

HYDROCARBON SPECIES IN THE EXHAUST OF DIESEL ENGINES EQUIPPED WITH ADVANCED EMISSIONS CONTROL DEVICES

**Final Report
CRC Project No. AVFL-10b-2**

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January 28, 2005

Prepared for:



**Coordinating Research Council, Inc.
3650 Mansell Road, Suite 140 - Alpharetta, Georgia 30022**

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Abstract

The following report will illustrate the variation in hydrocarbon (HC) species that can exist in modern diesel engine exhaust when a variety of NO_x emissions control methods are used. Modern diesel engines operate at high efficiency and typically have very low HC concentrations in diesel exhaust. Therefore, because diesel exhaust is fuel lean, some type of HC addition is required to enable the reduction of NO_x in a net oxidizing environment. The required increase in HCs, in most cases, means that the low concentrations of HC species that are present in conventional engine operation are overwhelmed by the added HCs. The blend of fuel and the HC introduction strategy are both critical to the composition of the HCs in the exhaust. A set of appendices are included to give as much specific information on individual species as possible. Because many devices will likely use a finishing oxidation catalyst, the work presented here is by no means intended to describe tailpipe emissions, but rather the HC species that must work in concert with the aftertreatment to reduce NO_x.

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Acronyms

NOx	oxides of nitrogen
LNT	lean NOx trap
NSR.....	NOx storage and reduction
HC SCR.....	hydrocarbon selective catalytic reduction
HECC	high-efficiency clean combustion
FEERC.....	Fuels, Engines and Emissions Research Center
ORNL	Oak Ridge National Laboratory
MCNARD	Measurement and Characterization of NOx Adsorber Regeneration and Desulfation
CRADA	Cooperative Research and Development Agreement
ITEC.....	International Truck and Engine Corporation
DEM	delayed, extended, main injection
FTIR.....	Fourier Transform Infrared
FID.....	HC analyzer signal
DPF	diesel particulate filter
DOC.....	diesel oxidation catalyst
OM668.....	Merc-Benz 1.7L direct injection compression ignition engine
ECU	engine control unit
EGR.....	exhaust gas recirculation
SOI.....	start of injection
SOF.....	Soluble Organic Fraction (of particulate matter)

Introduction

Diesel aftertreatment typically requires the creation of a locally oxygen-depleted condition in the catalyst or combustion chamber environment to effect the reduction of oxides of nitrogen (NO_x). This requirement has led to the development of different approaches which can be broadly grouped into three categories: 1) NO_x trapping and “batch” regeneration, as with a NO_x adsorber catalyst [also lean NO_x trap (LNT) or NO_x storage and reduction catalyst (NSR)]; 2) hydrocarbon selective catalytic reduction (HC SCR), or lean NO_x catalysis; and 3) engine-based NO_x reduction strategies such as high EGR and high-efficiency clean combustion (HECC). The HC species created in each of these categories is dependent upon the particular fuel that is used as well as the specific strategy employed to introduce the HC to the exhaust.

The Fuels, Engines and Emissions Research Center (FEERC) at the Oak Ridge National Laboratory (ORNL) has had an active program in the HC speciation of diesel exhaust since 1997, with particular emphasis on diesel aftertreatment systems. This report will present available FEERC data collected on light-duty and medium-duty engines equipped with each of the three categories of diesel aftertreatment in order to guide the development of relevant HC mixes for bench scale studies of diesel aftertreatment. Charts will be used to illustrate general trends in this report and a complete data set is available in tabular form in the Appendix.

Regenerative catalysts

Lean NO_x traps (LNTs) trap or store NO_x during lean operation and then typically utilize periodic fuel-rich events to desorb and convert trapped NO_x to N₂. The strategies used to create these conditions will likely encompass both in-cylinder techniques as well as in-pipe introduction of fuel HCs. ORNL-FEERC personnel have studied both of these strategies on a light-duty and medium-duty engine.

The light-duty engine project is titled Measurement and Characterization of NO_x Adsorber Regeneration and Desulfation (MCNARD) and involves the use of a Mercedes-Benz 1.7 L turbocharged, direct-injection engine equipped with a full-pass engine control. The engine control system allows multiple injection events as well as periodic changes in the main injection event, throttling of the intake, and control of EGR to create the periodic fuel-rich conditions necessary to regenerate the LNT. The medium-duty project is a Cooperative Research and Development Agreement (CRADA) project with International Truck and Engine Corporation (ITEC), focusing on regeneration of LNTs using intake throttling and in-pipe injection of fuel to create rich conditions on a 7.3 L engine. Although the CRADA prevents complete disclosure of the data, previously-published information will be shown in this document for trends.

Experimental Description For the light-duty project, two strategies highlighted in this report include a delayed, extended main injection (DEM) and a post injection event (Post 80°) in which additional fuel is injected into the cylinder after the main injection. The engine operating point is 1500 rpm, 5 bar BMEP, and regeneration events are fixed at 60 sec intervals. The engine is equipped with a diesel oxidation catalyst as well as a LNT, as shown in Figure 1. Diesel oxidation catalysts can function as reformers under rich conditions, cracking fuel HC species to lighter, often more reactive compounds. For the

in-cylinder strategies described, high concentrations of H₂ and CO are generated by the engine, are still available at the LNT inlet, and are utilized to release and reduce the trapped NO_x. In these studies, both FTIR and gas chromatography-mass spectrometry (GC-MS) are used to identify the HC species created. Typically, FTIR of raw exhaust (Nicolet REGA 7000 with 10m heated gas cell) is used to identify the C₁ – C₄ HCs created, and GC-MS is used to identify the higher MW species collected in dilute exhaust. For the GC-MS samples, exhaust is diluted with a micro-diluter and samples are collected in a bag over a fixed number of regeneration cycles, usually 5-10. The bag samples are then concentrated using an Entech 7100 pre-concentrator which focuses the HC species at the head of the GC column for analysis.¹

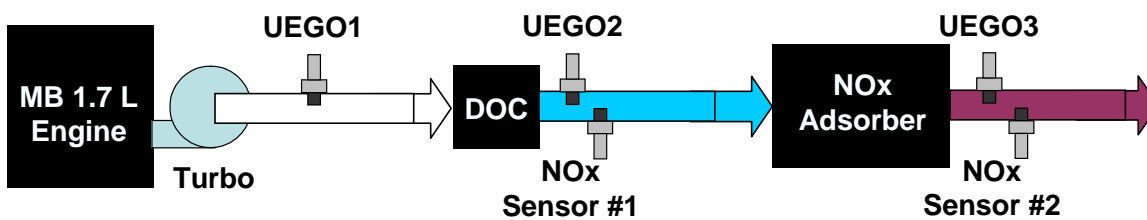


Figure 1. Schematic of LNT system . Samples described in this report were obtained downstream of the turbo.

Figure 2 illustrates the variation in species obtained with each strategy. Despite similar nominal air-fuel ratios, the DEM produces less total HC analyzer (FID) signal because more fuel HC is being converted to CO, H₂ and soot carbon in-cylinder. In addition, the lightest HC species in the DEM account for most of the HC concentration reported by the FID, which supports the idea of significant fuel reforming occurring in-cylinder. Conversely, the Post 80° injection has a large quantity of “other” HCs which represents hundreds of individual compounds, typically fuel HCs and cracking products over the boiling range of the fuel.

HCs resulting from the DEM strategy

This strategy employs throttling as well as a broader main injection to create rich conditions in the exhaust. Compounds created under these conditions include greatly increased concentrations of those HCs typically found in lean diesel exhaust such as ethene, propene, formaldehyde and acetaldehyde. In addition, high concentrations of methane and ethyne (a.k.a. acetylene) are produced, *which are typically very low in lean exhaust*. Figure 3 shows the *average* concentration of the top 4 HCs as a function of indicated air-fuel ratio for normal lean operation and DEM regeneration. Note that the *peak* concentration is likely 20X as high, because the engine is fuel-rich for only 3 sec out of every 60 sec. Typically, a rich air-fuel ratio is required to sustain the high performance of the LNT catalyst. The ethyne increases 30-fold over the base lean operation. In addition to being a potent soot precursor, the triple bond will likely cause the compound to have different properties on the catalyst. On the other hand, the methane is likely to be non-reactive in a catalyst system, or require significant energy to reform. These factors are critical to consider when designing benchflow reactor experiments for LNT research.

