Effects of iso-octane/ethanol blend ratios on the observance of Negative Temperature Coefficient behavior within the Ignition Quality Tester

Gregory E. Bogin Jr.^{1*}, Jon Luecke², Matthew A. Ratcliff², Eric Osecky¹, Bradley T. Zigler²
¹Colorado School of Mines, ²National Renewable Energy Laboratory

gbogin@mines.edu

Abstract

An ignition delay study investigating the reduction in low temperature heat release (LTHR) and negative temperature coefficient (NTC) region with increasing ethanol concentration in binary blends of ethanol/isooctane was conducted in the Ignition Quality Tester (IQT). The IQT is advantageous for studying multi-component fuels such as iso-octane/ethanol which are difficult to study at lower temperatures covering the NTC region in traditional systems (e.g., shock tubes, rapid compression machines, etc.). The high octane numbers and concomitant long ignition delay times of ethanol and iso-octane are ideal for study in the IQT allowing the system to reach a quasi-homogeneous mixture; allowing the effect of fuel chemistry on ignition delay to be investigated with minimal impact from the fuel spray due to the relatively long ignition times. NTC behavior from *iso*-octane/ethanol blends was observed for the first time using an IQT. Temperature sweeps of *iso*-octane/ethanol volumetric blends (100/0, 90/10, 80/20, 50/50, and 0/100) were conducted from 623 – 993 K at 0.5, 1.0 and 1.5 MPa and global equivalence ratios ranging from 0.7 to 1.0. Ignition of the iso-octane/ethanol blends in the IQT was also modeled using a 0-D homogeneous batch reactor model. Significant observations include: 1) NTC behavior was observed for ethanol/iso-octane fuel blends up to 20% ethanol. 2) Ethanol produced shorter ignition delay times than iso-octane in the high temperature region. 3) The initial increase in ethanol from 0% to 10% had a lesser impact on ignition delay than increasing ethanol from 10% to 20%. 4) The 0-D model predicts that at 0.5 and 1.0 MPa ethanol produces the shortest ignition time in the high-temperature regime, as seen experimentally.

Keywords: IQT, *Iso*-octane, Ethanol, Ignition, NTC, fuel blends

1.0 Introduction

The development of clean-burning and energy-efficient internal combustion engines (ICEs) depends on improved combustion strategies, which in turn increasingly depend on computational models that include chemical kinetic mechanisms. Advanced combustion strategies can potentially leverage improved fuel properties that may be provided by oxygenated renewable fuels such as alcohols, esters, furans, and ethers. Ethanol has become the most widely used biofuel for on-highway transportation. This is mostly related to its high octane numbers that are important for more efficient spark ignition (SI) engines [1]; however, other types of ICEs such as compression ignition (CI) [2] and homogeneous charge compression ignition (HCCI) [3] may benefit as well. Ethanol can be blended with gasoline and has also been utilized as a single fuel with minor engine modifications [4]. The research (ASTM D2699) [5] and motor (ASTM D2700) [6] octane number methods use iso-octane and n-heptane mixtures to calibrate the knock (i.e., end-gas autoignition) resistance of fuels for SI engines. Autoignition is a critical combustion behavior for ICE engines. In the case of SI engines, autoignition is an unwanted behavior leading to knock, which, if sufficiently severe, damages engine hardware. However, in a CI engine autoignition is exploited to initiate combustion and having a fundamental understanding of the impact of kinetics on ignition delay in a CI engine introduces the possibility of using autoignition kinetics as a tuning parameter for optimizing engine efficiencies; through advanced combustion strategies. Research has shown that octane numbers alone are not always adequate to characterize the autoignition propensity of advanced combustion engines, and that autoignition would be ideally defined by modeling the autoignition chemistry as function of temperature and pressure [7-9]. In this work, new ignition data for iso-octane/ethanol blends were obtained to assist the development and validation of chemical kinetic models capable of predicting autoignition, which could ultimately be

utilized in optimization of combustion control strategies. The high octane numbers and concomitant long ignition delay times of ethanol and iso-octane are ideal for study in the Ignition Quality Tester (IQT) in that they allow the system to reach a quasi-homogeneous mixture, which allows the effects of fuel chemistry on ignition delay to be investigated with minimal impact from the fuel spray physics. Commercially available constant-volume chambers (e.g., IQT, Fuel Ignition Tester (FIT)) have been used successfully to investigate multi-component fuel blends (e.g., gasoline and diesel surrogates) [10,11] as well as the impact of blending alcohol (e.g., butanol, ethanol) on *n*-heptane autoignition [12,13]. However, there remains a need for additional data to provide insight into the effects of ethanol blending on *iso*-octane across a wide temperature range, capturing the effects in the high-temperature, low-temperature, and negative temperature coefficient (NTC) region with the IQT. Alkanes have low-temperature oxidation chemistry involving peroxy radicals and hydroperoxyalkyl radicals which play a crucial role in their early ignition kinetics and produce the characteristic negative temperature coefficient (NTC) region and low temperature heat release [14]. The NTC region is important to low-temperature oxidation kinetics and the overall ignition of alkanes which is important for developing advance combustion control strategies. Accurate characterization of the ignition kinetics of fuels is even more important for low-temperature combustion engines, such as homogeneous charge compression ignition, and premixed charge compression ignition and other variations of the low-temperature combustion regimes. The ignition characterization provided by the IQT at engine relevant conditions provides additional insight into the fundamental autoignition kinetics and validation for existing and developing chemical kinetic mechanisms that will be used in developing control strategies for advanced combustion engines.

