

Detailed Characterization of Negative Valve Overlap Chemistry by Photoionization Mass Spectroscopy

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ABSTRACT

For next-generation engines that operate using low-temperature gasoline combustion (LTGC) modes, a major issue remains poor combustion stability at low-loads. Negative valve overlap (NVO) enables enhanced main combustion control through modified valve timings to retain combustion residuals along with a small fuel injection that partially reacts during the recompression. While the thermal effects of NVO fueling on main combustion are well understood, the chemical effects of NVO reactions are less certain, especially oxygen-deficient reactions where fuel pyrolysis dominates. To better understand NVO period chemistry details, comprehensive speciation of engine samples collected at the end of the NVO cycle was performed by photoionization mass spectroscopy (PIMS) using synchrotron generated vacuum-ultraviolet light. Two operating conditions were explored: 1) a fuel lean condition with a short NVO fuel injection and a relatively high amount of excess oxygen in the NVO cycle (7%), and 2) a fuel-rich condition with a longer NVO fuel injection and low amount of NVO-cycle excess oxygen (4%). Samples were collected by a custom dump-valve apparatus from a direct injection, single-cylinder, automotive research engine operating under low-load LTGC and fueled by either isooctane or an 88-octane research certification gasoline. Samples were stored in heated stainless steel cylinders and transported to the Lawrence Berkeley National Laboratory Advanced Light Source for analysis using a Sandia National Laboratories flame sampling apparatus.

For all isooctane fueled conditions, NVO cycle sample speciation from the PIMS measurements agreed well with previously reported GC sample measurements if the sum total of all isomer constituents from the PIMS measurements were considered. PIMS data, however, provides richer speciation information that is useful for validation of computational modeling approaches. The PIMS data also revealed that certain species for the GC diagnostic were either misidentified during the calibration process or not identified at all. Examples of unidentified species include several classes of oxygenates (e.g., ketenes, aldehydes, and simple alcohols) and simple aromatics (e.g., benzene and toluene). For the gasoline fueled NVO cycles, performance characteristics were well matched to corresponding isooctane fueled NVO cycles. However, significant PIMS cross-talk from a wide range of gasoline components restricted the sampling analysis to a handful of species. Nonetheless, it was confirmed that for fuel-lean NVO operation there was a comparable increase in acetylene with NVO injection timing retard that is attributed to the prevalence of locally-rich, piston-surface pool fires caused by fuel spray impingement.

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INTRODUCTION

The relentless drive for clean and efficient automotive engines has motivated research in low-temperature gasoline combustion (LTGC) strategies [1, 2]. Next-generation LTGC engines can achieve excellent fuel economy while still meeting ultra-low emissions standards. For LTGC, compression-induced auto-ignition is used to avoid high flame temperatures that result in nitrogen oxide formation typically associated with spark ignition. However, auto-ignition control is a challenge, especially at low specific engine output power operating points when mixture compositions are highly dilute and charge temperatures are low [3, 4].

The negative valve overlap (NVO) strategy has been used to overcome the low-load challenge via retained cylinder-combustion products in a recompression stroke along with a small injection of fuel [4, 5]. The subsequent main-cycle combustion stability is enhanced through a combination of charge heat addition from retained exhaust energy and NVO-period fuel oxidation [3, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22], along with enhanced mixture reactivity from partial fuel reformation [3, 10, 11, 12, 17, 22, 23, 24]. Despite extensive research characterizing products of NVO fueling via laser diagnostics [25, 26] and, more recently, using direct engine sampling [22, 24, 27], much remains uncertain about NVO chemistry.

Detailed end-cycle NVO speciation is needed to improve the fundamental understanding of the dominant chemical effects. Species characterization during NVO is complicated by the fact that intermediates are retained and consumed during the subsequent main combustion cycle. Laser-based absorption and fluorescence diagnostics enable spatially and/or temporally resolved measurements of charge temperature and number density for select species [14, 16, 18, 26, 28, 29], but are generally insufficient for comprehensive mixture speciation. Direct sampling with follow-on analysis by either gas chromatography (GC) or Fourier transform infrared spectroscopy (FTIR) diagnostics has provided important speciation details at the start and end of the NVO cycle [22, 24, 27, 30, 31, 32]. These methods hinge on the application of suitable gas-sampling systems that are free of biases from quenching or mixture stratification.

