

Investigation of Fuel Effects on In-Cylinder Reforming Chemistry Using Gas Chromatography

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ABSTRACT

Negative Valve Overlap (NVO) is a potential control strategy for enabling Low-Temperature Gasoline Combustion (LTGC) at low loads. While the thermal effects of NVO fueling on main combustion are well-understood, the chemical effects of NVO in-cylinder fuel reforming have not been extensively studied. The objective of this work is to examine the effects of fuel molecular structure on NVO fuel reforming using gas sampling and detailed speciation by gas chromatography. Engine gas samples were collected from a single-cylinder research engine at the end of the NVO period using a custom dump-valve apparatus. Six fuel components were studied at two injection timings: (1) iso-octane, (2) n-heptane, (3) ethanol, (4) 1-hexene, (5) cyclohexane, and (6) toluene. All fuel components were studied neat except for toluene - toluene was blended with 18.9% nheptane by liquid volume to increase the fuel reactivity. Additionally, a gasoline surrogate matching the broad molecular composition of RD587 gasoline was formulated using the chosen fuel palette and tested. The energy content of the injected fuel mass was kept constant for the sampled NVO cycle and the excess oxygen was relatively low (2.4%) compared to previous studies by the authors. The later injection timing studied resulted in useable recovered fuel energy near 70% and improved reformat yield of hydrogen and C1-C4 hydrocarbons compared to the earlier injection timing for all fuels except toluene/n-heptane. Analysis of the RD587 surrogate reformat compared to the individual component reformates suggests that fuel component interactions depend on injection timing, potentially through the in-cylinder equivalence ratio distribution.

CITATION: Wolk, B., Ekoto, I., and Northrop, W., "Investigation of Fuel Effects on In-Cylinder Reforming Chemistry Using Gas Chromatography," *SAE Int. J. Engines* 9(2):2016, doi:10.4271/2016-01-0753.

INTRODUCTION

Low-temperature gasoline combustion (LTGC) engines that employ compression induced auto-ignition can achieve excellent fuel economy and good emissions characteristics through the use of staged, flameless combustion. Efficiency gains are realized through higher compression and mixture specific heat ratios as well as reduced heat transfer and pumping losses [1, 2]. The main challenge facing LTGC engines has been the ability to achieve and control stable combustion across a range of relevant engine speeds and loads, while keeping noise and emissions characteristics at an acceptable level.

For elevated loads, indicated mean effective pressures (IMEP) of up to 10 bar have been achieved in naturally-aspirated engines through the use of positive valve overlap (PVO) strategies that retain exhaust thermal energy for the subsequent cycle through valve re-breathing [3]. Intake pressure boost and partial fuel stratification, particularly with the use of ϕ -sensitive fuels, have been used to extend the high-load limit above 20 bar IMEP without excessive ringing [1, 4]. Additionally, strategies such as spark-assisted compression ignition (SACI), where spark ignition is used to initiate flame propagation so that combustion phasing is optimized and combustion noise modulated, have shown promise [5].

Challenges also exist for LTGC at low loads due to poor combustion stability that can lead to partial burns or misfires that adversely impact fuel economy and emissions, namely carbon monoxide (CO) and hydrocarbons (HC) [1]. Negative valve overlap (NVO) has been used to extend low-load stability limits by retaining exhaust thermal energy for the subsequent cycle through modified valve lift and timing events that form a recompression stroke [6, 7]. Often, NVO-period pilot fuel injections are used to further heat the charge [7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21] or to alter the main-period fuel reactivity through in-cylinder reformation or partial oxidation of the injected pilot fuel [7, 12, 13, 16, 20, 21, 22, 23, 24, 25, 26].

The products resulting from the recompression heating of fuel in an oxygen-deficient environment, or reformat, contain a mixture of species including high concentrations of CO, hydrogen (H_2), and unburned hydrocarbons. An example is the dedicated exhaust gas recirculation (D-EGR) concept where a single engine cylinder operates with fuel-rich combustion to create power along with a continuous reformat stream in a modified EGR loop. The reformat stream contains mole fractions up to 6% CO and 2% H_2 to improve the knock-resistance of all cylinders [27]. Reformate products may also contain high ν -reactive species such as acetylene

(C₂H₂), which can improve auto-ignition reactivity for LTGC or serve to increase flame speeds for spark-ignited combustion (both of which extend dilution tolerance) [27]. Szybist et al. [28, 29] show that NVO-period reformat generated under oxygen deficient conditions can be used to increase the total available chemical fuel energy through the use of exhaust-heat driven endothermic reactions that convert the parent fuel into components with higher overall energy content. This process, termed thermochemical recuperation, can offset NVO-period pumping losses [7] by converting sensible exhaust thermal energy into available chemical energy for subsequent main-period combustion.

