

Effect of Cetane Improvers on Gasoline, Ethanol, and Methanol Reactivity and the Implications for RCCI Combustion

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ABSTRACT

The focus of the present study was to characterize the fuel reactivity of high octane number fuels (i.e., low fuel reactivity), namely gasoline, ethanol, and methanol when mixed with cetane improvers under lean, premixed combustion conditions. Two commercially available cetane improvers, 2-ethylhexyl nitrate and di-tert-butyl peroxide, were used in the study. First, blends of the primary reference fuels iso-octane and n-heptane were port injected under fixed operating conditions. The resulting combustion phasings were used to generate effective PRF number maps. Then, blends of the aforementioned base fuels and cetane improvers were tested under the same lean premixed conditions as the PRF blends. Based on the combustion phasing results of the base fuel and cetane improver mixture, the effective PRF number, or octane number, could be determined. In all three base fuels it was found that 2-ethylhexyl nitrate is more effective at increasing fuel reactivity compared to di-tert-butyl peroxide. However, 2-ethylhexyl nitrate has a potential disadvantage due its nitrate group, which can manifest itself as NO_x emissions. The relationship between the fuel-bound nitrate group and the engine-out NO_x emissions was extensively characterized in the present study. It was also observed that methanol's response to cetane improvers was better than that of ethanol, in spite of the fact that they have similar octane numbers in their neat form. Once the reactivity of the base fuels was characterized, two mixtures of methanol and cetane improvers were selected and compared to diesel fuel as the high reactivity fuel (i.e., direct injected) for RCCI combustion.

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INTRODUCTION

RCCI Background & Motivation for Current Study

In an effort to reduce NO_x and soot emissions while maintaining high thermal efficiency, many new compression ignition combustion strategies have been proposed. Homogeneous Charge Compression Ignition (HCCI) is a concept that has been researched for many years and was initially studied in four-stroke engines [1]. HCCI combustion has been shown to have superior characteristics in terms of thermal efficiency, which results from lower heat transfer losses and shorter combustion durations. In addition, the lean, low temperature combustion process yields near zero NO_x and soot emissions.

Although fully premixed HCCI combustion appears thermodynamically attractive, it is entirely controlled by chemical kinetics, which means the in-cylinder temperature, pressure, equivalence ratio, and fuel reactivity (i.e., octane number) will govern when ignition occurs. This presents a controllability challenge because there is no direct means to

control the timing of combustion on a cycle-to-cycle basis when the fuel is completely premixed. However, utilizing fuel injections during the negative valve overlap (NVO) period has shown promise as a means to control HCCI combustion phasing [2]. These results have been confined to low-load operation and require costly variable valve train systems. In addition, the HCCI combustion process is very rapid which leads to excessive pressure rise rates and possible engine damage.

Finally, Bessonette et al. [3] demonstrated experimentally that the best fuel for HCCI operation has autoignition qualities between that of diesel fuel and gasoline, depending on the operating condition. For instance, they demonstrated that at 16 bar BMEP the most suitable fuel had an octane number of ~81. However, at 2 bar BMEP a cetane number of ~45 (i.e., a traditional diesel fuel) was required for stable operation. Thus, it seems that exploring fuel blends for specific operating conditions would be beneficial. These advantages and challenges of HCCI combustion have motivated the investigation of Partially Premixed Combustion (PPC) concepts.

Reactivity Controlled Compression Ignition (RCCI) is a dual fuel partially premixed combustion concept developed by Kokjohn et al. [4]. In this strategy, a low reactivity fuel, such as gasoline, is premixed via port fuel injection (PFI) and a high reactivity fuel, such as diesel fuel, is direct injected (DI) during the compression stroke. This process of in-cylinder fuel blending develops fuel reactivity gradients in the combustion chamber. The stratification of fuel reactivity results in a broad combustion event and reduced pressure rise rates compared to fully premixed HCCI combustion. Using a suite of optical diagnostics Kokjohn has gone on to demonstrate that RCCI is a chemically controlled combustion process, similar to HCCI [5]. The direct injection events are sufficiently early during the compression stroke that the peak equivalence ratio at the start of combustion remains very lean (i.e., equivalence ratio < 0.5). This results in sequential autoignition events beginning at the regions of highest fuel reactivity and progressing down the reactivity gradient. In addition, Kokjohn has shown that flame propagation plays an indistinguishable role during the combustion process due to the very lean equivalence ratios [5].