It was observed during previous sampling studies that the products of rich combustion (e.g., acetylene and ethylene) increased for a globally lean NVO operation point as the NVO start of injection (SOI) was retarded [22]. The increase was attributed to pyrolysis reactions from piston surface pool fires as fuel spray impingement increased [17]. Conversely, these same rich products were observed with NVO SOI advanced for a globally rich operating point, which was thought to be from increased residence time for overly rich bulk-gas reactions [24, 27]. Sampling measurements have provided valuable data, although information supplied by the GC and FTIR diagnostics has so far been incomplete. The GC flame ion detector (FID) is not sensitive to aldehydes and cannot distinguish hydrocarbon isomers due to identical elution times. FTIR measurements on the other hand have been inconclusive due to large amounts of channel cross-talk that is difficult to account for during calibration. Accordingly, attempts to model NVO-cycle chemistry effects have largely been inconclusive due to a lack of complete speciation data [10, 12, 17, 33].

To overcome previous diagnostic difficulties, comprehensive species characterization of collected samples was performed via photoionization mass spectroscopy (PIMS) using vacuum-ultraviolet (VUV) light. Experiments were carried out using a Sandia-developed flame-sampling apparatus located at the Lawrence Berkeley National Laboratory Advanced Light Source (LBNL ALS) [34]. Multiple samples from a sweep of NVO fuel injection timings for a low and high excess oxygen NVO condition were collected at Sandia National Laboratories into heated stainless steel sample bottles. Samples were diluted by argon and transported to the ALS where they were analyzed using a predefined protocol.

The goal of the current study was to perform detailed speciation of engine samples collected at the end of the NVO cycle using PIMS. These data are then used to (1) provide validation measurements for NVO-cycle combustion modeling, (2) elucidate dominant constituents responsible for enhanced main combustion phenomena, and (3) provide calibration information for a complementary in-house GC diagnostic.

APPROACH

Engine

An optically accessible single-cylinder research engine configured for LTGC operation was used, with all-metal components replacing quartz windows for the current experiments. The flat-top piston from the

optical configuration has been preserved. The pent-roof cylinder head contains one exhaust and two intake valves along with a centrally mounted, vertically oriented, 8-hole direct injector (see Figure 1). Exhaust valve closing (EVC) and intake valve opening (IVO) occurred 75 crank angle degrees (CAD) before and after NVO top dead center (TDC_{NVO}) respectively, with roughly 50% of the residual exhaust gases retained. NVO samples were collected using a custom dump-valve apparatus previously described in detail by Steeper and Davisson as well as by Peterson et al. [22]. The dump-valve assembly has direct access into the cylinder through one of two spark plug ports, with the other port used to house an embedded thermocouple so that head surface temperature can be continuously monitored.

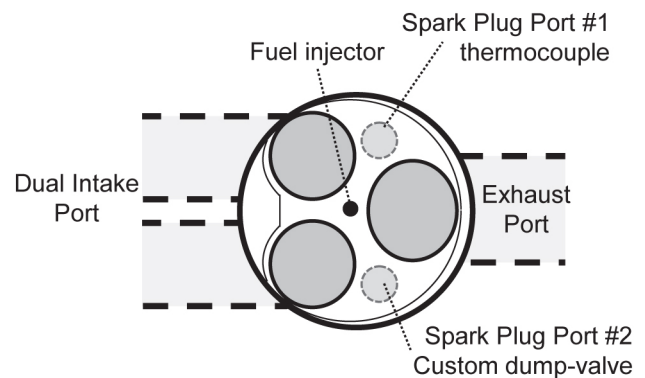


Figure 1. Schematic of the pent-roof cylinder head valve, spark plug, and injector arrangement.

To simplify sample gas speciation and facilitate future NVO-cycle modeling, isooctane was selected as a gasoline surrogate. For comparison, sampling and performance data were also acquired from the engine fueled by an 88-octane research gasoline (RD587) that contained 10% ethanol by volume for the globally lean NVO operating condition. Characteristics for the research gasoline are summarized in Table 1. Fuel injection rates for both the NVO and main cycles were set using custom injection timings from a predefined calibration map. Total fuel injection rate was monitored using a Max Machinery Model 213 flow meter. While the NVO fueling rate was fixed for both fuels, the main fueling rate for the RD587 gasoline was adjusted such that the total fuel energy injected was matched. The overall difference in fueling rates for the respective fuels was minor since the increased density of the reference gasoline was mostly offset by the larger isooctane heating value.