A key objective of the NVO-period reactions is to improve the overall cycle efficiency through a combination of extracted work and recovered fuel energy, with minimal NVO-period losses (e.g. heat transfer, pumping losses). From a full-cycle perspective, work directly extracted during the NVO period is more valuable than an equivalent amount of recovered fuel energy due to inevitable losses during main-period combustion [26]. However, the amount of work extracted during the NVO period relative to the amount of fuel consumed is generally poor due to a combination of low compression ratio (CR) from non-optimal valve timings, increased heat transfer losses, and slow reaction rates [2]. The additional thermal energy at intake valve opening (IVO) will also negatively impact volumetric efficiency during induction. Other considerations include factors that impact main-period reactions such as the formation of reformat species and charge heating from NVO-period fuel oxidation.

The effect of fuel type on NVO engine operation has been investigated previously for test and/or reference fuels [30,31,32,33,34] as well as for primary reference fuels (PRF) [30], neat iso-octane and nheptane [33], alcohol blends [34], and diesel [32]. However, main-period combustion performance (load limits, efficiency, emissions, etc.) was the primary focus of these studies. In addition to consideration of main-period combustion parameters, detailed speciation of NVO reformat composition has been performed for neat iso-octane and ethanol [24, 25, 28] as well as methanol and isobutanol [28]. The current study experimentally examines the effect of parent fuel molecular structure on NVO-period heat release and reformat yield in a 0.63 liter, single-cylinder research engine using dump-sampling and detailed speciation by gas chromatography. The fuels tested were iso-octane, n-heptane, ethanol, 1-hexene, cyclohexane, and toluene, along with a 5-component gasoline surrogate. The heat release and speciation data are used to evaluate energy recovery pathways and losses during the NVO period. Additionally, constant-pressure, single-zone chemical kinetics simulations are used to elucidate the experimental observations.

APPROACH

Sandia Single-Cylinder LTGC Engine

An optically accessible single-cylinder research engine configured for LTGC operation was used for all experiments. All-metal components replaced quartz windows, as optical visualization was

not required (a metal flat top piston was retained). Relevant engine geometric and operating characteristics are summarized in Table 1. Two NVO injection timings were studied: SOI_{NVO} = -65 and -40 CAD_{NVO}, where NVO top dead center TDC_{NVO} = 0 CAD_{NVO}. SOI_{NVO} = -65 CAD_{NVO} provides a longer residence time in the NVO period, which should favor the relatively slow reforming reactions. SOI_{NVO} = -40 CAD_{NVO} was shown in [26] to result in better reformat yield of CO, H₂, methane (CH₄), and acetylene/ethylene (C₂H₂/C₂H₄) compared to earlier or later SOI_{NVO}. Lower exhaust excess O₂ concentration was also shown in [26] to be favorable - the exhaust excess O₂ concentration of 2.4% studied in this work was the lowest achievable while maintaining stable main-period combustion. The resulting NVO-period bulk-averaged equivalence ratio (ϕ) was ≈ 3 . To achieve the low exhaust O₂ concentration, the intake air was diluted with house nitrogen; the O₂ concentration of the intake air/N₂ mixture was $\sim 16.5\%$.

The pent-roof cylinder head has two intake valves and one exhaust valve, as sketched in Figure 1. A Bosch, step-hole, valve covered orifice (VCO) injector with 8 holes and a 60° included angle is centrally mounted and oriented vertically downward. The current injector is similar to the injector used in previous studies [24, 25] except that the included angle has been reduced from 70° to 60°. The NVO recompression period started with exhaust valve closing (EVC) at -75 CAD_{NVO} and ended with intake valve opening (IVO) at +75 CAD_{NVO}. Approximately 45%-47% of the burned gases were retained. The head surface temperature was monitored by an embedded thermocouple placed in one of the available spark plug ports.

Table 1. Engine specifications and operating conditions.