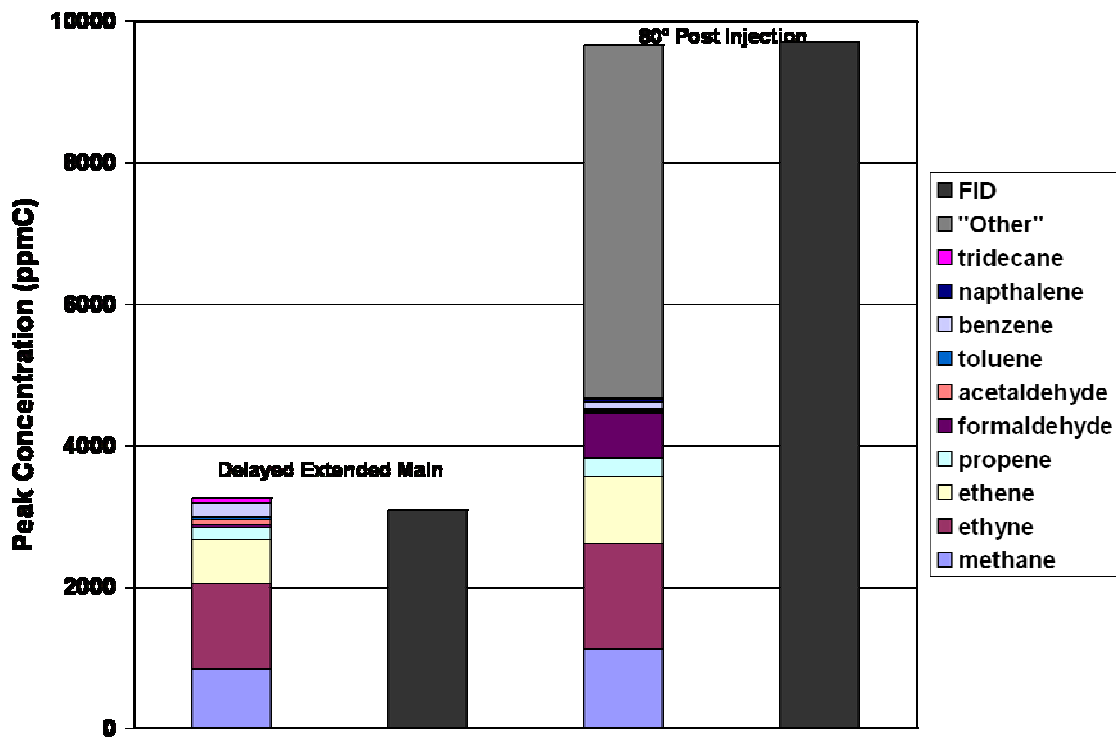


Figure 2. Major HC species obtained with DEM and Post Injection at 80° ATDC. Note that the total HC signal (FID, above) is accounted for by only 10 compounds for the DEM strategy

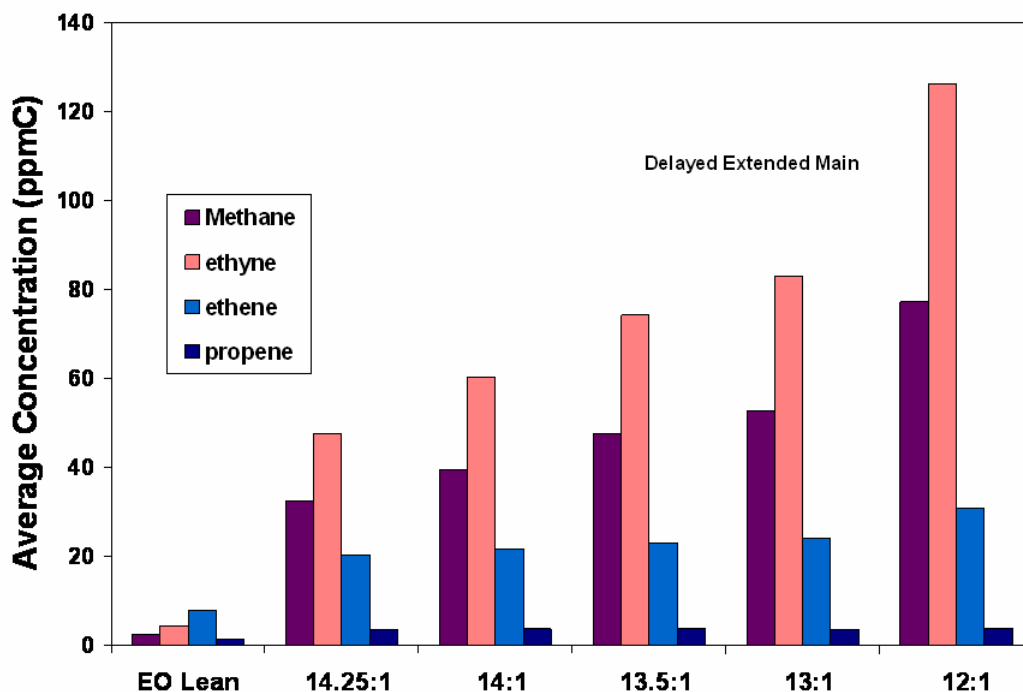


Figure 3. Delayed, extended main injection for periodic rich operation results in high amounts of short chain HCs. EO lean air-fuel ratio is 34:1.

HCs resulting from post-injection strategy

Post injection utilizes additional fuel injection after the main injection to create rich conditions. In order to contrast regeneration strategies in MCNARD, a post injection condition was chosen that resulted in a different reductant pool for the LNT, as shown in Figure 2. The post 80° strategy was chosen after assessing the HCs from a sweep of post-injection timing. Figure 4 shows how this sweep of post injection timing identified a significant difference in some of the HC species occurring beyond about 75° ATDC. At earlier post injection events, the species pool is closer to that of DEM, with H₂ and CO dominating. After 78°, the total HC increases dramatically, despite the same amount of excess fuel being used. Figure 5 shows a plot of average concentration values for the lightest HC species for the Post 80° injection strategy at different A/F values. Note that the scale is the same as in Figure 3. Unlike the DEM strategy, air-fuel ratio has little effect on the concentration of these components. Both Figure 3 and Figure 5 illustrate the importance of considering regeneration strategy when designing a HC species pool for modeling and bench reactor studies. Appendix A.1 has all of the available species data for these two strategies.

- Lighter compounds increase between 70 & 80 deg
- Heavier compounds remain flat throughout timing sweep