Two operating conditions were explored: (1) a globally lean NVO operating point with elevated excess oxygen (7%) and a small NVO fuel injection (1.3 mg/inj.), and (2) a globally rich NVO operating point with little excess oxygen (4%) and a comparatively larger NVO fuel injection (6.0 mg/inj.). For both conditions, the intake air pressure was fixed at 100 kPa and the engine speed was kept a constant 1200 rpm. The intake air temperature was increased from 88°C for the globally rich NVO condition to 120°C for the globally lean NVO condition so that good combustion stability was maintained (~3% coefficient of variation). The NVO-cycle SOI was swept from shortly after EVC until at or just past NVO top dead center (TDC_{NVO}). Engine specifications and operating conditions along with NVO-cycle fueling rates and bulk mixture conditions for each condition are listed in Table 2.

Table 1. Specifications for the reference isooctane and RD587 research fuels.

Distillation Temperature(s) [K] Isooctane RD587 (10%, 50%, 90%)	372.1 330.5, 371.4, 429.3
Isooctane Element [Wt%]	Carbon: 84.12% Hydrogen: 15.88%
RD587 Element [Wt%]	Carbon: 82.67% Hydrogen: 13.68% Oxygen: 3.65%
RD587 Composition [Vol%]	Ethanol: 9.9% Saturates: 66.5% Olefins: 4.7% Aromatics: 18.9%
Heat of Combustion [MJ/kg] Isooctane RD587	44.31 41.87
Density @ 15.56°C [g/mL] Isooctane RD587	0.692 0.748
Octane Number (RON + MON)/2 Isooctane RD587	100 88.4

Table 2. Engine Specifications and Operating Conditions.

Displaced volume [liter]	0.633
Stroke [mm]	95.25
Bore [mm]	92
Compression ratio	11.3:1
Number of Valves	3 (2 intake, 1 exhaust)
Inlet Valve Open & Close	+75 CAD _{NVO} & -140 CAD _{MAIN}
Exhaust Valve Open & Close, EVO	+140 CAD _{MAIN} & -75 CAD _{NVO}
Residual Gas Fraction	0.50
NVO Duration [CAD]	150
Valve Lift [mm]	3
Speed [rpm]	1200
Intake Air Pressure [kPa]	100
Fuel Pressure [bar]	100
Exhaust Excess O ₂ [%]	7 & 4
Intake Temperature [°C] 7% Exhaust Excess O ₂ 4% Exhaust Excess O ₂	88 120
Main Fueling Rate [mg/inj.] 7% Exhaust Excess O ₂ 4% Exhaust Excess O ₂	Isooctane/RD587 8.3/8.1 9.9/N/A
Main SOI [CAD _{MAIN}]	-270
NVO Fueling Rate [mg/inj] 7% Exhaust Excess O ₂ 4% Exhaust Excess O ₂	1.3 6.0
NVO Global Equivalence Ratio 7% Exhaust Excess O ₂ 4% Exhaust Excess O ₂	0.45 2.13
NVO SOI (CAD _{NVO}) 7% Exhaust Excess O ₂ 4% Exhaust Excess O ₂	-55, -30, -20, -10, -5 -40, -10, 10

Gas-Sampling

The 8-mm dump-valve head diameter was designed to fit into the 14-mm threaded spark-plug port described earlier, and has a valve lift of 3.2 mm. A vacuum evacuated sample manifold connected the dump valve to a 1-liter, Teflon-lined, stainless steel sample bottle (see

the illustration in Figure 2). All sample system components were insulated and kept at a constant 90°C by electric tape heaters connected to PID controllers to avoid water and hydrocarbon condensation. Exhaust stream gas sampling was also performed to measure the change in EVC input constituents.