2.0 Experimental Procedure

2.1 IQT Overview

The IQT is a constant-volume combustion apparatus with a spray injection system designed for direct measurement of liquid fuel ignition delay, as depicted in Figure 1. Experimental parameters such as initial charge-air pressure and temperature, chamber wall temperature, oxygen concentration, and mass of fuel injected are well controlled. A pressure transducer installed in the combustion chamber measures the pressure rise during the combustion event. The time interval between the start of injection and the rise in combustion pressure to the “pressure recovery point” (calculated as 138 kPa above the initial chamber pressure prior to injection, based on measurements using ASTM D6890 conditions) defines ignition delay, [15 – 17] as seen in Figure 2. For this study, a fixed pressure point (FPP) of 551 kPa (0.551MPa) pressure rise above the initial chamber pressure was used to compensate for low-temperature heat release-induced pressure increases and therefore more accurately determine the start of ignition. This FPP definition was also compared with a “maximum rate of change in pressure” definition and the calculated definition based on measurements using ASTM D890 methods, as shown in Figure 3. Several temperature points comparing the new FPP definition vs. “maximum rate of change in pressure” are presented in Table 1; 100% *iso*-octane was used because this fuel produced the greatest pressure rise from low-temperature heat release (LTHR), and consequently would be expected to produce the largest differences among the ignition delay definitions. As seen in Table 1, there were slight differences (<4.5%) in the ignition delay times. Because the FPP definition requires much less post-processing, it will be used to determine the ignition delay times presented in this manuscript. The IQT apparatus and setup were described in more detail previously. [18,19]

2.2 Fuel Specifications and Preparations

The binary fuel mixtures consist of iso-octane (2,2,4-trimethylpentane, anhydrous 99.8%, density = 0.692 g/mL, vapor pressure = 5.5 kPa, heat of vaporization = 36.1 kJ/mol) (Sigma-Aldrich) and ethanol (ACS reagent, $\geq 99.5\%$, density = 0.789 g/mL, vapor pressure = 5.95 kPa, heat of vaporization = 42.5 kJ/mol) (Sigma-Aldrich). The various volumetric fuel blend ratios were obtained by converting the desired volume percentages to mass using the known density of each fuel. Once this conversion was complete, each component of the fuel blend was weighed at $150 \text{ g} \pm 10 \text{ mg}$ using a high-precision balance (Mettler PB303-S) to obtain the desired volumetric blend ratio.

The mass of fuel injected into the chamber was controlled using a variable volume injection pump (standard on the IQT), which utilizes metal shims to vary the relative position of the fuel plunger, allowing either a smaller or a larger volume of fuel to be injected. The mass of fuel injected was calculated based on the fuel's density and utilizing a mass calibration curve developed with *n*-heptane as the calibration fuel. This mass calibration curve was used to determine the amount of fuel injected for the various blends based on their respective densities. The accuracy of the mass calibration curve for the various blends was determined by taking actual mass measurements at select points, which are presented in Table 2. It can be seen that the measured values and calculated values using the mass calibration curve vary between 0% and 6.6% depending on the relative *iso*-octane/ethanol blend. The actual fuel mass injected was measured using the ASTM D6890 standard method for mass measurement, which takes an average of three measurements, each consisting of 10 injections. The variability of injection-to-injection was also measured and resulted in a standard deviation of less than 1 mg of fuel as seen in Table 3. Note that the mass injection tests presented in Table 2 and Table 3 are at different set-points.

2.3 Experimental Conditions

Temperature sweeps were performed by heating the charge-air (20.9% oxygen balanced in nitrogen) in the constant-volume vessel to the desired temperature. The chamber heaters were then turned off, and after each fuel injection, the constant-volume vessel was purged (charge-air flowed through the vessel for one second and then the vessel was charged to the operating pressure and then evacuated prior to re-charging for the next fuel injection). This process was repeated as the chamber temperature dropped, resulting in lower charge-air temperatures before each subsequent injection. Approximately 20 seconds elapsed between injections, allowing the charge-air temperature to come to steady state. The air temperature dropped approximately 3 K between injections providing high-resolution ignition delay measurements across the temperature sweep. The temperatures reported here are based on the air temperature thermocouple located in the main portion of the chamber, which is representative of the bulk air temperature prior to injection of fuel. It should be noted that the gas temperature prior to ignition would be lowered due to the evaporative cooling of the fuel. Temperature sweeps of *iso*-octane/ethanol volumetric blends (100/0, 90/10, 80/20, 50/50, and 0/100) were conducted from 623 – 993 K at 0.5, 1.0, and 1.5 MPa and global equivalence ratios ranging from 0.7 to 1.0. Temperature sweeps at a constant equivalence ratio of 1.0 were also conducted at select *iso*-octane/ethanol volumetric blends (100/0, 90/10, and 0/100) for comparison.