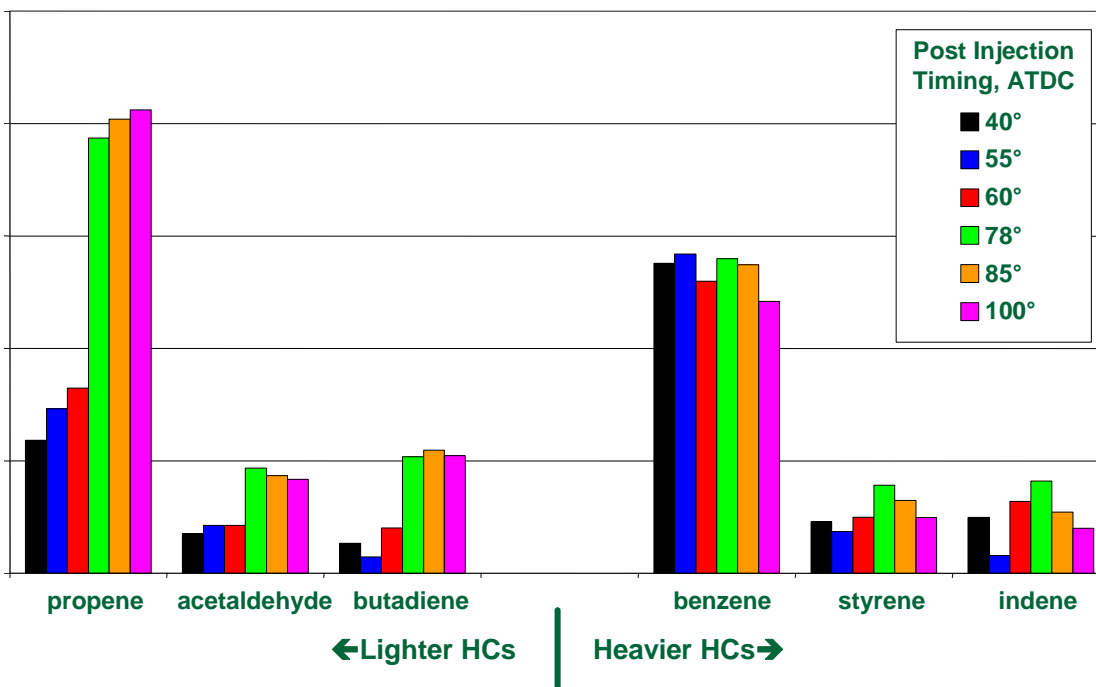


Figure 4 Post injection timing sweep increases light HCs with advanced timing of post injection. Scale is relative abundance using GC/MS.

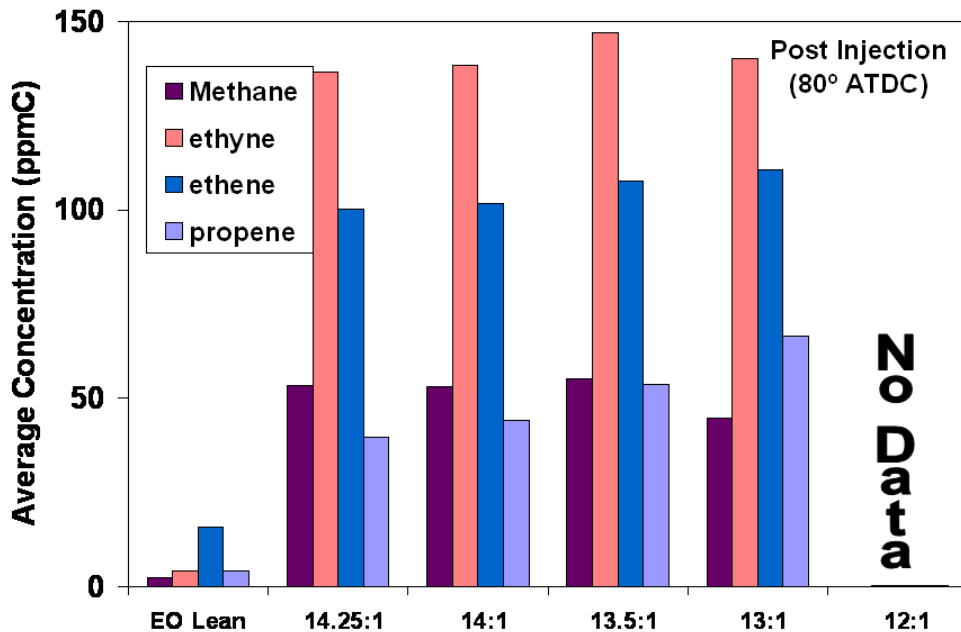


Figure 5. Air-fuel ratio sweep for Post 80° Regen

HCs resulting from in-pipe injection strategy

The ORNL/ITEC LNT CRADA project at FEERC focuses on using in-pipe injection and engine throttling to create periodic fuel-rich conditions for regeneration. While many of the details are protected under terms of the CRADA, the important influences of fuel and pre-NO_x-adsorber treatment including the use of a diesel particulate filter (DPF) and/or a diesel oxidation catalyst (DOC) have been approved for release and were presented at DEER in 2003². Figure 6 shows a schematic of the exhaust setup for these experiments. Figure 7 compares chromatograms of the dilute exhaust from an operating point under the same conditions. This shows the extent of cracking when a DOC is used ahead of the CDPF and LNT. The exhaust is sampled just prior to the LNT in both cases. The rich pulse traveling over the DOC causes cracking of the fuel and subsequent production of light HCs which appear to be better utilized by the LNT. In Figure 5, the large HC “hump” from 20-30 minutes elution time in the GC column gets much smaller, and the concentrations of C₄, C₅, and C₆ alkanes and alkenes increase dramatically. In some ways this is comparable to the Post 80° in the light-duty case described previously, except that it is a much later injection event (actually in-pipe raw diesel fuel).

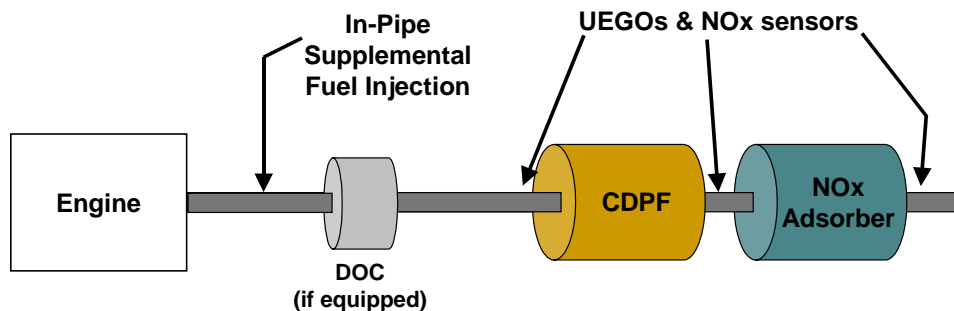


Figure 6. Schematic of in-pipe regeneration system for a LNT

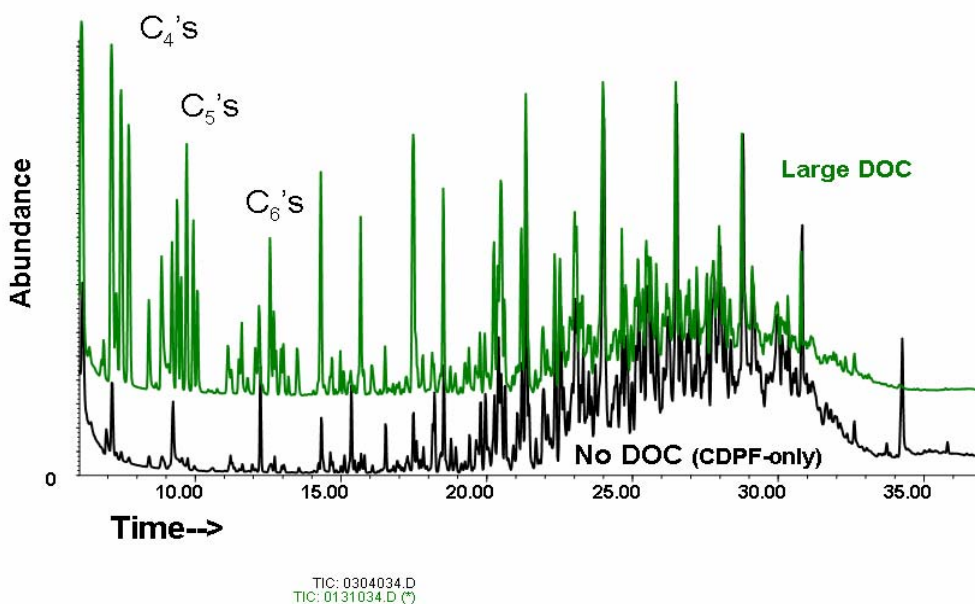


Figure 7. GC/MS trace of diluted exhaust from 7.3L International T444E. Engine was at rated speed, 2300 RPM, 450 ft-lbs. ECD-1 fuel was injected into the exhaust pipe upstream of the CDPF or DOC. Each spike represents a different chemical compound separated by the GC.