The majority of RCCI combustion research conducted to date has used port injected gasoline and direct injected diesel fuel [6]. There are potential disadvantages of a combustion strategy that requires two different base fuels (e.g., two fuel tanks). However, considering that RCCI combustion only requires that a fuel reactivity gradient be present in the combustion chamber, it has been proposed to use port injected low reactivity fuel and direct inject the same low reactivity fuel mixed with a small percentage of a cetane improver to serve as the high reactivity fuel. With this approach, the vehicle would require a single fuel tank (i.e., the low reactivity fuel, such as gasoline) and an additive tank, which would need to be roughly the same size as a diesel exhaust fluid (DEF) tank, depending on the additive doping level [7]. Thus, the main goal of the present study was to characterize the potential of low reactivity fuels, namely gasoline, ethanol, methanol, and blends of the alcohols and gasoline when mixed with cetane improvers to understand how they will perform as the high reactivity fuel during RCCI operation.

Previous Research with Cetane Improvers EHN & DTBP

Splitter et al. [7] were among the first to investigate the aforementioned concept on a heavy duty diesel engine, in which they port injected gasoline and direct injected gasoline mixed with small amounts of di-tert-butyl peroxide (DTBP). They found that RCCI combustion could be achieved by mixing as little as 2% by volume DTBP into the direct injected gasoline. Kaddatz et al. [8] conducted similar research on a light duty diesel engine. Considering that the majority of pump gasoline in the United States today has been blended with up to 10% ethanol by volume (i.e., E10), Kaddatz et al. investigated using E10 mixed with 3% by

volume 2-ethylhexyl nitrate (EHN) as the high reactivity fuel for RCCI combustion. They made comparisons to gasoline/diesel RCCI and found that more E10+EHN was required compared to diesel fuel to achieve similar combustion phasing. This suggests that diesel fuel is more reactive than E10 mixed with 3% by volume EHN. Kaddatz et al. also showed that for RCCI operation with gasoline/diesel, if the direct injection timings were sufficiently advanced, start of injection command of -36° ATDC and earlier, the NOx emissions went to essentially zero. However, as the direct injection timings were advanced using E10+EHN as the high reactivity fuel, the NOx emissions converged to one-third of the fuel-bound NO from the EHN. This potential disadvantage of using EHN as a reactivity enhancer will be discussed in detail in the present study.

The impact of cetane improvers on fully premixed HCCI combustion has previously been investigated as well. Mack et al. [9] demonstrated the effect of adding DTBP to blends of ethanol and diethyl ether during HCCI combustion. They found that the addition of DTBP did not elongate the heat release nor did it allow for stable retardation of the combustion phasing. However, they found that the combustion did advance by approximately 3° CA for 3% DTBP in ethanol. Eng et al. [10] studied the effect of adding DTBP to gasoline during HCCI operation with the goal of extending the low load limit. They found that from 0 to 2% DTBP addition, the low load limit was reduced by 23%. However, from 2% to 15% DTBP addition the low load limit was only reduced by an additional 10%. This data suggests that DTBP added to gasoline exhibits a very non-linear behavior in terms of increasing the gasoline's reactivity. In both of the aforementioned studies on HCCI combustion with cetane improvers (i.e., [9, 10]) it was discussed that the effects of ignition promoters are currently not totally understood. There is some evidence that suggests the ignition promoting effect is due simply to a temperature increase, stemming from low temperature heat release. However, other researchers argue that the effect is chemical in nature and due to the fact that chain propagating and chain branching reactions are accelerated by the decomposition of the cetane improver. The present study supports the latter chemical effect.