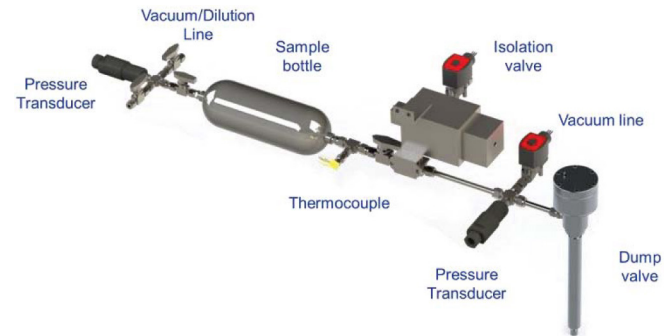


Figure 2. Illustration of the custom dump valve system and sample bottle.

During engine warm-up, port-fueled DME injections were used to quickly heat cylinder surfaces to 120°C. The DME injections were then replaced by direct isooctane or RD587 injections, with the total fueling rate set to achieve the desired exhaust O₂ concentration. Once cylinder wall temperatures reached 127°C, the dump-valve cycle sequence was activated (illustrated in Figure 3). The sequence began with a dump-cycle that featured a custom NVO injection rate, no main injection, and activation of the dump-valve system. The dump-cycle was then followed by continuous motored cycles. During the dump-cycle, dump-valve actuation began at -200 CAD_{MAIN} and continued until just after main-cycle TDC as a mix of NVO-cycle gasses plus fresh intake air collected in the sample bottle.

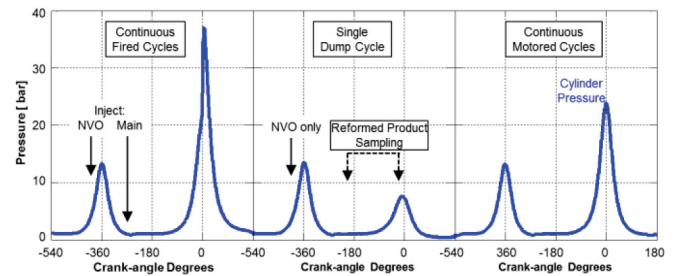


Figure 3. Schematic of the dump-valve cycle-sequence. Note that injection timings are reported with respect to the dump-cycle NVO TDC.

To estimate NVO species concentrations prior to IVO, the effect of sample dilution by the freshly mixed intake charge was compensated during post-processing. Note that Peterson et al. [24] compared GC speciation of engine exhaust samples with NVO samples without NVO fuel injection, and concluded the sampling system does not significantly impact intake breathing. Dump-sampling was repeated until the bottle pressure slightly exceeded atmospheric pressure. At this point, the engine was stopped with the sample bottle isolated and the bottle temperature and pressure recorded. The sample bottle was filled with pure argon until the bottle pressure reached roughly 3 bar. Sample bottle pressure and temperature were again recorded so that the amount of added dilution argon could be determined.

Two chromatograms created from an analysis of engine sample by in-house GC are presented in Figure 4, with known peaks from single-point calibrations identified. From the FID#1 column used to identify large hydrocarbon intermediates, it is apparent that numerous large hydrocarbon species that may be soot precursors have not been identified. From the FID#2 column, small concentrations of smaller hydrocarbon intermediates remain unidentified. Furthermore, it remains unclear if the calibrated species have been misidentified.

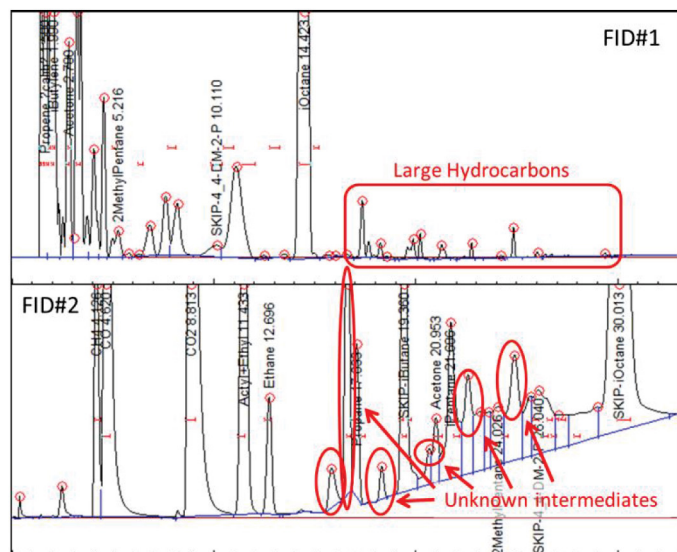


Figure 4. Sample chromatograms from the two FID detectors during a typical sampling run. Several intermediate species remain unidentified, including numerous hydrocarbons larger than the parent isooctane fuel.