In Figure 8, the influence of fuel chemistry is shown qualitatively on the make up of the HC species created by in-pipe injection and the DOC under rich conditions. Both the DECSE 3 ppm S fuel and ECD-1, or fuels like them, are potential 2007 on-road fuels. DECSE has less sulfur by taking a narrow cut and then blending back in aromatics and other compounds to get the aromatic content and distillation curve to match certification diesel fuel. ECD-1 is made by deeper hydrodesulfurization which results in a lower aromatic content and more paraffinic structures. In Figure 8, the ECD-1 fuel creates a broader range of HCs at the inlet of the LNT catalyst, likely due to the larger number of compounds in the base fuel. Whether or not HC species diversity has much influence on aftertreatment performance is very dependent upon other conditions – the type of LNT, the temperature of the exhaust gas, and the overall air-fuel ratio are among the key parameters which can affect LNT performance.

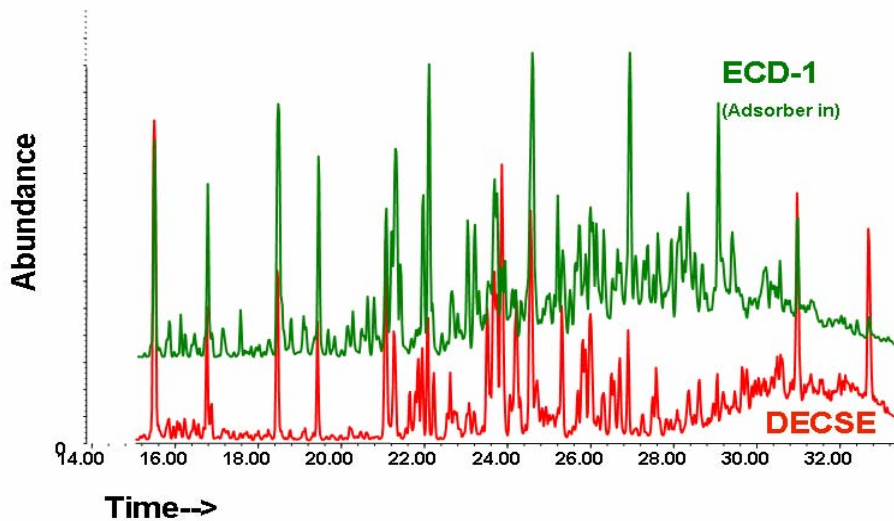


Figure 8. GC/MS trace of diluted exhaust from 7.3L International T444E. Engine was at rated speed: 2300 RPM, 450 ft-lbs. ECD-1 fuel and DECSE fuel were injected into the exhaust pipe in the same quantity.

Propene is often used as a model HC in many NO_x catalyst studies. Fortunately, propene is found in normal raw diesel exhaust, but certainly its use in the laboratory is also driven by the convenience of using a bottled gas. In many ways, propene is an idealized reductant because it is a reactive, small molecule and relatively little energy is required to convert it to H₂ and CO, which are critical for LNT function. In Figure 9, the relative amounts of propene production are shown as a function of pre-treatment and fuel amount. The samples were taken at the LNT inlet. With the CDPF only, as little as 1 ppm propene is measured (average FTIR concentration, 27s lean, 3s rich). In contrast, with the large DOC and the higher fueling rate, 20 ppm propene is measured. Note that very little of the propene exits the LNT, indicating high usage. As in Figures 3 and 5, the concentration is the average over the rich and lean periods, so the peak concentration is closer to 10X the value shown.

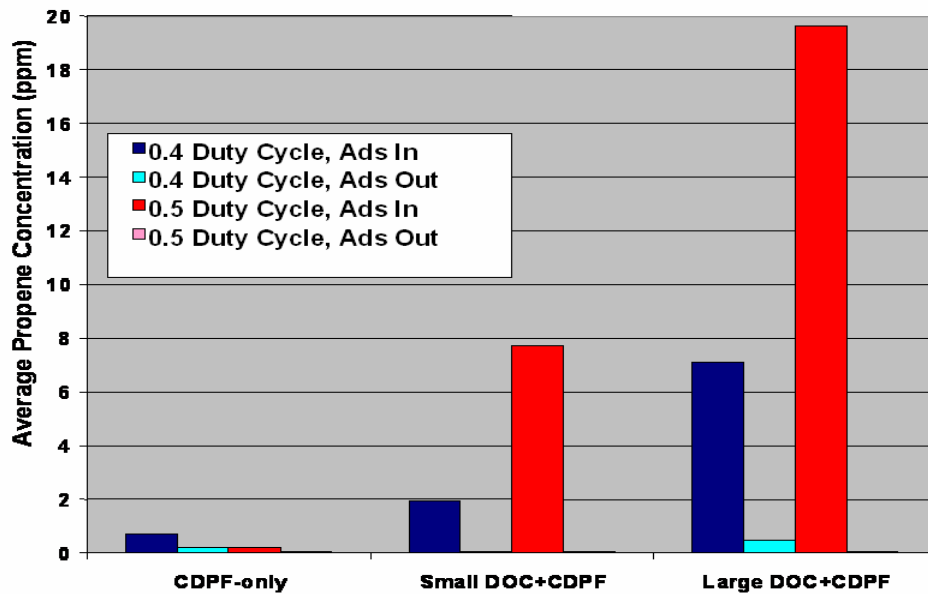


Figure 9. More aggressive oxidation catalysts promote propene formation, which is readily used by LNT catalyst. Data from FTIR, raw exhaust. Duty cycle refers to fractional time of injection.

Lean NOx Catalysis and Selective Catalytic Reduction

In lean NOx catalyst systems, HCs, typically fuel, are added to the exhaust continuously to provide reductant for the catalyst to convert NOx to N₂. No throttling is used and the overall air-fuel ratio remains lean, in contrast to LNT systems. Although these systems were among the first to be developed,³ their poor performance (20%-40% NOx conversion) and tendency to make N₂O at light-duty temperatures made the higher performing urea-SCR and LNT systems more attractive. Recently, though, advances in engine controls have lowered the requirements for the aftertreatment, making lean NOx systems and their relative simplicity more attractive. Our discussion here focuses not on the catalyst, but on the HC pool that can be created under a variety of conditions through in-pipe or late post injection.

Experimental description – lean NOx

In these experiments, a 1994-spec Navistar T444 7.3L engine was modified to enable a second, late injection of fuel from 120° ATDC to 280° ATDC. In addition to in-cylinder injection, the exhaust was also fitted with an automotive fuel injector to allow in-pipe injection of diesel fuel. In either case, excess fuel delivery was continuous, not periodic as with the LNT). Because this was a 5 g/bhp-hr engine, a considerable mass of fuel was required to get the desired HC/NOx ratios of 3:1, 6:1, and 9:1, thought at the time to be the most useful for lean NOx catalysis. Nonetheless, the exhaust conditions were overall still very lean (in contrast to the LNT work described in the previous section). Engine conditions were the peak torque speed, 1900 rpm, at 0%, 20%, 40%, 60%, 80% and 100% load, and at the rated speed of 3000 rpm for 20%, 40%, 60%, 80% and 100% load. Fuel was Phillips No.2 certification diesel fuel. Bag samples were taken from a mini-dilution tunnel and concentrated on a glass cartridge containing Tenax™ beads. These

cartridges were then thermally desorbed into the GC with cryo-focusing of the analytes on the front of the GC column. This method is similar to the method used by Ford to analyze exhaust HC species from a series of light-duty vehicles.⁴ Additionally, DNPH cartridges were used to examine the aldehyde concentrations at many of these engine points. Semivolatile HC species were trapped on Empore™ C-18 membrane separation disks and analyzed using a method previously described.⁵

Results – lean NOx catalysis

A series of experiments were conducted to determine the optimum position of the post-injection. The most promising positions were 120° ATDC and 220° ATDC, with the latter providing the highest HC/NOx ratio for a given injection amount. Figure 10 shows the difference in typical species, a light alkene, an aromatic, and a fuel-like alkane. Note that the earlier injection produced more propene (propylene on the chart) and less decane, Figure 10 indicates that more fuel cracking was occurring with the earlier injection, which is expected due to the higher temperature and pressures at the earlier crank angle.