Of course, the effect of cetane improvers on diesel fuel under mixing limited conditions (i.e., high equivalence ratios) has been studied extensively. Schwab et al. [11] studied the effect of EHN and DTBP on two different diesel fuels. [Figure 1](#) illustrates their findings, in which regardless of the cetane number of the base fuel, as the cetane improvers are added, the cetane number increase (i.e., reactivity increase) is more rapid with EHN than with DTBP.

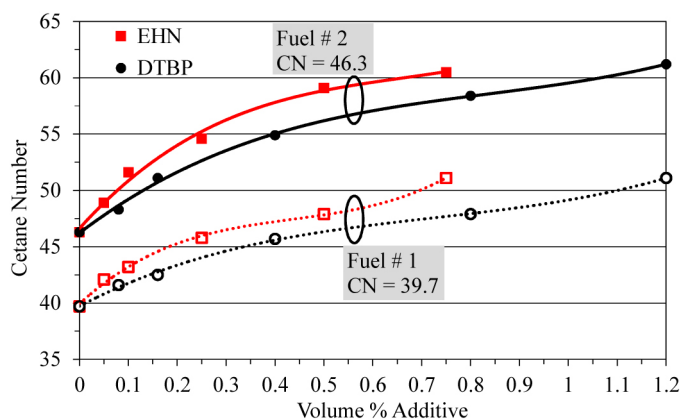


Figure 1. Effect of EHN & DTBP on the cetane number of diesel fuel under conventional diesel operation [11].

Characterizing High Octane Number Fuels Mixed with Cetane Improvers

As mentioned previously, the main goal of this work was to characterize low reactivity fuels mixed with cetane improvers to evaluate how well they will perform as the high reactivity fuel during RCCI operation. First, an experiment representative of the thermodynamic conditions experienced by the directed injected fuel during RCCI combustion needed to be selected. Figure 2 shows a representative RCCI operating condition in which 85% of the total fuel is premixed gasoline and the remaining 15% is direct injected diesel fuel. The diesel was injected using a double injection strategy with the first injection at -61° ATDC and the second at -41° ATDC.

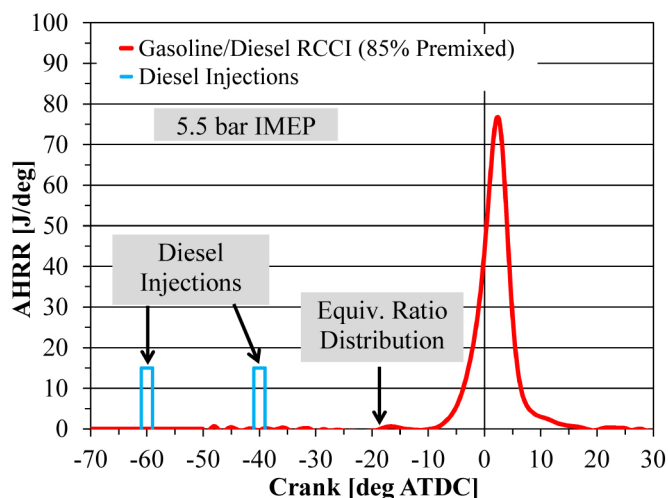


Figure 2. Typical RCCI injection strategy and subsequent AHRR operating with gasoline & diesel fuel.