Displaced volume [liter]	0.633
Bore/Stroke [mm]	92/95.25
Compression ratio	11.3:1
Connecting Rod [mm]	166.7
Intake Valve Open/Close	+75 CAD _{NVO} / -140 CAD _{MAIN}
Exhaust Valve Open/Close	+140 CAD _{MAIN} / -75 CAD _{NVO}
Valve Lift [mm]	3
Speed [RPM]	1200
Intake Pressure [kPa]	100
Intake Temperature [°C]	75 – 132
Fuel Pressure [bar]	100
Residual Gas Fraction [%]	$\sim 45 - 47$
Exhaust Excess O ₂ [%]	2.4
Exhaust Temperature [°C]	345 – 379
NVO Duration [CAD]	150
SOI _{NVO} [CAD _{NVO}]	-65, -40
NVO Inj. Fuel Energy (LHV basis) [J/cycle]	265
NVO Bulk-Averaged Equiv. Ratio	~ 3.0 (see Table 3)
SOI _{MAIN} [CAD _{MAIN}]	-270
Total Inj. Fuel Energy (LHV basis) [J/cycle]	604

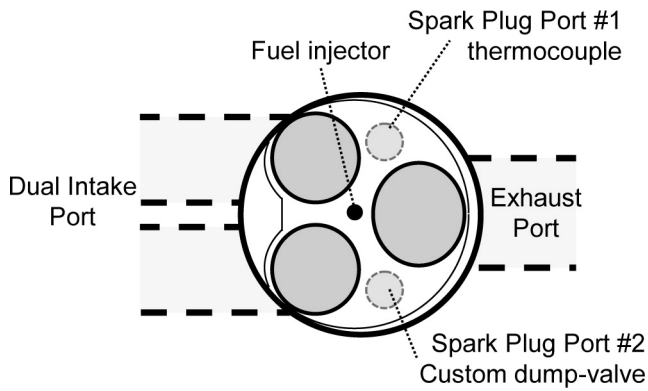


Figure 1. Pent-roof cylinder head valve, spark plug, and injector schematic.

The custom dump valve apparatus had an 8 mm head diameter with 3.2 mm lift and was housed in a body that fit into the remaining 14 mm spark plug port. The sampling system consisted of a manifold connected to a vacuum evacuated, 1-liter, Teflon-lined, stainless-steel sample bottle. A schematic of the apparatus is presented in Figure 2. Solenoid-operated isolation and vacuum valves were used to minimize gas contamination from subsequent dump cycles and any potential engine blow-by across the dump-valve. All sampling system components were insulated and electrically heated to 90°C to avoid water and hydrocarbon condensation.

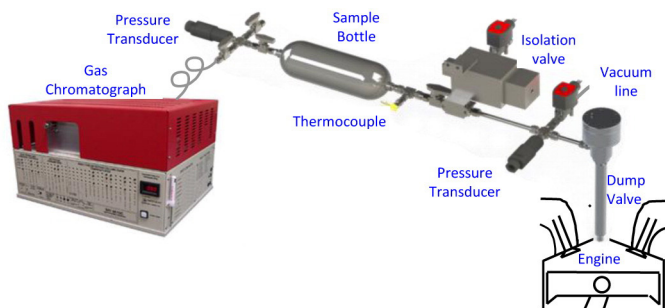


Figure 2. Illustration of the custom dump valve system, 1-liter sample bottle, and gas chromatograph.

Six fuel components were studied: (1) iso-octane, (2) n-heptane, (3) ethanol, (4) 1-hexene, (5) cyclohexane, and (6) toluene. All fuel components were studied neat except for toluene - toluene was blended with n-heptane to increase the fuel reactivity (81.1% toluene, 18.9% n-heptane by liquid volume). In addition, a 5-component gasoline surrogate matching the broad molecular composition of RD587 research gasoline was formulated using the chosen fuel palette. The use of a surrogate simplifies analysis of detailed speciation, as speciation of the true gasoline results in significant column elution cross-talk for the GC diagnostic [24].