Chamber air pressures were limited to 1.5 MPa because of the potential for fuel boiling in the fuel injector, which is partially exposed to the high air temperatures and pressures. At higher chamber pressures, there is an increase in heat transfer to the injector tip and because of limitations of the cooling system it was difficult to keep the fuel nozzle tip at the desired 323 K. It is expected that fuel boiling was occurring, which resulted in the injection profile being severely impacted (reducing the maximum needle-lift to half of the typical needle-lift displacement) and subsequently impacting the ignition delay. Typically the fuel in the nozzle tip is maintained at 0.34 MPa prior to injection with the coolant around

the nozzle tip maintained at 323 K. However, the combination of increased heat transfer and the moderate boiling temperatures of iso-octane and ethanol (372 K and 351 K at 0.1 MPa, respectively) along with the relatively high vapor pressure compelled limiting the chamber pressure to ensure high quality data.

3.0 Results and Discussion

The IQT's ability to capture two-stage ignition for alkanes and the effects of alcohol blend concentration on the reduction of LTHR provide important new kinetic data that complement those from shock tubes and rapid compression machines. These data allow validation of chemical kinetic mechanisms, and consequently for optimizing the design of low-temperature combustion engines through simulation.

The magnitude of global evaporative cooling (as measured by the chamber pressure drop) from the injection of the fuel increased with increasing fuel mass, with the minimum pressure dropping by 0.1 MPa with an addition of increasing the mass injected from 34 mg to 80 mg. However, little to no effect as a result of increasing ethanol concentration was observed, as there was no noticeable change in minimum chamber pressure between iso-octane and ethanol with equivalent mass injected. This result is explained in the work by Chupka et al., [20] which shows that the heat of vaporization differences between ethanol and *iso*-octane decreases with increase in temperature in the range tested in the IQT. Tests conducted at various temperatures also showed little to no impact on the amount of global evaporative cooling for constant mass injection. These results indicate that the resultant drop in air temperature after fuel was injected was nearly constant across the temperature range investigated.

For iso-octane and low ethanol concentration blends, two-stage ignition was observed after fuel injection and the drop in chamber pressure (due to evaporative cooling), with LTHR causing a small

increase in chamber pressure above the initial chamber pressures prior to the main ignition event as shown in Figures 4a-c.

In experiments at 1.0 MPa and 773 K, LTHR from pure *iso*-octane and from 10% ethanol was apparent from the 45 – 100 kPa pressure rise above the initial charge pressure before the main ignition event, as seen in Figure 4a. LTHR was suppressed as the ethanol concentration increased, with little to no LTHR observed above 20% ethanol. Increasing ethanol concentration did not linearly increase ignition delay times, as increasing ethanol concentration from 10% to 20% had a much larger impact than the first 10% of the ethanol added; while adding another 30% (50/50 blend) produced a much smaller increase in ignition delay time as seen in Figure 4a. Furthermore, the 20% and 50% ethanol blends had longer ignition delay times than pure ethanol.

Figure 4b shows the effects as the initial chamber pressure was increased from 1.0 MPa to 1.5 MPa, where a noticeable increase in pressure rise from LTHR was observed. Moreover, the 20% ethanol fuel blend displayed LTHR at 1.5 MPa (which was not apparent at 1.0 MPa), indicating that the effects of higher oxygen partial pressure on *iso*-octane's LTHR outpaced the additional ethanol's suppression of LTHR. As noted above, 100% ethanol produced a shorter ignition delay time than the 20% and 50% ethanol blends at 1.0 MPa. However, at 1.5 MPa the 20% ethanol blend's ignition delay was shorter than for 100% ethanol. This change is associated with the appearance of LTHR for the 20% ethanol blend at this pressure, which was not present at 1.0 MPa. For both 1.0 MPa and 1.5 MPa at 773 K, a 50% ethanol fuel blend produced the longest ignition delay times. At the lower gas temperature of 723 K at 1.5 MPa, the LTHR magnitude increased as seen in Figure 4c and in Table 4. Along with lowering the gas temperature to 723 K, the ignition delay times increased and the 50% ethanol fuel blend was not investigated.

The increase in LTHR with reduction in temperature and increase in pressure produced larger discrepancies in the ignition delay determination using the ASTM D6890 definition. This is clearly seen when comparing various definitions of ignition delay across the temperature sweeps (global equivalence ratio varies because the mass of fuel injected is kept constant and the charge temperature is reduced) of *iso*-octane shown in Figure 5a and Figure 5b. An NTC region was observed with all three definitions of ignition delay; however, the ASTM D6890 definition produced shorter ignition delays at low temperatures because LTHR increased the pressure above the ASTM D6890 definition. An FPP of 551 kPa (which is above the largest measured LTHR for this set of fuel blends and conditions) is used for defining ignition delay for rest of this manuscript, because there were only slight differences between this FPP ignition delay and the $dP/dt_{\max}$ definition (the latter requires significantly more data post-processing to calculate and filter appropriately to maintain consistent determination of ignition delay times).

3.1 Constant Mass Temperature Sweep

The NTC region is important to low-temperature oxidation kinetics and the overall ignition of alkanes. Therefore, if the IQT is to be a complementary research apparatus to Rapid Compression Machines (RCMs) and shock tubes for validating chemical mechanisms of low multi-component fuels, the ability to capture NTC and LTHR behavior is essential. Several temperature sweeps for the various fuel blends were obtained across several pressures (0.5 MPa, 1.0 MPa, and 1.5 MPa) with NTC observed for fuel blends with 20% ethanol or less, and no NTC observed at 0.5 MPa as seen below in Figures 6–8.