Equivalence Ratio (Φ) Distribution

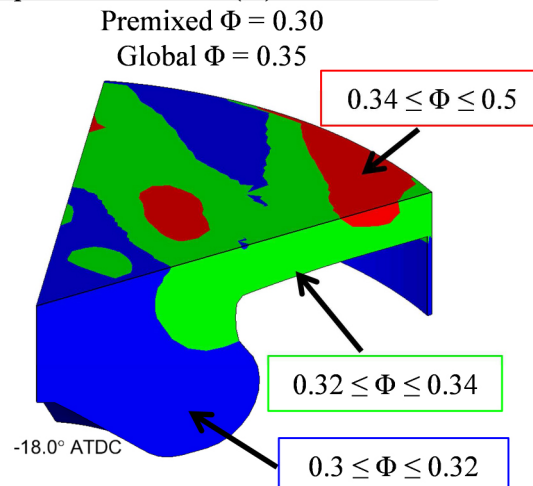


Figure 3. Predicted equivalence ratio distribution from CFD simulations with 85% premixed gasoline and 15% direct injected diesel fuel.

Figure 2 also shows the resulting apparent heat release rate (AHRR) for this mid-load operating condition. Figure 3 shows the equivalence ratio distribution in the combustion chamber at -18° ATDC predicted by CFD simulations using KIVA3V. As can be seen, the background equivalence ratio from the premixed gasoline is 0.3. The direct injected diesel fuel provides some equivalence ratio stratification, with a peak equivalence ratio in the chamber of 0.5. The majority of the direct injected fuel exists at an equivalence ratio between 0.32 and 0.34, which is nearly the background equivalence ratio. Thus, a lean, premixed combustion experiment would serve as a representative operating condition for the high reactivity fuel during RCCI operation.

Objectives

The main focus of the current study was to investigate RCCI combustion in a light duty engine using a single low reactivity fuel, mainly alcohols, and the low reactivity fuel mixed with cetane improvers to serve as the high reactivity fuel. This concept has been demonstrated previously by Splitter et al. [7] and Kaddatz et al. [8], but the amount of cetane improver used was arbitrarily chosen. In this study, the reactivity of the base fuels (i.e., gasoline, ethanol, methanol, and alcohol/gasoline blends) was characterized when mixed with cetane improvers EHN and DTBP. The goal was to understand how the base fuel's reactivity changes and if these low reactivity fuels could be utilized as high reactivity fuels for RCCI combustion when mixed with cetane improvers.

SINGLE CYLINDER LIGHT DUTY DIESEL ENGINE LABORATORY

The experiments were carried out on a light duty, four-stroke diesel engine based on the General Motors 1.9L



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platform. Table 1 shows the engine and fuel injector specifications and Figure 4 provides a schematic of the single cylinder engine laboratory. With a bore of 82.0 mm and stroke of 90.4 mm this engine is representative of a light duty automotive diesel engine with four valves per cylinder driven by dual overhead cams. A stock four-cylinder head is installed atop a single cylinder block with only the valves for cylinder #2 activated by the cams.

Table 1. GM 1.9L Single Cylinder Engine Specifications

Engine Geometry	
Base Engine	GM 1.9L Diesel
Compression Ratio	17.4
Displacement (Liters)	0.477
Stroke (mm)	90.4
Bore (mm)	82.0
Intake Valve Closing	-132° aTDC
Exhaust Valve Opening	112° aTDC
Swirl Ratio	2.2
Piston Bowl Type	Stock (Re-entrant)
Port Fuel Injector	
Model Number	TFS-89055-1
Included Spray Angle	20°
Injection Pressure (bar)	2.5 to 3.5
Rated Flow (kg/hr)	25
Common Rail Injector	
Model	Bosch CRI2.2
Number of Holes	7
Hole Diameter (mm)	0.14
Included Spray Angle	148°
Injection Pressure (bar)	250 to 1000 bar

Multiple combustion strategies were investigated in this study, namely HCCI and RCCI. HCCI operation was achieved with two port fuel injectors mounted in the intake runner. The point of fuel injection is approximately 30 cm upstream of the intake valves. For RCCI operation, the low reactivity fuel was delivered through the same port fuel injectors and the high reactivity fuel was delivered with a centrally mounted common rail injector.