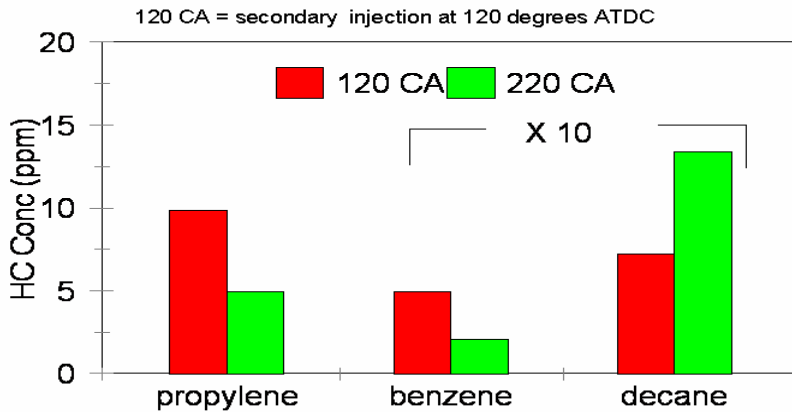


Figure 10. Representative HC species produced during post injection of fuel under lean conditions. Engine at 1900 rpm, 60% load . Overall HC concentration ~ 1200 ppmC

The in-pipe injection gave a different HC mix which looked primarily like the fuel profile. To compare the in-cylinder and the in-pipe injection, the same total HC concentration was maintained with either the in-cylinder or in-pipe injection. Figure 11 shows the differences with three representative compounds. The benzene is a cracking product of aromatics in the fuel since there was very little benzene in the fuel itself.

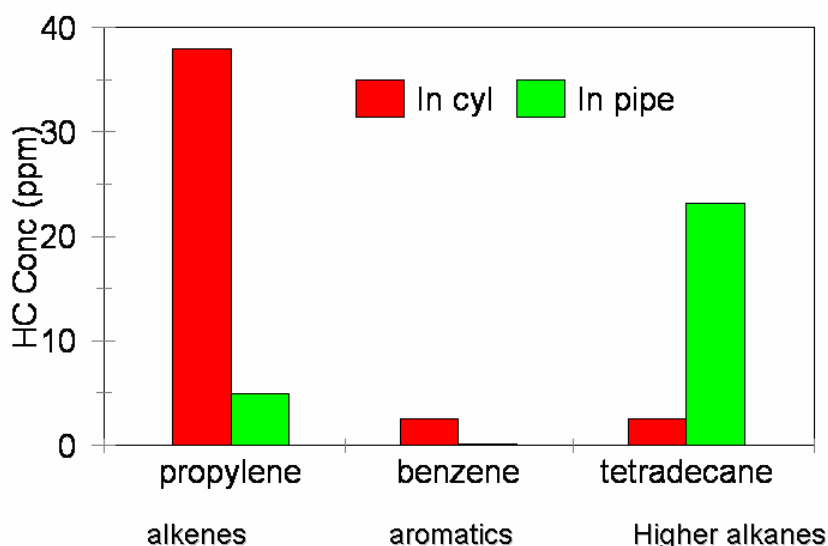


Figure 11. In-cylinder vs. in-pipe injection at 1900 rpm, 100% load

Table 1 summarizes the overall breakdown of HC species for the experiments. Higher loads, and thus higher temperatures, resulted in more cracking taking place, which accounts for the ranges of values. Appendix A.2 contains an extensive listing of all of the HC species for the various loads and speeds.

Compounds	Fraction of total HCs	
	HC in-cyl	HC in-pipe
	(percentages change with load)	
Alkenes (e.g. propylene)	20-50%	1-5%
Higher alkanes (> heptane)	10-20%	30-50%
Branched alkanes	5-15%	10-30%
Mono-aromatics (e.g. benzene)	5-50%	5-25%
Oxygenated aromatics (e.g. phenol)	0-5%	0-5%
Aldehydes (> propanal)	0-5%	0-5%
Napthalenes, PAHs	5-10%	1-10%

Table 1. Breakdown of HC species observed from the addition of fuel to exhaust

Urea-SCR HC species

ORNL's experience with urea SCR systems has shown that there are frequently very low levels of HCs present in the exhaust. Because most urea SCR systems utilize a DOC to achieve a mixture of NO and NO₂ prior to the SCR catalyst, the concentration of HC species is very low. Furthermore, the zeolite-based SCR formulations for light-duty applications are sensitive to HC poisoning, so it is important that these levels are low.

Engine-based NO_x reduction: HC species found during high-efficiency, clean combustion (HECC)

In the past five years, advances in electronic engine controls and high-pressure common rail fuel injection have enabled new combustion modes that result in very low engine-out NO_x with simultaneous reduction in PM. The ORNL-FEERC has been examining the use of EGR and ignition timing to effect low NO_x, low PM combustion.^{1,6} The most

recent study examined the HC species that resulted from this mode of operation.¹ In general, increasing EGR and/or timing retardation with EGR resulted in an increase in partially-oxygenated HCs and the formation of unsaturated HCs.

Experimental description – HECC

This study was performed using a modified Mercedes-Benz 1.7 L turbocharged, direct-injection compression ignition engine (OM668). The factory engine control unit (ECU) was replaced with a rapid prototype control system to allow departures from the factory engine calibration. Although similar to the Mercedes engine used for the An intake throttle was added to the engine to provide higher exhaust gas recirculation (EGR) rates than was possible with the factory engine configuration. Finally, a production EGR cooler (heat exchanger) was added to cool the EGR gases using engine coolant. The engine was installed on an eddy-current dynamometer. The fuel used in all of the HECC experiments presented in this report was a low-aromatic (10 wt%) California certification diesel fuel.

As in previous work at ORNL with these combustion regimes, two approaches were used to achieve low-NO_x, low-PM combustion.⁵ Table 2 shows the operating conditions for both approaches. In the first approach, EGR rate was swept by opening the EGR valve until it was fully open. When the EGR valve was fully open, EGR was further increased by gradually closing the intake throttle to restrict fresh air intake. No changes were made to the fuel injection strategy to enter this combustion regime, but fuel injection changes were used to provide a means for recovering power and fuel economy losses resulting from operating at the higher EGR levels.⁵ The rate of fuel injection was fixed at the baseline condition (0.5cc/s). As the EGR rate increased, the apparent air/fuel ratio decreased but remained lean of stoichiometry at all times.

The second approach achieved low-NO_x, low-PM combustion in a different manner. First, the EGR valve was again opened to the fully open position to allow operation at a higher EGR level. At this point, the main injection timing was gradually retarded. The intake throttle was left completely open. In this case, load and fuel economy recovery utilized a higher fuel injection rail pressure.⁵ Once again, the fuel rate was fixed at the baseline condition (0.5cc/s). Apparent air/fuel ratio changed as the EGR valve was opened fully, then remained constant at a point lean of stoichiometry.

Table 2. Engine Operating Characteristics

Characteristic	Approach 1	Approach 2
Base Torque, lb-ft	25	25
Speed, RPM	1500	1500
Rail Pressure, Bar	334	334
Main PW, ms	0.592	0.592
Main Timing, CAD	2 BTDC	Varies
Pilot PW, ms	0.270	0.270
Pilot Gap, ms	1.8	1.8
EGR Rate, %	Varies	Varies

A microdiluter device was configured to provide a dilute (non-condensing) exhaust stream for analyzing exhaust chemistry. Various samples were extracted from the diluted sample stream and trapped for off-line analysis. DNPH cartridges were used to capture aldehydes and ketones in the dilute exhaust stream for analysis. Tedlar™ bags were used to collect dilute samples which were then analyzed with the Entech 7100 as described above. A supercritical CO₂ extraction technique was utilized to remove non-polar soluble organic compounds from the particulate sample filter. The extraction method exposes the sample filter to CO₂ at a pressure of 335 atmospheres and a temperature of 80 °C for 10 minutes. The extracted solubles were collected in dichloromethane and analyzed by GC/MS. The FTIR was unavailable at the time of this study, so no C₁ – C₄ HC information is presented with the exception of the aldehydes.