The surrogate for RD587 was developed to match the broad molecular composition of the true gasoline as determined by a chemical analysis from Paragon Laboratories. As part of the chemical analysis, the ethanol content of RD587 was determined using gas chromatography. The amount of saturates, olefins, and aromatics were determined using the fluorescent indicator absorption (FIA) method. Toluene was used as the aromatic surrogate compound, 1-hexene as the olefin surrogate compound, and iso-octane and nheptane as the saturate surrogate compounds. Because the ratio of

iso-saturates to n-saturates was not specified by the chemical analysis, the amount of iso-octane and n-heptane in the surrogate was determined such that the Research Octane Number (RON) of the 5-component surrogate matched the measured RON of RD587 (RON = 92.1) assuming a linear blending rule for all components. The composition of the RD587 surrogate used in this work was: 54.9% iso-octane, 11.6% n-heptane, 9.9% ethanol, 4.7% 1-hexene, and 18.9% toluene by liquid volume.

Compared to the real RD587 gasoline, the surrogate has a slightly higher H/C ratio (surrogate = 2.02; actual = 1.97), slightly lower heating value (surrogate = 41.70 MJ/kg; actual 41.87 MJ/kg), and slightly lower density (surrogate = 0.732 g/mL; actual = 0.780 g/mL). To evaluate if the linear blending assumption for RON was reasonable, the RON of the surrogate was estimated using the methodology of Ghosh et al. [35]. The resulting estimate was RON = 93.5, only slightly larger than the target RON = 92.1, indicating that the linear blending assumption and the chosen RD587 surrogate composition were reasonable.

Fuel and injection properties for the seven fuels tested in this study are presented in Table 2 (the RON presented for the fuel blends assumes linear blending). Main and NVO fuel injection rates were set using custom timings from a predefined calibration, with the total fuel injection quantity monitored by a Max Machinery Model 213 volumetric flow meter. The NVO fueling rate of 5.97 mg/cycle for iso-octane was shown in [25] to result in the lowest relative amount of unburned fuel compared to other NVO fueling rates. The fueling rate for each fuel was adjusted such that the total energy injected was equivalent to the iso-octane condition on a Lower Heating Value (LHV) basis.

Table 2. Fuel and injection properties, along with intake and exhaust temperatures.

	Iso-Octane	n-Heptane	Ethanol	1-Hexene	Cyclohexane	Toluene/n-Heptane	RD587 Surrogate
Liquid Density [g/mL]	0.690	0.684	0.789	0.673	0.779	0.832	0.732
LHV [MJ/kg]	44.43	44.57	26.86	44.43	43.45	41.21	41.70
Research Octane Number	100	0	108.6	76.4	82.5	97.3	92.1
Total Fueling Quantity [mg/cycle]	13.60	13.55	22.41	13.60	13.90	14.66	14.41
NVO Injection Quantity [mg/cycle]	5.97	5.95	9.83	5.98	6.10	6.44	6.32
NVO Injection Duration [CAD]	3.19	3.20	4.71	3.27	2.91	2.88	3.18
Intake Temperature [°C]	132	75	132	90	91	132	125
Exhaust Temperature [°C]	364	345	360	352	344	379	372



The operating conditions replicated low-load engine operation where combustion stability can be problematic. The engine speed was set to 1200 RPM using a motoring dynamometer and the intake air pressure was fixed at 100 kPa to mimic naturally-aspirated operation without throttling. The exhaust oxygen concentration was adjusted to 2.4% using a combination of nitrogen dilution of the intake air and main-period fueling. The intake air temperature and main/NVO fuel injection split were adjusted to maintain stable combustion with exhaust temperatures between 345 - 380 °C.

Port-fuel injected dimethyl ether (DME) was used to rapidly warm engine cylinder surfaces before being replaced by direct injections of liquid fuel. Total fueling rates were fixed at 604 J/cycle on a LHV basis. Once cylinder wall temperatures (measured in the cylinder head) were steady, the dump-cycle sequence illustrated in Figure 3 was activated. Following a similar procedure to that described in [20], the dump-cycle sequence featured a custom NVO injection rate (265 J/cycle on a LHV basis), no main injection, and activation of the dump-valve system shortly after IVO ($-200 \text{ CAD}_{\text{MAIN}}$ to $50 \text{ CAD}_{\text{MAIN}}$), before concluding with continuous motored cycles. Accordingly, the dump cycle collected a mix of end-period NVO reformat and heated intake air. Dump sampling was repeated until the sample bottle pressure exceeded atmospheric pressure ($\sim 6\text{-}8$ dump samples). The engine was then stopped with the sample bottle isolated. Due to the unique nature of the NVO dump-cycle, exhaust-gas emissions measurements, lambda values, and main-period engine performance data for this cycle are unavailable. Bulk temperatures and residual gas fractions (RGF) at EVC were calculated using a custom 1-D engine model previously described by Fitzgerald et al. [36] that was validated over a wide range of NVO operation. The calculated RGF was used to correct for dilution of the reformat sample with intake air. By correcting for intake air dilution, NVO reformat species concentrations at IVO are obtained. Peterson et al. [25] confirmed that exhaust gas speciation results using this procedure are not significantly impacted by intake air scavenging.