Engine controls and data acquisition were handled through National Instruments LabView software. A Kistler 6125A pressure transducer in series with a Kistler 4010 charge amplifier was used to measure the in-cylinder pressure. A shaft encoder with 1440 pulses per revolution was used, which supplies a resolution of 0.25 crank angle degrees. For each operating point 300 consecutive cycles of cylinder pressure data were acquired. Each individual cycle's pressure data was smoothed using a Fourier series low-pass filter with a Gaussian roll-off function having a transmission of 100% from 0 to 1600 Hz and dropping to 1% at 6720 Hz. Once filtered, the collected cycles were ensemble averaged to yield a representative cylinder pressure trace, which was used to calculate the apparent heat release rate (AHRR) and, in turn, determine combustion phasing. The AHRR is essentially the chemical heat release rate minus the heat loss rate to the combustion chamber walls and is given by

$$AHRR = \frac{dQ}{d\Theta} \Big|_{chem} - \frac{dQ}{d\Theta} \Big|_{wall} = \frac{1}{\gamma-1} V \frac{dP}{d\Theta} + \frac{\gamma}{\gamma-1} P \frac{dV}{d\Theta} \quad (1)$$

From the AHRR, the accumulated heat release can be determined. The combustion phasing was calculated to be the crank angle at which the accumulated heat release had reached 50% of its maximum, denoted as CA50.

CHARACTERIZATION OF HIGH OCTANE NUMBER FUELS MIXED WITH CETANE IMPROVERS

Engine Operating Conditions & Reference Combustion Phasing Maps

As mentioned previously, the RCCI direct injection strategy creates equivalence ratio and octane number stratification in the combustion chamber. In Figure 3 it was shown that the equivalence ratio distribution just prior to ignition remains lean (equivalence ratios < 0.5). Therefore, lean fully premixed HCCI combustion was chosen as the strategy to study the impact of cetane improvers on high octane number fuels. The engine operating conditions that were used to create the reference maps is shown in Table 2. These engine operating parameters were fixed throughout the study regardless of the base fuel, and two different equivalence ratios were investigated: 0.26 and 0.3.