For this set of experiments, the mass injected was kept constant, resulting in a change in the global equivalence ratio due to the change in air temperature. However, this allowed rapid temperature sweep ignition characterization of the fuels. The constant mass injected produced an equivalence ratio of

1.0 at 973 K, which decreased to 0.7 at 673 K, because the charge-air density increases at lower temperatures. It is also noted that constant equivalence ratio experiments were conducted and are presented in the section 3.1. Little difference was observed between the constant mass and constant equivalence ratio temperature sweeps for the various fuel blends.

As seen in Figure 6, at 0.5 MPa 100% ethanol produces the shortest ignition delay times, with ignition delay times increasing with increase in iso-octane concentrations. This observation is the opposite of what would be expected using octane number as the comparative basis. Because ethanol has a higher Research Octane Number (RON) than iso-octane and using the traditional association of higher-octane fuels having longer ignition delay times, one would expect ethanol to produce longer ignition delay times compared to iso-octane. No NTC region was observed for iso-octane/ethanol blends at 0.5 MPa, most likely due to system limitations as the ignition delays became extremely long (>700 ms) in the expected NTC region. Longer times were avoided to minimize the potentially large impact of surface reactions on ignition times.

For 1.0 MPa (see Figure 7) at the higher temperatures ($1000/T < 1.2$), ahead of the NTC region, the 100% ethanol produced the shortest ignition delay. In this high temperature region, ignition delay times increased with a decrease in ethanol concentration. In the NTC region ($1000/T > 1.25$) 100% iso-octane produced the shortest ignition delay times, with ignition delay times increasing with an increase in ethanol. There was no NTC region observed for ethanol concentrations above 20% at 1.0 MPa.

Similar observations were made at 1.5 MPa (see Figure 8) with 100% iso-octane producing the longer ignition delay times at high temperatures ($1000/T < 1.2$), with 100% ethanol producing longer ignition delay times than 100% iso-octane at lower temperatures (within iso-octane's NTC region, $1000/T > 1.2$). Additionally, the blends up to 20% ethanol displayed NTC behavior, while 50% ethanol produced the longest ignition delay times overall partly because of ethanol's suppression of NTC, as seen in Figure 8.

This observation of 20% and 50% ethanol blends producing longer ignition times compared to 100% ethanol in the NTC region as shown earlier in the pressure plots of Figure 4 and now in the temperature sweeps in Figure 7-8 is consistent with results seen in Foong et al. [21] which showed that the RON values for 20% ethanol blended in *iso*-octane were higher than neat ethanol, and with the 40% ethanol blended in *iso*-octane producing the highest RON . The decrease in ignition times with increase in ethanol concentration in the high temperature region also follows the results seen in Foong et al. [21] with increase in ethanol concentrations resulting in lower Motored Octane Numbers (MON).

3.2 Constant Equivalence Ratio Temperature Sweep

The previous temperature sweeps were conducted using constant mass injected because the temperature sweep experiments can be performed quickly. Another set of experiments was conducted using a constant global equivalence ratio by varying the mass injected to correspond with the mass of air in the chamber, which increases as the temperature of the chamber decreases. The global equivalence ratio was determined by measuring the mass of air and of fuel injected. The global equivalence ratio was maintained at 1.0, and the results were compared to the constant mass temperature sweeps as shown in Figures 9 – 11. Overall, using a constant equivalence ratio of $\Phi = 1.0$ produced results similar to those for constant mass (where the global equivalence ratio changed from 1.0 to 0.7 as the air temperature decreased from 973 K to 673 K). Several temperature and mass injection points were also fixed for several injections at each condition to determine the variability in ignition delay times, as presented in Table 5. The longer ignition delay times of ethanol at low temperatures have more variance, most likely related to the possibility for surface reactions altering the measured ignition delay times in the 400 – 500 ms range.

3.3 *Iso-octane/Ethanol Blends in Shock Tubes and Rapid Compression Machines*

Investigation of *iso*-octane/ethanol blends were conducted by Cancino et al. [22 – 24] in a shock tube with the 100% ethanol producing a shorter ignition delay time compared to 25% ethanol at higher temperatures ($1000/T \leq 1.0$) as seen in Figure 12. Figure 12 shows that at 1,000 K, 100% ethanol produces an ignition time of 547 μ s compared to 791 μ s for a 75% *iso*-octane/25% ethanol blend. Also, for the next higher temperature shown, 100% ethanol (1,045 K) produces a residence time that is 267 μ s compared to 404 μ s for a 75% *iso*-octane/25% ethanol (1,059 K) blend. The shorter ignition delay times observed with 100% ethanol in shock tubes are similar to our observations with the IQT in the high temperature regime for 0.5 – 1.5 MPa. Yahyaoui et al. [25] also observed a reduction in ignition times with increasing ethanol concentration from 10% to 20% in a three-component gasoline surrogate blend; it was also observed that 50% ethanol produced longer ignition time compared to 20% ethanol above 1,300 K. Although their studies were done with a multi-component gasoline surrogate, the trends are also similar to what was observed with the IQT. Song et al. [26] investigated *iso*-octane/ethanol blends in a RCM at 2.7 MPa and found that increasing ethanol concentration to 10% resulted in an increase in the ignition delay times in the lower temperature region (750 K – 900 K); this trend also agrees with our observation that increasing ethanol concentrations results in increased ignition times in the NTC region observed in the IQT. The similar trends seen between the data from IQT, shock tubes, and RCMs show that the resulting impact of increasing ethanol concentration is highly dependent on the temperature (whether in the NTC or high temperature region) suggests that the IQT is capable of capturing key ignition characteristics and can serve as a complementary device to shock tubes and RCMs for investigating ignition behavior of various single and multi-component fuel blends.