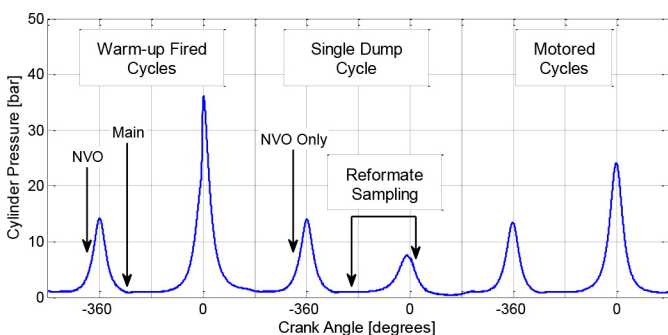


Figure 3. Illustration of the dump-sample collection procedure. First, the engine underwent continuous warm-up fired cycles with main and NVO fuel injections. When the head temperature was steady, a single dump cycle was activated that had only a custom NVO fuel injection (no main fuel injection). The dump valve was opened from $-200 \text{ CAD}_{\text{MAIN}}$ to $50 \text{ CAD}_{\text{MAIN}}$ during the single dump cycle to collect the NVO reformat sample (mixed with intake air). The single dump cycle was followed by continuous motored cycles. This process was repeated until the 1-liter sample bottle pressure exceeded atmospheric pressure ($\sim 6\text{-}8$ samples).

The sample bottle was connected to a compact SRI Instruments Multi-Gas Analyzer #3 gas chromatograph (GC) that houses three gas column detectors capable of detecting a wide range of sample stream constituents. The first of two flame ionization detectors (FID#1) was connected to a Restek MXT-1 60 meter capillary tube and was primarily used to identify large intermediate hydrocarbons. A second FID (FID#2) with a slower eluting 2 meter Restek Haysep-D column was used to resolve smaller hydrocarbons ($\text{C}_1\text{-C}_2$), with a methanizer used to detect CO and CO_2 . Note that FID#2 could not distinguish between C_2H_2 and C_2H_4 due to similar column elution times. However, C_2H_2 and C_2H_4 have similar GC response and the cumulative measurement of $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ is reported in this paper. A 2 meter Restek Molecular Sieve-13x column that fed a thermal conductivity detector (TCD) was used to detect hydrogen and oxygen, and was connected in series to the FID#2 column.

The gas sample characterization methodology was similar to the procedures described in [20], with an updated calibration gas mix based on detailed NVO-period speciation measurements obtained via photoionization mass spectrometry [24]. In addition, two new assumptions were made during GC data processing. First, p-xylene and m-xylene could not be distinguished due to similar column elution times; the cumulative values are reported in this paper. Second, toluene/n-heptane had significant unidentified peaks at molecular weights above toluene that were assumed to be small polycyclic aromatic hydrocarbons (PAH). The PAHs were assumed to follow the same calibration as toluene and have energy content equivalent to toluene on a per carbon basis. On an energy basis, the identified PAH accounted for approximately 2% of the input fuel energy for toluene/n-heptane.

RESULTS AND DISCUSSION

Engine Performance Data

Ensemble-averaged NVO-period in-cylinder pressure and heat release rate (HRR) traces for the seven fuels at $\text{SOI}_{\text{NVO}} = -65 \text{ CAD}_{\text{NVO}}$ are presented in Figure 4a. The HRR was determined by correcting the apparent heat release rate (AHRR) with the computed heat loss using a modified Woschni model [37]. The modified Woschni model constants were tuned using the motored pressure for the NVO period (EVC to IVO). The modified Woschni temperature coefficient was decreased slightly from 0.73 to 0.71 while the unsteady gas velocity coefficient was increased from 0.20 to 0.25 (same as [26]). The cumulative NVO-period modeled heat loss agrees within 10% (1.5 J) of the computed change in sensible energy for the motored cases across the conditions studied.