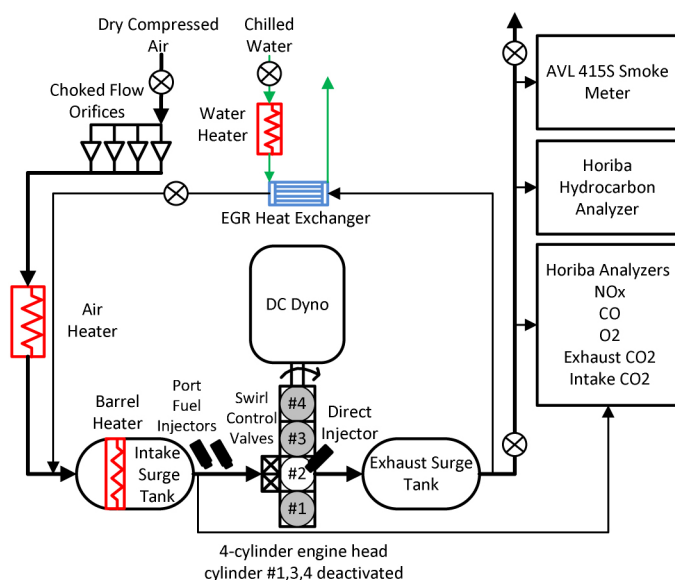


Figure 4. GM 1.9L Single Cylinder Engine Laboratory

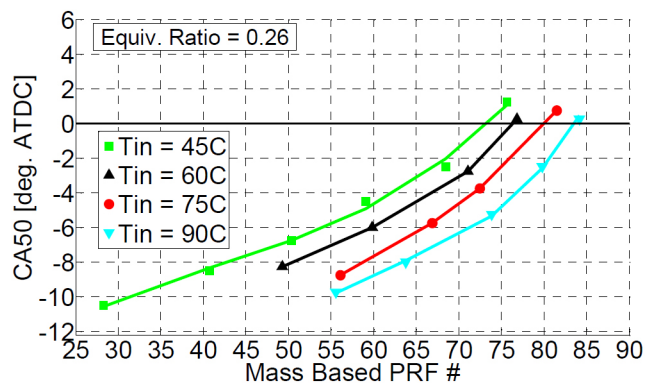
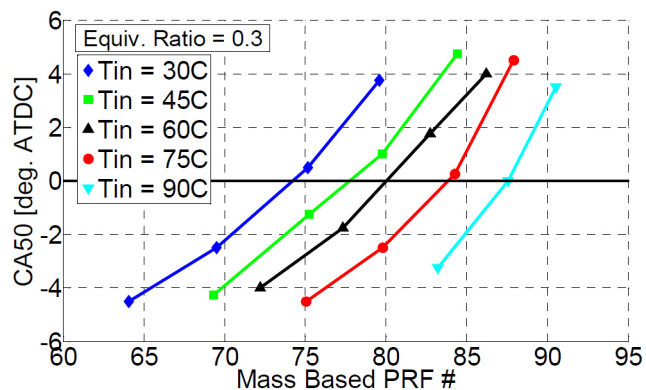
Table 2. Fixed Engine Operating Conditions for HCCI

Engine Speed [rpm]	1500
Oil & Coolant Temperature [°C]	80
Intake Surge Tank Pressure [bar]	1.1
Exhaust Surge Tank Pressure [bar]	1.2
Global Equivalence Ratio	0.26, 0.30

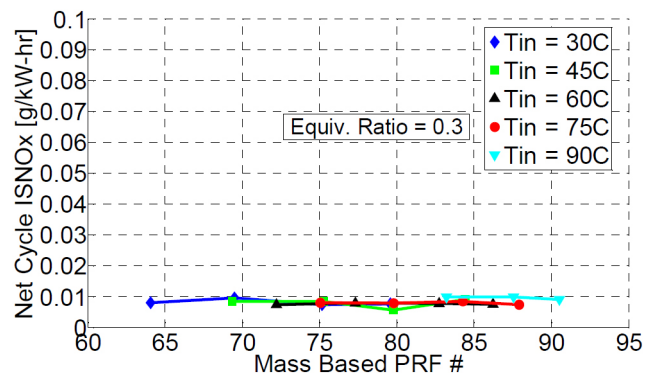
In order to characterize the reactivity of the base fuels (i.e., gasoline, ethanol, and methanol) under lean, premixed combustion conditions, a reference combustion phasing map was created. This was accomplished by blending the primary reference fuels, iso-octane and n-heptane, in the intake runner via separate port fuel injectors (PFIs). In order to span a wide range of reactivities (i.e., PRF numbers), the intake temperature was varied widely in steps of 15°C. The resulting combustion phasing maps are shown in [Figure 5](#) and [Figure 6](#). In these figures, the combustion phasing (CA50) is plotted as a function of the mass based PRF number, which is defined in [Equation \(2\)](#). As can be seen in the figures, at a fixed intake temperature, as the PRF # is increased, the combustion phasing is retarded. In addition, at a fixed PRF #, as the intake temperature is decreased, the combustion phasing is retarded.

$$PRF \# = \frac{\dot{m}_{iso-octane}}{\dot{m}_{iso-octane} + \dot{m}_{n-heptane}} \quad (2)$$

Limits were set on the peak pressure rise rate and the coefficient of variation (COV) of engine load (i.e., indicated mean effective pressure, IMEP), at 10 bar/deg. and 10%, respectively. Thus, at a given intake temperature, the most advanced combustion phasing produced a peak pressure rise rate of 10 bar/deg. and the most retarded phasing had a COV of IMEP approaching 10%. These combustion phasing results with primary reference fuels will serve as references to determine the effective PRF # of the base fuels mixed with cetane improvers.