Samples were transported to the LBNL ALS to be analyzed using a flame sampling apparatus owned and operated by Sandia's Combustion Chemistry department. Key details of the sampling apparatus are described below. Every effort was made to minimize the time between sample collection at Sandia and sample characterization at the ALS. Fresh samples were produced in the Sandia engine using the protocol described above, and then transported to the ALS (~1 hour drive). The largest time lag between sample generation and characterization was ~4 hours. Even for fresh samples, there was no chance to capture and identify short-lived intermediates. However, many of these species were likely quenched by the NVO-cycle expansion, with the surviving intermediates expected to be metastable. To investigate if species composition was impacted by long time delays, 4 samples at select operating points were intentionally generated 24 hours before characterization. No significant variation was observed.

Flame Sampling Apparatus Description

Detailed characterization of collected engine samples was performed using a Sandia owned flame-sampling apparatus originally designed for *ex situ* flame species measurements. A brief discussion is presented here, but the reader is referred to Cool et al. [34] for more details about the apparatus and Hansen et al. [35] for details about the PIMS diagnostic. Within the flame chamber, samples were expanded to a pressure of $\sim 10^{-4}$ Torr through a quartz nozzle. The effusive flow

was further expanded through a nickel skimmer to a pressure of $\sim 10^{-6}$ Torr to create the desired molecular beam. Tunable VUV light from the LBNL ALS Chemical Dynamics beamline was used to continuously ionize the molecular beam in the extraction region of a high-resolution, reflectron, time-of-flight mass spectrometer. Ions were extracted into a flight tube at a 30 kHz repetition rate and with mass spectra up 250 atomic mass units (AMU) detected on a multichannel plate detector.

The low-pressure flame chamber was modified to accept direct input from the heated sample cylinders. Samples were metered into the flame chamber by an MKS 1179 flow controller at a low flow rate (85 cc/min) to maximize the sampling duration and hence the collected signal. A PID controller connected to the bottle heat tape with temperature feedback from an embedded thermocouple was used to keep sample bottle temperatures warm ($\sim 50^\circ\text{C}$). Engine sample speciation was accomplished by scanning across a range of relevant the photon energies (9.7-12.3 eV in 0.05 eV increments). An energy scan was also performed on a calibration bottle that contained 1000 ppm each of 8 hydrocarbons with a range of molecular weights (methane, acetylene, ethylene, propene, 1-butene, cyclopentene, benzene, and toluene).

PIMS Signal Post-Processing

For each energy scan, background noise was subtracted from the ion count signal, with wavelet filters applied for further noise reduction. Signal time-of-flight measurements were correlated to the ion mass by a predefined calibration, with the signal counts binned in 1 AMU units to maximize signal-to-noise (SNR) and facilitate spectral analysis. Processed signal from each energy scan was then stitched together to form an energy scan image as a function of photon energy and AMU. An example is provided in the top image in Figure 5.

A custom algorithm was developed to determine species constituents from the each energy scan image. Signal post-processing was simplified from the method described by Cool et al. [34], to reflect the fact that the metered engine samples were isothermal. Accordingly, the ion count S for mass i at energy E is related to the species mole fraction χ as:

$$1. S_i(E) = \chi_i \cdot \sigma_i(E) \cdot D_i \cdot \Phi(E) \cdot PD_{eff}(E) \cdot SW(E) \cdot C(E)$$

Here, σ is the photoionization cross-section (PICS), D is a mass discrimination factor that depends on mass spectrometer ion focusing, Φ is the photon flux, and PD_{eff} is the corresponding photodetector efficiency. Note that photo-dissociation processes can result in the formation of smaller ion fragments, which accordingly result in multiple photoionization terms for each energy level. Comprehensive photoionization cross-section libraries for 335 hydrocarbon species, oxidants, diluents, and flame intermediates across a range of energies were consolidated from several sources. For cross-section libraries missing data at higher energies (i.e., up to 12.3 eV), these values were estimated from linear extrapolation of lower energy values. Extrapolated libraries were found to agree well with the calibration datasets, but nonetheless introduced additional uncertainty during