It can be seen in Figure 4a that minimal HRR is observed for all fuels with the exception of ethanol. Due to the low amount of available oxygen, the heat release is extended over much of the NVO period (from about $-25 \text{ CAD}_{\text{NVO}}$ to $15 \text{ CAD}_{\text{NVO}}$). The increased NVO-period reactivity of ethanol compared to iso-octane was also observed in [26]. The trends in HRR with fuel type are very similar for $\text{SOI}_{\text{NVO}} = -40 \text{ CAD}_{\text{NVO}}$, as seen in Figure 4b. Noise in the HRR trace during the NVO injection and subsequent charge cooling are observed around $-40 \text{ CAD}_{\text{NVO}}$.

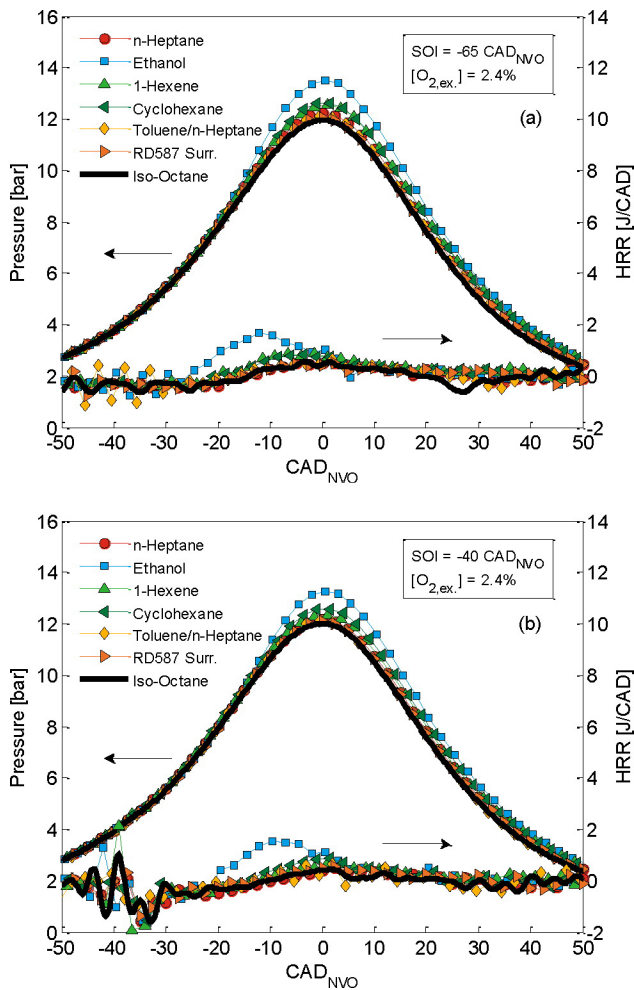


Figure 4. Ensemble-averaged NVO-period in-cylinder pressure and HRR (corrected for heat transfer) traces for the 7 fuels tested at 2.4% oxygen with (a) $SOI_{NVO} = -65 \text{ CAD}_{NVO}$ and (b) $SOI_{NVO} = -40 \text{ CAD}_{NVO}$. The fuels show similar HRR and pressure behavior, except for ethanol. Ethanol exhibits the highest peak HRR and pressure during the NVO period.

The total heat release (HR) corrected for heat loss during the NVO period is presented in Figure 5 for $SOI_{NVO} = -65$ and -40 CAD_{NVO} . The HR was determined by integrating the HRR presented in Figure 4 while the HRR trace is positive (near TDC_{NVO}). The maximum bulk-averaged in-cylinder temperature (T_{max}) for each case is also indicated in Figure 5. As expected from the higher HRR, ethanol (EtOH) exhibits drastically increased HR compared to the other fuels. Aside from ethanol, cyclohexane (CHex) and 1-hexene (1Hex) show the next most HR. Additionally, iso-octane (iO), n-heptane (nH), toluene/n-heptane (T/nH), and the RD587 surrogate (RD587) show similar HR magnitudes at $SOI_{NVO} = -65 \text{ CAD}_{NVO}$. However, iso-octane and n-heptane release less heat at $SOI_{NVO} = -40 \text{ CAD}_{NVO}$ compared to toluene/n-heptane and the RD587 surrogate. Most surprisingly, n-heptane shows very similar HR during the NVO period compared to iso-octane despite their drastically different main-period reactivity. There is also increased HR for $SOI_{NVO} = -65 \text{ CAD}_{NVO}$ compared to $SOI_{NVO} = -40 \text{ CAD}_{NVO}$ for all fuels.