3.4 Zero Dimensional Modeling of Iso-octane/Ethanol Blends

The CHEMKIN-PRO software package [27] was used to model the IQT using a homogeneous batch reactor model. Previous CFD results have predicted a quasi-homogeneous zone in the chamber at longer (>40 ms) ignition delay times [28]. This suggests that the homogeneous batch reactor could work for predicting ignition delay times in the IQT at relatively long ignition delay times of >60 ms. A gasoline surrogate mechanism developed by Mehl et al. [29] at Lawrence Livermore National Laboratory (LLNL) was used to predict ignition of the iso-octane/ethanol fuel blends. Figure 13a&b shows the model results for 0.5 MPa; it is noted that 1.0 MPa and 1.5 MPa model results produce similar trends as the 0.5 MPa model, and are not shown for brevity. At the higher pressure (1.5 MPa), the 50% *iso*-octane/50% ethanol blend began to show NTC and the differences in ignition times in the high temperature region for 100% ethanol and the other blends diminish. Figure 14 shows comparison with the 0-D model and experiments at 0.5 MPa. The 0-D model results predict that 100% ethanol produces the shortest ignition delay time in the high temperature region prior to the NTC region. As the ethanol concentration is reduced, the ignition delay times increase with 100% *iso*-octane producing the longest ignition delay times in the high temperature region, as observed experimentally with the IQT. Once entering the NTC region, the ignition times for 100% *iso*-octane display the shortest ignition delay times with an increase in ethanol concentration producing longer ignition delay times. This was also observed experimentally in the IQT. The difference in ignition delay times between 100% ethanol and 100% *iso*-octane increases with reduction in chamber pressure in the high temperature region. This increase in ignition delay time is also observed between 100% ethanol and 90% ethanol. Further investigation into the chemical kinetics of the *iso*-octane/ethanol blends via 0-D modeling, multi-zone and computational fluid dynamics are currently underway.

4.0 Conclusions

New ignition data are provided for *iso*-octane/ethanol blends across a range of temperatures and pressures, including blending effects on NTC and LTHR that are presented for the first time. Several key experimental observations were made:

(1) No NTC region was observed with fuel blends $\geq 50\%$ ethanol concentration.

(2) No NTC region was observed for *iso*-octane/ethanol blends at 0.5 MPa, most likely due to system limitations as the ignition delays became extremely long ($>700\text{ms}$) in the expected NTC region.

(3) At 1.0 MPa and 1.5 MPa, increasing the ethanol concentration from 0% to 20% resulted in an increase in ignition delay beginning in the NTC region ($\leq 723\text{K}$), while increasing the ethanol concentration from 20% to 50% produced much smaller increases in ignition delay.

(4) LTHR decreased as ethanol concentration increased.

(5) The 0-D model predicts shorter ignition times for ethanol in the higher temperature region with *iso*-octane producing the longest ignition times, as seen experimentally in the IQT.

(6) At 0.5 MPa, increased ethanol concentrations produced shorter ignition delay times across the range of temperatures (823 – 993K) investigated. This observation of shorter ignition delay with 100% ethanol was also seen in a shock tube study.

These results show the importance of characterizing fuel autoignition chemistry as a function of temperature and pressure to ensure optimal utilization in advanced combustion engines. The IQT is capable of capturing the NTC behavior of binary blends, distinguishing between autoignition characteristics for both alkanes and alcohol fuels, and can serve as an additional validation tool for multi-component chemical kinetic mechanisms.

Acknowledgements

The authors thank the U.S. Department of Energy's (DOE's) Vehicle Technologies Office and Fuel Technologies Program Manager Kevin Stork for their support of this fuels research. This work was supported by the DOE under Contract No. DE-AC36-08-GO28308 with the National Renewable Energy Laboratory. This research was conducted as part of the Co-Optimization of Fuels & Engines (Co-Optima) project sponsored by the U.S. DOE Office of Energy Efficiency and Renewable Energy (EERE) and the Bioenergy Technologies and Vehicle Technologies Offices. The Co-Optima project is a collaborative project of multiple national laboratories initiated to simultaneously accelerate the introduction of affordable, scalable, and sustainable biofuels and high-efficiency, low-emission vehicle engines.