**Figure 5. Reference combustion phasing (CA50) map with PRF fuels at an equivalence ratio of 0.26****Figure 6. Reference combustion phasing (CA50) map with PRF fuels at an equivalence ratio of 0.3**

[Figure 7](#) shows the net cycle indicated specific NOx emissions (ISNOx) when operating with the PRF fuels at equivalence ratio of 0.3. Regardless of the PRF #, which as indicated in [Figure 6](#) spans a combustion range of 8° CA, NOx emissions are very low at less than 0.01 g/kW-hr. This suggests that the peak in-cylinder temperatures are low. This observation will be important when comparing to results with EHN, which has a fuel-bound nitrate group and has the potential to yield fuel-bound NOx emissions.

**Figure 7. Indicated specific NOx emissions as a function of the PRF # at an equivalence ratio of 0.3**

Fuel Properties & Intake Temperature Corrections for the Base Fuels

The physical and chemical properties of the primary reference fuels, the tested base fuels, and the cetane improvers are shown in [Table 3](#). All the fuels used in this study are extremely volatile, which ensured that a homogeneous premixed charge was created in the combustion chamber. As can be seen in the table, a marked difference between the fuels is the enthalpy of vaporization and the stoichiometric air-fuel ratio. The alcohol fuels have much higher charge cooling potential and a smaller stoichiometric air fuel ratio compared to gasoline and the primary reference fuels. Thus, to achieve the fixed global equivalence ratios shown in [Table 2](#), the fueling rate for the

alcohol fuels must be increased. This serves to amplify the charge cooling effect of the alcohols. Considering the focus of this study is the combustion kinetics of the base fuels with cetane improvers, it is important that the bulk gas temperature at the start of compression (i.e., intake valve closure, IVC) remain constant for a given intake temperature (T_{in}). Therefore, corrections were made to the intake temperature when using the alcohol fuels based on estimates from one dimensional cycle simulations which accounted for the charge cooling from port injected alcohols [12]. It should be noted that because the enthalpy of vaporization of gasoline and the reference fuels is similar, no intake temperature corrections were made for gasoline. Figure 8 illustrates these parameters in the current experimental setup. The engine intake temperature (T_{in}) is measured at the exit of the intake surge tank, just prior to the point of port fuel injection. The intake temperature, amount of fuel port injected, intake runner wall temperature, and in-cylinder wall temperatures are all boundary conditions for the cycle simulation.

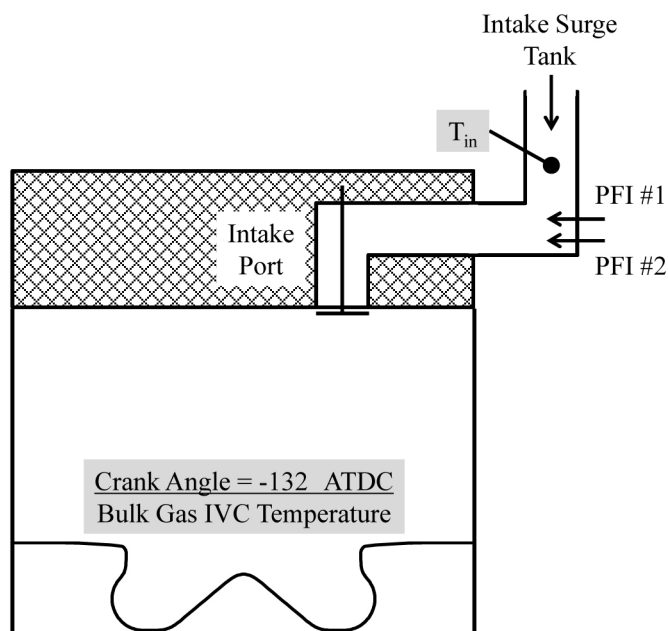


Figure 8. Illustration of the engine parameters for HCCI combustion experiments. (Note the piston profile shown in this illustration is the stock piston used in both the HCCI and RCCI experiments).