Results – HC speciation during HECC

Figures 12 and 13 illustrate the decrease in NO_x and PM observed for Approach 1 and Approach 2, respectively. The total HCs continue to increase, even when the PM drops.

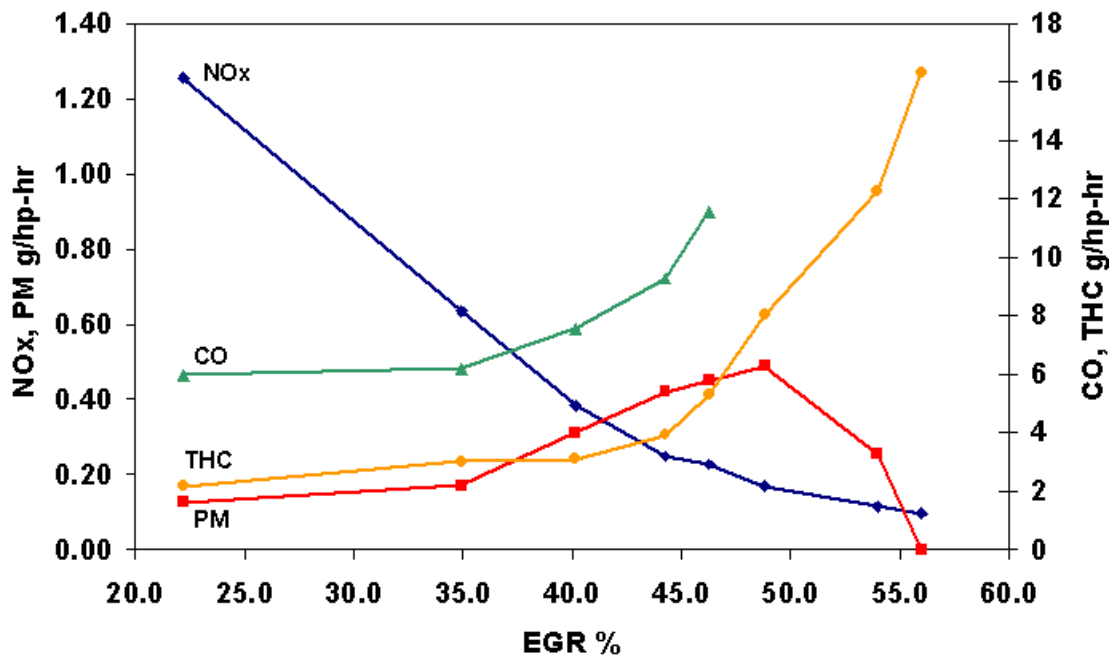


Figure 12. NOx, PM, CO, and THC emissions for Approach 1.

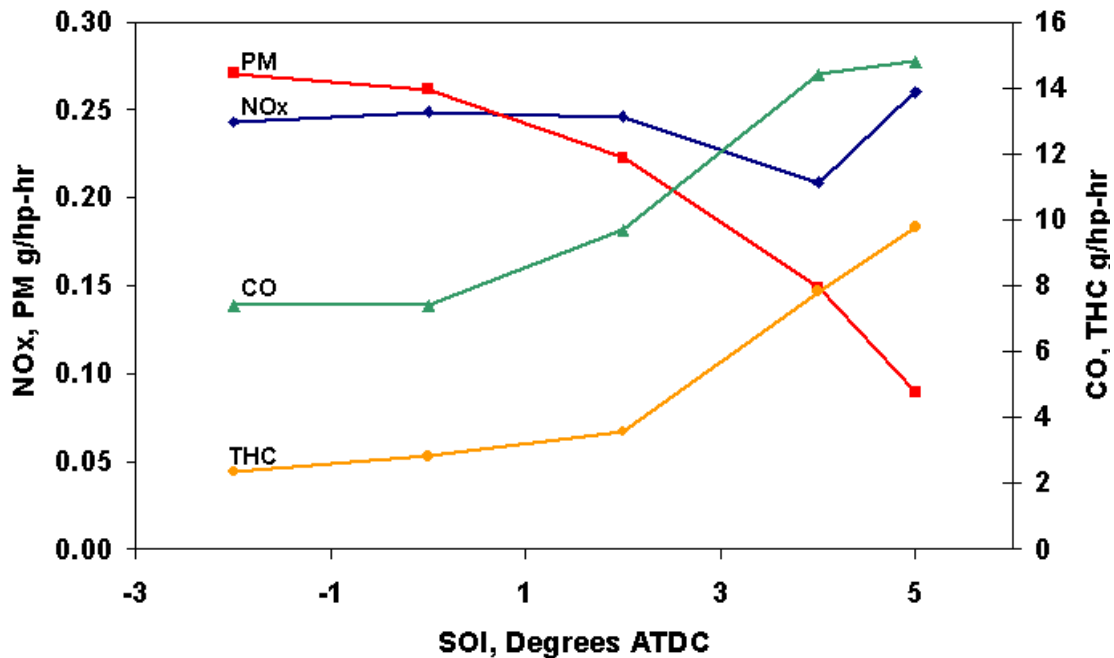


Figure 13. NOx, PM, CO, and THC emissions for Approach 2.

The HC speciation results will therefore refer to Approach 1 and Approach 2. Because standards were not available for all compounds, the following results for gaseous HCs refer to relative abundance based on integrated peak areas from the GC-MS results. In Appendix A.3, raw exhaust concentration values for those species with available

standards are given for the two different approaches. The graphs are provided here to illustrate the important changes in HC species that can occur with the onset of HECC.

Results from the GC-MS analyses of sample bags collected with Approach 1 are shown in Figure 14. Results are normalized to the baseline so that the baseline case shows a result of 1 for each compound. The 44.3% EGR case is missing because of an analytical problem with the collected sample. As the EGR rate increases, the normalized emission rate of benzene and naphthalene increases considerably, without displaying any significant effects on NO_x and PM emissions (see Figure 12). Propene is a product of hydrocarbon-cracking that takes place during the combustion and fuel reformation processes, and increases steadily until the engine transitions between combustion modes. At the transition point, the emissions of propene no longer increase but remain relatively steady. Cyclopentadiene has never been observed by the authors in other diesel exhaust speciation projects. It is likely formed by cracking of fuel paraffins. Cyclopentadiene is distilled commercially from the light oil ends of coke manufacturing.⁷