References

- [1] Balat, M., Balat, H., “Recent trends in global production and utilization of bioethanol fuel,” *Appl Energy* 86: 2273–2282 (2009).
- [2] Hansen, A.C., Zhang, Q., Lyne, P.W.L., “Ethanol–diesel fuel blends – a review,” *Bioresour Technol* 96: 277–285 (2005).
- [3] Sjöberg, M., Dec, J.E., “Effects of EGR and its constituents on HCCI autoignition of ethanol,” *Proc. Comb. Inst.* 33: 3031–3038 (2011).
- [4] Delgado, R.C.O.B., Araujo, A.S., Fernandes Jr., V.J., “Properties of Brazilian gasoline mixed with hydrated ethanol for flex-fuel technology,” *Fuel Process. Technol.* 88: 365–368 (2007).
- [5] *Standard Test Method for Research Octane Number of Spark-Ignition Engine Fuel*, ASTM D2699-15a, ASTM International, October 1, 2015.
- [6] *Standard Test Method for Motor Octane Number of Spark-Ignition Engine Fuel*, ASTM D2700-16, ASTM International, January 1, 2016.
- [7] Kalghatgi, G.T., “Auto-ignition quality of practical fuels and implications for fuel requirements of future SI and HCCI engines,” SAE paper 2005-01-0239 (2005).
- [8] Andrae, J.C.G., Björnborn, B., Cracknell, R.F., Kalghatgi, G.T., “Autoignition of toluene reference fuels at high pressures modeled with detailed chemical kinetics,” *Comb. Flame* 149: 2–24 (2007).
- [9] Fikri, M., Herzler, J., Starke, R., Schulz, C., Roth, P., Kalghatgi, G.T., “Autoignition of gasoline surrogates mixtures at intermediate temperatures and high pressures,” *Comb. Flame* 152: 276–281 (2008).
- [10] Perez, P.L., Boehman, A.L. “Experimental investigation of the autoignition behavior of surrogate gasoline fuels in a constant-volume combustion bomb apparatus and its relevance to HCCI combustion,” *Energy Fuels*, **2012**, 26, 6106 – 6117.
- [11] Zheng, Z., Badawy, T., Henein, N., Sattler, E., Johnson, N. “Effect of cetane improver on autoignition characteristics of low cetane sasol IPK using Ignition Quality Tester (IQT),” In ASME 2013 Internal Combustion Engine Division Fall Technical Conference, ICEF 2013. (Vol. 2). ICEF2013-19061, 2013
- [12] Haas, F.M., Ramcharan, A., Dryer, F.L., “Relative reactivities of the isomeric butanols and ethanol in an Ignition Quality Tester,” *Energy Fuels*, **2011**, 25, 3909 – 3916.
- [13] Baumgardner, M.E., Sarathy, S.M., Marchese, A.J., “Autoignition characterization of primary reference fuels and n-heptane/n-butanol mixtures in a constant volume combustion device and homogeneous charge compression ignition engine,” *Energy Fuels*, **2013**, 27, 7778 – 7789.

- [14] Bogin Jr., G. E., Osecky, E.; Ratcliff, M. A.; Luecke, J.; He, X.; Zigler, B. T.; Dean, A. M. *Energy & Fuels* **2013**, 27 (3), 1632–1642
- [15] *Standard Test Method for Determination of Ignition Delay and Derived Cetane Number (DCN) of Diesel Fuel Oils by Combustion in a Constant Volume Chamber*, ASTM D6890-16, ASTM International: West Conshohocken, PA, April 2016.
- [16] Allard, L.N., Webster, G.D., Hole, N.J., Ryan, T.W., Ott, D., Fairbridge, C.W., *Diesel fuel ignition quality as determined in the Ignition Quality Tester (IQT)*, SAE Report No. 961182, SAE International 1996.
- [17] Allard, L.N., Webster, G.D., Ryan, T.W., Ott, D., Beregszaszy, A., Fairbridge, C.W., Cooley, J., Mitchell, K., Richardson, E.K., Elliot, N.G., Rickeard, D.J., *Diesel fuel ignition quality as determined in the Ignition Quality Tester (IQT™) - Part II*, SAE Report No. 971636, SAE International 1997.
- [18] Bogin Jr., G.E., DeFilippo, A., Chen, J.Y., Chin, G., Luecke, J., Ratcliff, M.A., Zigler, B.T., Dean, A.M., “Numerical and experimental investigation of n-heptane autoignition in the Ignition Quality Tester (IQT).” *Energy Fuels*, **2011**, 25 (12), 5562-5572.
- [19] Bogin, G., Dean, A.M., Ratcliff, M.A., Luecke, J., Zigler, B.T., “Expanding the experimental capabilities of the Ignition Quality Tester for autoigniting fuels,” *SAE Int. J. Fuels Lubr.* **2010**, 3, 353-367.
- [20] Chupka, G., Christensen, E., Fouts, L., Alleman, T. et al., "Heat of Vaporization Measurements for Ethanol Blends Up to 50 Volume Percent in Several Hydrocarbon Blendstocks and Implications for Knock in SI Engines," *SAE Int. J. Fuels Lubr.* 8(2):2015, doi:10.4271/2015-01-0763.
- [21] Foong, T.M., Morganti, K.J., Brear, M.J., da Silva, G., Yang, Y., Dryer, F.L. “The octane numbers of ethanol blended with gasoline and surrogates.” *Fuel* 115 (2014) 727 – 739.
- [22] Cancino, L.R., Fikri, M., Oliveira, A.A.M., Schulz, C. “Ignition delay times of ethanol-containing multi-component gasoline surrogates: Shock-tube experiments and detailed modeling.” *Fuel* 90 (2011) 1238 – 1244.
- [23] Cancino, L.R., Fikri, M., Oliveira, A.A.M., Schulz, C., “Thermal oxidation of ethanol: experimental and numerical analysis of ignition chemistry of ethanol-air mixtures in shock-heated gases,” Paper 30074, 27th International Symposium on Shock Waves, St. Petersburg, Russia, 2009.
- [24] Cancino, L.R., Fikri, M., Oliveira, A.A.M., Schulz, C. “Autoignition of binary mixtures of gasoline surrogates, ethanol – iso-octane blends in air: Numerical and experimental study in a high-pressure shock tube,” 20th International Congress of Mechanical Engineering, Gramado, RS, Brazil, 2009.
- [25] Yahyaoui, M., Matheiu, O., Dotoum, C., Chaumeix, N., Paillard, C.-E. Autoignition of Gasoline Surrogate Containing Various Blend Ratios of Ethanol: Shock Tube Experiments and Detailed Kinetic Modeling, Proc. 7th Mediterranean Combustion Symposium, Cagliari, Sardinia, Italy, 2011.