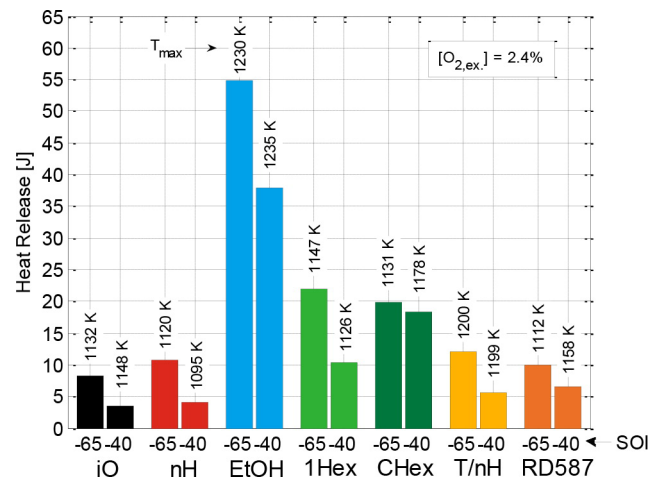


Figure 5. Ensemble-averaged NVO-period HR for the 7 fuels tested at 2.4% oxygen and $SOI_{NVO} = -65$ and -40 CAD_{NVO} . The supplied NVO-period fuel energy was 265 J. The HR decreases for all fuels as SOI_{NVO} is delayed from -65 CAD_{NVO} to -40 CAD_{NVO} . Ethanol has significantly higher HR than the other fuels at both NVO injection timings. The maximum bulk-averaged in-cylinder temperature (T_{max}) for each case is also indicated.

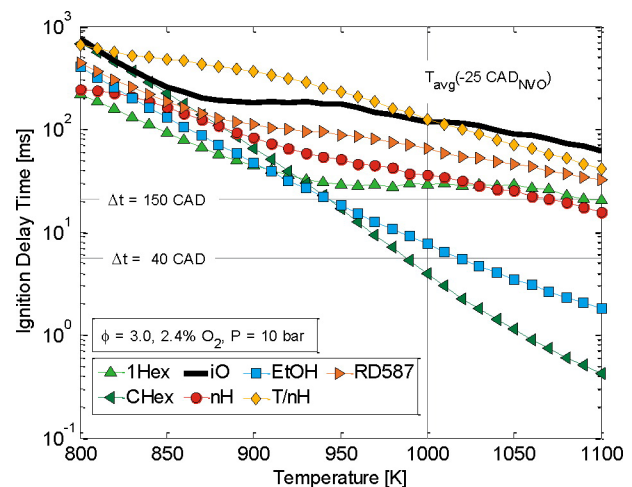


Figure 6. Ignition delay times (constant pressure) for the 7 fuels tested at 2.4% oxygen (in N_2), $\phi = 3.0$, and 10 bar. The horizontal lines represent the time duration of 150 CAD (EVC to IVO) and 40 CAD (-25 CAD_{NVO} to 15 CAD_{NVO} ; the crank angle range of heat release) at 1200 rpm. The vertical line at 1000 K is representative of the average in-cylinder temperatures at -25 CAD_{NVO} . Ethanol and cyclohexane are the only fuels of the fuels tested that have sufficiently short ignition delay times relative to the time duration of 40 CAD, which explains the much larger NVO-period HR observed for ethanol and the relatively strong HR for cyclohexane.

In order to clarify the observations about heat release in Figures 4 and 5, representative ignition delay times were calculated for the 7 fuels tested using CHEMKIN-PRO [38]. The LLNL gasoline surrogate detailed mechanism [39] was used for all fuels except cyclohexane; the cyclohexane ignition delay times were calculated using the LLNL cyclohexane detailed mechanism [40]. The mixture composition used in the computations was $\phi = 3.0$ with 2.4% oxygen in N_2 , which is representative of the in-cylinder mixture after fuel injection neglecting residual HC and mixture stratification. The computed constant-pressure ignition delay times at 10 bar are presented in Figure 6. The horizontal lines in Figure 6 indicate the time duration of 150 CAD (the entire NVO