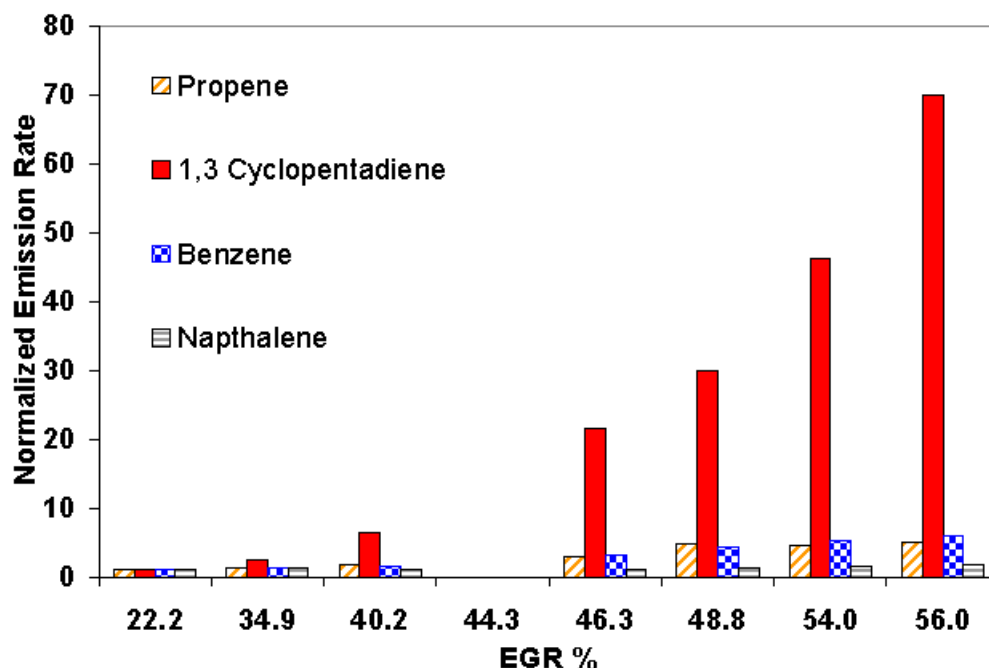


Figure 14. Relative abundance of selected HC species in Approach 1

The normalized emission rate of cyclopentadiene increased much faster than the other hydrocarbons species with increasing EGR rate. As the GC/MS response factors for several of these compounds were not known, we were not able to determine the absolute emissions levels of these compounds. Therefore although cyclopentadiene exhibited the most significant change with EGR rate, it did not necessarily dominate the overall emission rate of hydrocarbons. The presence of the propene, cyclopentadiene, and benzene are all indicators of fuel cracking and reforming occurring in the engine, despite an overall lean air-fuel ratio. Although a sharp rise in these species was not observed at the transition point, their increase is consistent with a locally rich, lower temperature zone of combustion.

Figure 15 shows the gas-phase hydrocarbons for Approach 2. Cyclopentadiene exhibited a nearly linear increase in its rate of emission and reached a maximum increase of 24 times what was observed at the base engine condition as opposed to a 70-fold increase for Approach 1. Propene exhibited an increase in its emission rate but failed to demonstrate a marked change with the transition to low-NO_x, low-PM combustion in Approach 2. Increases in benzene and naphthalene were much lower than in Approach 1 but generally increased as the SOI was retarded.

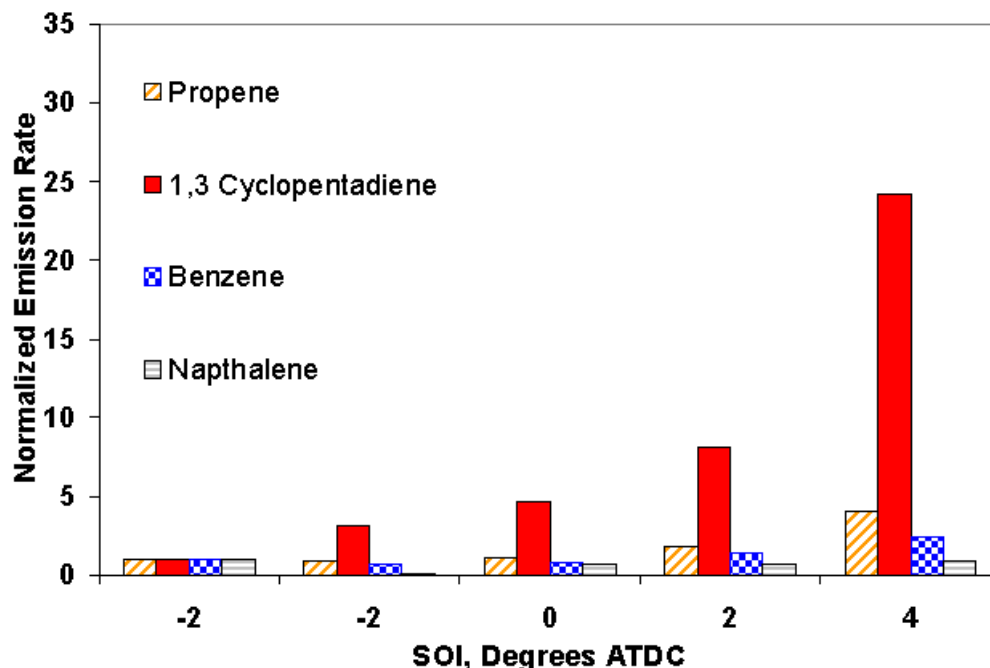


Figure 15. Relative abundance of selected HC species for Approach 2

Because the aldehydes were quantified, it is possible to calculate brake specific values for these species as shown in Figures 16 and 17. Note that the emission rate shown for formaldehyde is divided by 3. In Figure 16, the baseline case (EGR 22%) exhibited some emissions of formaldehyde, acetaldehyde, acrolein, propionaldehyde, and benzaldehyde. The emissions of all of these compounds initially decreased as the EGR rate increased. The reason for this decrease is unclear. A possible explanation is that the aldehydes began to adhere to the increasing particulate emissions, which prevented them from being trapped on the DNPH cartridges for analysis. Also note that emissions of the higher molecular weight aldehydes did not drop as much as those of acetaldehyde and formaldehyde. The emissions of aldehydes increased once the engine entered the low-NO_x, low-PM combustion regime. This increase was particularly dramatic for formaldehyde and acetaldehyde but was also observed for benzaldehyde, propionaldehyde, and acrolein. The rapid increase in partial oxidation products is a clear signal that different combustion phenomena are occurring. High aldehyde emissions would be consistent with a low-temperature combustion regime.

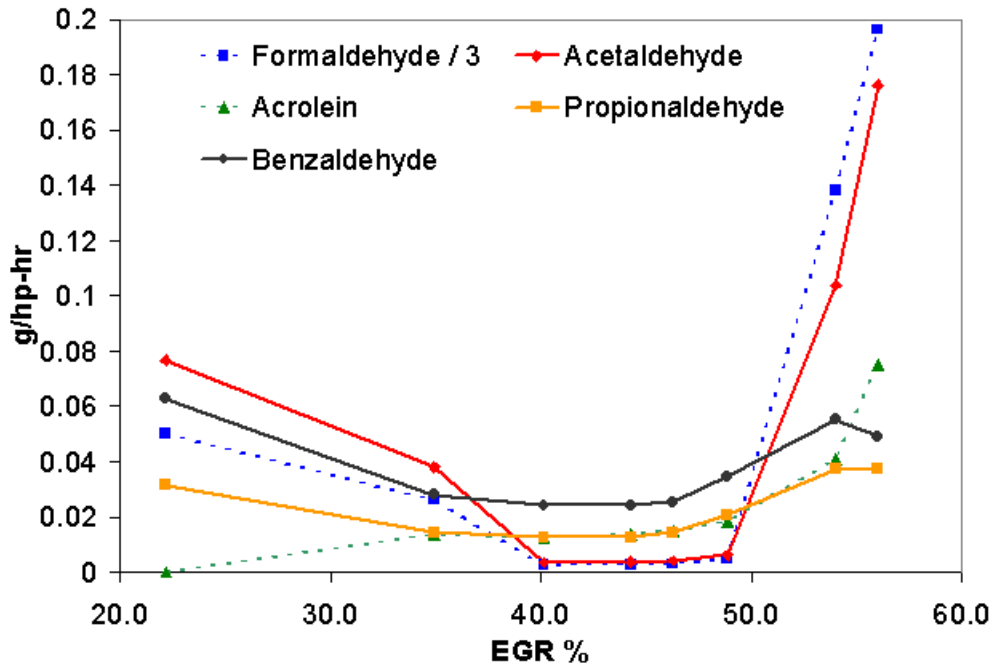


Figure 16. Brake specific aldehyde emissions for Approach 1

Figure 17 shows the aldehyde results for Approach 2. The vertical scale in Figure 17 is half that of Figure 16. As with Approach 1, aldehyde emissions drop to a very low level when the EGR valve is in its maximum open position. Retarding the SOI caused the emissions of aldehydes to rise, with acetaldehyde and formaldehyde emissions exhibiting an inflection point at 2° ATDC.