The results of the cycle simulations are shown in Figure 9 at an equivalence ratio of 0.26. The plot illustrates the estimated in-cylinder bulk gas temperature at IVC as a function of the intake temperature (T_{in}). As can be seen the nominal fueling rates were: PRF fuels and gasoline ~ 9 mg/cyc, ethanol ~ 14 mg/cyc, and methanol ~ 19 mg/cyc.

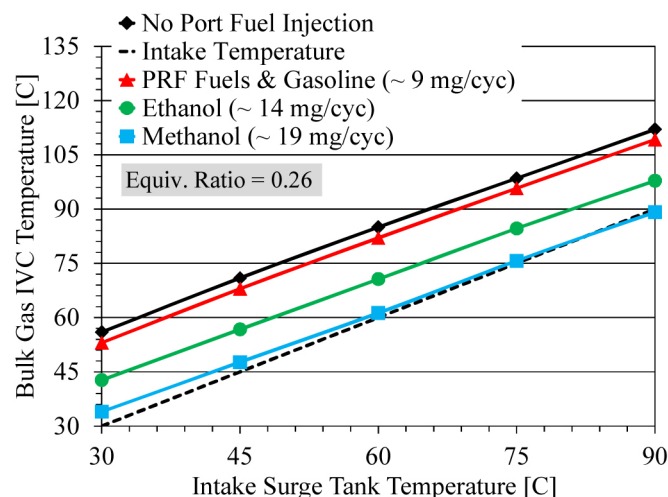


Figure 9. Cycle simulation results used to estimate the in-cylinder bulk gas temperature at IVC as a function of intake temperature and port injected fuel composition.

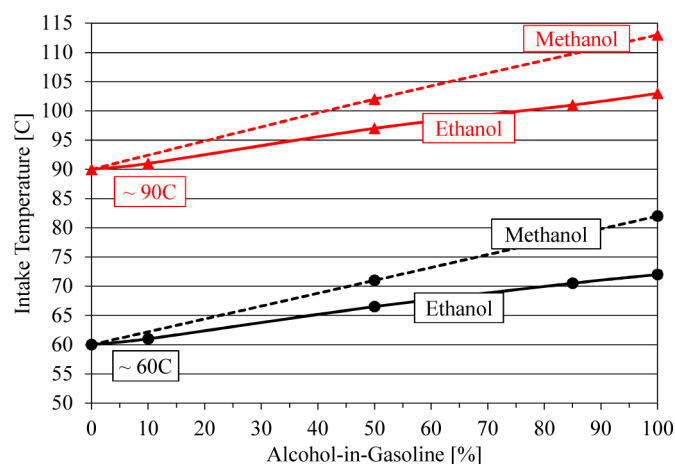


Figure 10. Required intake temperatures as a function of the volume % alcohol-in-gasoline to achieve a matched IVC temperature to the reference fuels.

With no port fuel injection at this operating condition, there is a nominal increase in the gas temperature from the intake surge tank to IVC of 28°C . If the PRF fuels or gasoline are port injected, it is estimated that a slight ($\sim 5^{\circ}\text{C}$) charge cooling effect will be experienced. However, if ethanol and methanol are port injected the charge cooling impact is much more significant. As mentioned previously, in order to study the chemical impact of cetane improvers on different base fuels, it is important that the thermodynamic conditions at the start of compression be matched to the reference fuels. Figure 10 shows the required intake temperature to achieve a fixed IVC temperature as a function of the volume % alcohol-in-gasoline. Two of the original intake temperatures used with the primary reference fuels are shown here, namely 60 and 90°C . At the far left (i.e., 0% alcohol-in-gasoline) are the