- [26] Song, H., Song, H.H. "Ignition delay measurements of iso-octane/ethanol blend fuel in a rapid compression machine," Proceedings of the European Combustion Meeting, 2015.
- [27] CHEMKIN-PRO 15131, Reaction Design: San Diego, 2013.
- [28] Bogin, Jr., G.E., Osecky, E., Chen, J.Y., Ratcliff, M.A., Luecke, J., Zigler, B.T., Dean, A.M. "Experiments and computational fluid dynamics modeling analysis of large n-alkane ignition kinetics in the Ignition Quality Tester," Energy Fuels 2014 28 (7), 4781-4794, DOI: 10.1021/ef500769j
- [29] Mehl, M., W.J. Pitz, C.K. Westbrook, H.J. Curran, "Kinetic modeling of gasoline surrogate components and mixtures under engine conditions," Proceedings of the Combustion Institute 33:193-200 (2011).

List of Tables:

Table 1. Comparison of ignition delay definitions at 1.0 MPa for 100% *iso*-octane at select temperatures.

Table 2. Calculated mass injected vs. measured mass injected

Table 3. Injection-to-injection variability for 10 injections

Table 4. Increase in chamber pressure due to LTHR comparison for *iso*-octane/ethanol blends

Table 5. Variability in ignition delay times for fixed mass injection and temperature.

List of Figure Captions:

Figure 1. Schematic of the IQT combustion chamber.

Figure 2. Needle-lift plot showing ASTM D6890 definition of Ignition Delay. Typical combustion pressure (dashed blue line) and needle-lift traces (solid black line) used to determine ignition delay; *iso*-octane, ignition delay = 81.98 ms, $P = 1.0$ MPa, $T = 773$ K. Start of injection (SOI) is based on a 0.076 mm increase.

Figure 3. Comparison of ignition delay definitions. 100% *iso*-octane at 1.0 MPa and 789 K. Unfiltered pressure trace (solid blue line), filtered pressure trace (black circles). FPP = Fixed Pressure Point above the initial charge pressure.

Figure 4a. Evaporative cooling and LTHR (maximum $\Delta P = \sim 0.1$ MPa) was observed before the main ignition. Initial charge pressure was 1.0 MPa, and temperature was 773 K. 100% *iso*-octane (solid line), 90% *iso*-octane/10% ethanol (dots), 100% ethanol (dashed line), 80% *iso*-octane/20% ethanol (double solid line), 50% *iso*-octane/50% ethanol (open dashed line).

Figure 4b. Evaporative cooling and LTHR (maximum $\Delta P = \sim 0.2$ MPa) was observed before the main ignition. Initial charge pressure was 1.5 MPa, and temperature was 773 K. 100% *iso*-octane (solid line), 90% *iso*-octane/10% ethanol (dots), 80% *iso*-octane/20% ethanol (double solid line), 100% ethanol (dashed line), 50% *iso*-octane/50% ethanol (open dashed line).

Figure 4c. Evaporative cooling and LTHR (maximum $\Delta P = \sim 0.3$ MPa). Initial charge pressure was 1.5 MPa, and temperature was 723 K. 100% *iso*-octane (solid line), 90% *iso*-octane/10% ethanol (dots), 80% *iso*-octane/20% ethanol (double solid line), 100% ethanol (dashed line). The 50/50 blend was not tested at this low temperature because of the extremely long ignition times.

Figure 5a. Temperature sweeps with different definitions of ignition delay. 1.0 MPa, $\Phi = 1.0 - 0.7$, 100% *iso*-octane. FPP = fixed pressure point. 138 kPa (black diamond), 551 kPa (open square), maximum rate of change in pressure (open triangle).

Figure 5b. Temperature sweeps with different definitions of ignition delay. 1.5 MPa, $\Phi = 1.0 - 0.7$, 100% *iso*-octane. FPP = fixed pressure point. 138 kPa (black diamond), 551 kPa (open square), maximum rate of change in pressure (open triangle).

Figure 6. Constant mass injection temperature sweeps ($1.0 < 1000/T < 1.3$) at 0.5 MPa providing a varying global equivalence ratio ($0.7 < \Phi < 1.0$). 100% *iso*-octane (black diamonds), 90% *iso*-octane/10% ethanol (blue squares), 80% *iso*-octane/20% ethanol (orange triangles), 50% *iso*-octane/50% ethanol (green dash), 100% ethanol (red circles). Data plotted every 25 K.

