constant, P is pressure (bar), b is the pressure exponential term,  $\chi_{\text{O}_2}$  is the oxygen mole fraction, c is the oxygen fraction exponential term,  $E_a$  is the apparent activation energy ( $\text{kJ mol}^{-1}$ ), R is the universal gas constant ( $8.314\text{E-}3 \text{ kJ mol}^{-1} \text{ K}^{-1}$ ), and T is temperature (K).

By applying this ignition delay model to Eq. (1), the ID of a given fuel can be characterized by a four-parameter fit, solving for A, b, c, and  $E_a$ . Regression analysis was used to determine the Arrhenius parameters for all nine of the FACE research fuels, resulting in R-squared values, as indicated in Table 1. Table 1 also lists the calculated ignition characterization parameters for the diesel FACE fuel set.

**Table 1. Arrhenius Relation Regression Results**

| FACE diesel | R <sup>2</sup> value | A      | b      | c      | $E_a$<br>[kJ mol <sup>-1</sup> ] |
|-------------|----------------------|--------|--------|--------|----------------------------------|
| FD1A        | 0.998                | 0.0682 | -1.002 | -0.729 | 44.28                            |
| FD2A        | 0.995                | 0.1431 | -1.053 | -0.787 | 39.95                            |
| FD3A        | 0.994                | 0.0215 | -0.902 | -0.732 | 50.65                            |
| FD4A        | 0.988                | 0.0802 | -1.035 | -0.992 | 41.50                            |
| FD5A        | 0.998                | 0.0115 | -0.836 | -0.788 | 48.83                            |
| FD6A        | 0.998                | 0.0139 | -0.866 | -0.788 | 48.53                            |
| FD7A        | 0.998                | 0.0111 | -0.850 | -0.749 | 51.30                            |
| FD8A        | 0.997                | 0.0144 | -0.866 | -0.777 | 48.65                            |
| FD9A        | 0.998                | 0.0168 | -0.917 | -0.750 | 50.15                            |

## FACE DIESEL DISCUSSION

These ignition characterization parametric study results allow predictions of ID time under a useful range of combustion conditions:

- Combustion air charge temperatures between 450°C and 550°C
- Combustion air charge pressures between 15 and 30 bar
- Oxygen volume fractions between 15.0% and 20.9% (balance nitrogen).

By applying Eq. (1) with the experimentally determined values for A, b, c, and apparent activation energy ( $E_a$ ), the ID time for each FACE fuel can be predicted. As a check of predictive accuracy, the experimentally measured ID time was compared with the predicted value, using the ASTM D6890 test conditions as inputs for each of the diesel FACE fuels, as shown in Table 2. The ID prediction errors for this test point are quite low, varying between 0.13% and 5.14% over-predicted.

**Table 2. Measured Ignition Delay Compared with Arrhenius Relation Predictive Ignition Delay for ASTM D6890-08 Test Conditions**

| FACE diesel fuel | Measured average ignition delay (ID) time (ms) | Predicted ID time (ms) | ID prediction error (%) |
|------------------|------------------------------------------------|------------------------|-------------------------|
| FD1A             | 6.044                                          | 6.355                  | +5.14                   |
| FD2A             | 6.196                                          | 6.424                  | +3.68                   |
| FD3A             | 6.369                                          | 6.602                  | +3.66                   |
| FD4A             | 6.454                                          | 6.462                  | +0.13                   |
| FD5A             | 3.696                                          | 3.767                  | +1.91                   |
| FD6A             | 3.801                                          | 3.842                  | +1.08                   |
| FD7A             | 4.563                                          | 4.674                  | +2.44                   |
| FD8A             | 4.082                                          | 4.098                  | +0.39                   |
| FD9A             | 4.645                                          | 4.720                  | +1.61                   |

As indicated by these predictive results, the parameters in Table 1 for A, b, c, and  $E_a$  are quantitative metrics of how the fuel ignition responds to changes in temperature, pressure, and EGR. These relationships provide more ignition behavior insight than DCN alone and may be used for engine control in combustion regimes such as partially mixed charge compression ignition (PCCI). For example, the apparent activation energy may be used to adjust the gain value on an intake air temperature controller for a given fuel to control combustion phasing [27]. Similarly, the pressure and oxygen fraction exponents (b and c values) may be used to adjust relative intake air pressure boost or EGR levels [27]. Furthermore, using the ignition delay expression in Eq. (1) and correcting the pre-exponential value (A) for engine-specific conditions, it is feasible that this type of formulation may be used to predict ignition timing over a range of conditions in an engine model [27].

Expanding IQT operating space beyond DCN conditions provides valuable new data, as demonstrated in the characterization study of the FACE fuels [29, 30]. This is illustrated in Table 3, which compares DCN and Arrhenius ignition delay predictive parameters to ASTM D613 engine-based CN results for the same fuels, which were independently tested by Chevron-Philips Chemical Company's Specialty Chemicals Group (CPCChem) and Southwest Research Institute (SwRI) under contract to Oak Ridge National Laboratory (ORNL) [29, 30]. Inspection of Table 3 shows that the four lowest CN fuels (FD1A, FD2A,