Figure 7. Constant mass injection temperature sweeps ($1.0 < 1000/T < 1.6$) at 1.0 MPa providing a varying global equivalence ratio ($0.7 < \Phi < 1.0$). 100% *iso*-octane (black diamonds), 90% *iso*-octane/10% ethanol (blue squares), 80% *iso*-octane/20% ethanol (orange triangles), 50% *iso*-octane/50% ethanol (green dash), 100% ethanol (red circles). Data plotted every 25 K.

Figure 8. Constant mass injection temperature sweeps ($1.0 < 1000/T < 1.6$) at 1.5 MPa providing a varying global equivalence ratio ($0.7 < \Phi < 1.0$). 100% *iso*-octane (black diamonds), 90% *iso*-octane/10% ethanol (blue squares), 80% *iso*-octane/20% ethanol (orange triangles), 50% *iso*-octane/50% ethanol (green dash), 100% ethanol (red circles). Data plotted every 25 K.

Figure 9. Temperature sweeps at 1.0 MPa. 100% *iso*-octane, constant equivalence ratio $\phi = 1.0$ [black diamond], constant mass $0.7 \leq \phi \leq 1.0$ [open square].

Figure 10. Temperature sweeps at 1.0 MPa. 90% *iso*-octane/10% ethanol, constant equivalence ratio $\phi = 1.0$ [black diamond], constant mass $0.7 \leq \phi \leq 1.0$ [open square].

Figure 11. Temperature sweeps at 1.0 MPa. 100% ethanol, constant equivalence ratio $\phi = 1.0$ [black diamond], constant mass $0.7 \leq \phi \leq 1.0$ [open square].

Figure 12. Comparison of 100% ethanol and a 75% *iso*-octane/25% ethanol blend at $\Phi = 1.0$, $P = 3.0 - 3.1$ MPa. Data extracted from Cancino et al. [21-23] in a shock tube.

Figure 13a&b. 0-D model at 0.5 MPa and $\Phi = 1$ using the detailed LLNL gasoline surrogate mechanism (left: $1000/T < 1.3$; right: $1000/T > 1.3$). 100% *iso*-octane (black open diamonds), 90% *iso*-octane/10% ethanol (blue open squares), 80% *iso*-octane/20% ethanol (orange open triangles), 50% *iso*-octane/50% ethanol (green asterisk), 100% ethanol (red open circles).

Figure 14. 0-D model at 0.5 MPa and $\Phi = 1$ using the detailed LLNL gasoline surrogate mechanism. 100% *iso*-octane (black diamonds), 80% *iso*-octane/20% ethanol (orange triangles), 100% ethanol (red circles). Open symbols represent model results, and closed symbols represent experimental results.

Tables:

Table 1. Comparison of ignition delay definitions at 1.0 MPa for 100% *iso*-octane at select temperatures.

Temperature	FPP (ms)	$dP/dt_{\max}$ (ms)	$dP/dt_{\max} - \text{FPP}$ (ms)	% difference
998 K	28.5	29.4	0.9	3.2
973 K	33.4	35.0	1.6	4.5
948 K	48.9	50.4	1.5	2.9
923 K	55.4	57.8	2.4	4.1
898 K	69.8	71.5	1.7	2.4

FPP = fixed pressure point above the initial charge pressure, FPP = 0.551 MPa

Table 2. Calculated mass injected vs. measured mass injected

Fuel	Calculated Mass (mg)	Measured Mass (mg)	% difference
100% <i>Iso</i> -octane	57.5	55.0	4.3
		55.5	3.5
		55.1	4.2
50% <i>Iso</i> -octane/50% Ethanol	61.6	61.8	0.3
		61.5	0.2
		61.6	0.0
100% Ethanol	65.6	69.6	6.1
		69.9	6.6
		69.6	6.1

Table 3. Injection-to-injection variability for 10 injections

Fuel	Range of Mass Injected (mg)	Average (mg)	Standard Deviation (mg)
100% <i>Iso</i> -octane	53 – 55	54	0.7
50% <i>Iso</i> -octane/50% Ethanol	58 – 60	59	0.8
100% Ethanol	67 – 69	68	0.7

Table 4. Increase in chamber pressure due to LTHR comparison for *iso*-octane/ethanol blends

Iso-octane %	ΔP (kPa) [1.0 MPa (773 K)]	ΔP (kPa) [1.5 MPa (773 K)]	ΔP (kPa) [1.5 MPa (723 K)]
100	93	200	335
90	45	160	220
80	-	75	155
50	-	-	-
0	-	-	-

Table 5. Variability in ignition delay times for fixed mass injection and temperature.

Fuel	# of Injections	Temperature (K)	Pressure (MPa)	Average Ignition Delay (ms)	Standard Deviation (ms)
Iso-octane	32	838	1.0	93.42	8.33
Iso-octane	10	744	1.5	93.67	5.40
Iso-octane	10	921	1.5	50.52	2.91
Ethanol	32	837	1.0	113.48	10.22
Ethanol	10	756	1.5	436.04	62.39
Ethanol	10	928	1.5	60.17	6.25

Figure 1

Figure 2

Figure 3

Figure 4a

Figure 4b

Figure 4c

Figure 5a

Figure 5b

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13a

Figure 13b

Figure 14