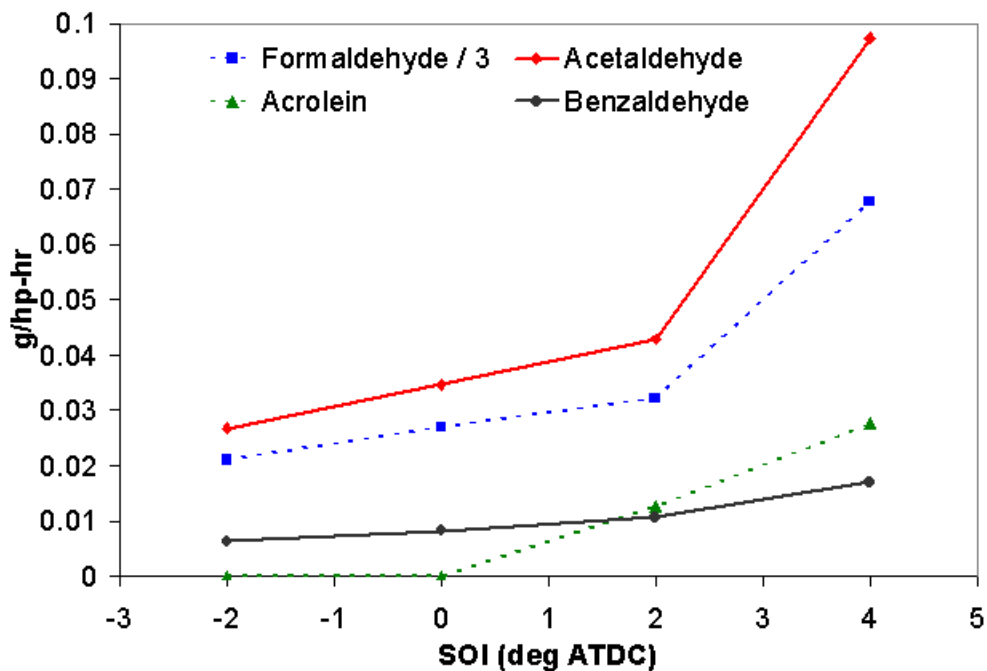


Figure 17. Brake-specific aldehyde emissions from Approach 2

Comparing the aldehyde emissions from the two approaches shows that the emissions of formaldehyde and acetaldehyde were more than 6 times higher for Approach 1 as compared to Approach 2, with formaldehyde being the dominant species for both approaches. Benzaldehyde and acrolein emissions were also lower for Approach 2 than for Approach 1. Propionaldehyde emissions were undetectable for most conditions used in Approach 2. Overall, the formation of aldehydes is an indicator of the partial oxidation of the fuel hydrocarbons. Both approaches demonstrate an increase in aldehyde emissions as the engine enters a low-NO_x low-PM combustion mode. The change in aldehyde behavior is sudden for Approach 1, as if the engine passed through a critical threshold that separated the two regimes. The transformation by Approach 2 is more gradual, possibly indicating a weaker transformation in combustion than was observed for Approach 1. This hypothesis is also supported by the generally lower levels of aldehydes observed for Approach 2 as compared to Approach 1.

A number of the SOF extracts were analyzed by GC-MS. Fluoranthene and pyrene were examined as representative PAH. Nonadecane was selected as representative unburned fuel hydrocarbon. GC-MS results for these compounds were cast as a pseudo-brake specific measurement by multiplying the mass abundance signal by the dilution ratio for the sample by the exhaust flow rate for the sample, and then dividing by the engine power for the sample. The resulting data were then normalized to the baseline condition. These results for Approach 1 are shown in Figure 18.

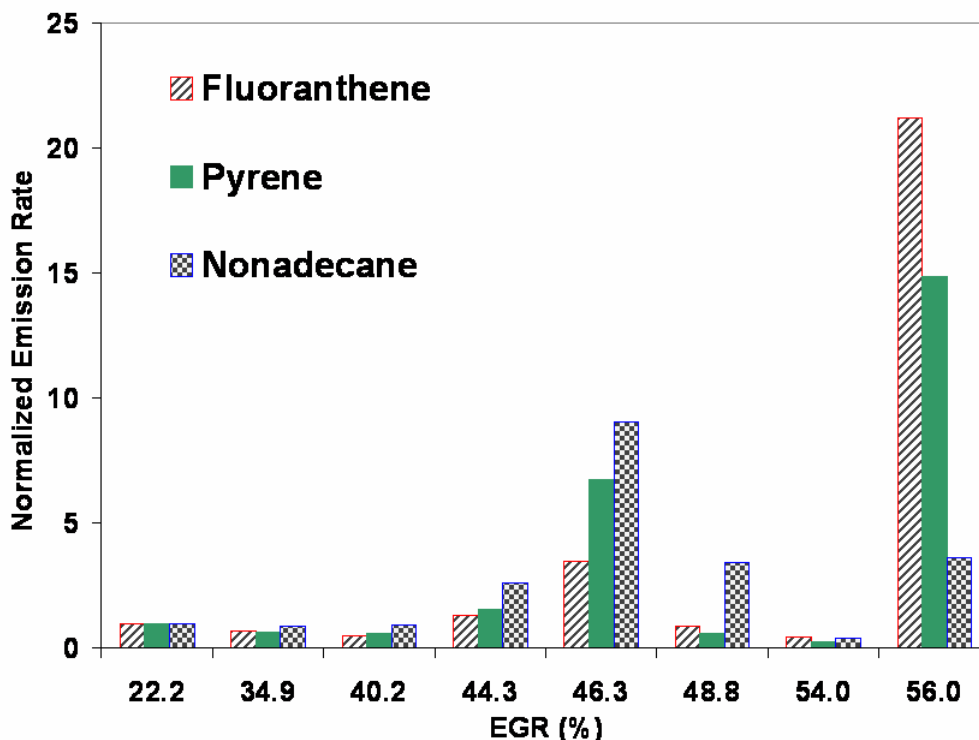


Figure 18. Representative SOF compounds for Approach 1

The total mass of SOF increased nearly linearly from 30% SOF at 46% EGR, to 70% SOF at 56% EGR. This increase indicates that there was a significant amount of the SOF emissions that was not well accounted for by this subset of the SOF compounds.

Moreover, these “missing” compounds must be of increasing importance as EGR increases from 46% to 56%. Benzo(ghi)fluoranthene was detected at the 46% EGR condition, but was not detected at other conditions. The “missing” SOF is most likely a collection of higher molecular weight partial oxidation products, such as long chain aldehydes and carboxylic acids. GC methods designed for PAH and fuel HC determination would not necessarily be very sensitive to polar and/or oxygenated compounds. In addition, the high increase in PAH for 56% EGR may indicate that a transition to a soot precursor regime has occurred. In other words, the lack of PM at this point (Figure 12) may be due to incomplete formation of soot and thus an abundance of soot precursors like PAH.

GC-MS analysis of the SOF extracts from Approach 2 showed that the soluble extract was composed principally of fuel alkanes and cracking products. Pyrene and fluoranthene were present but quickly disappeared as SOI was retarded. Nonadecane decayed as SOI was retarded, perhaps because of in-cylinder cracking of the longer-chain fuel hydrocarbons. Once again since the total SOF mass is increasing, there must be additional compounds that account for the mass since the cracking products and nonadecane are decreasing.

Overall, the transition to a low NO_x, low PM mode causes many changes in the HC profile of the exhaust. Total HCs are increasing, and the amounts of lighter species are indicative of extensive cracking of higher molecular weight compounds. Partial oxidation of HCs also occurs in this mode. This research was conducted at only one low load condition (1500 rpm, 2.6 BMEP); the HC species may well change under different load conditions. The results imply that aftertreatment requirements will likely change as engines operate more and more in the low NO_x, low PM modes. With “natural” HC:NO_x ratios > 100 and high CO, the possibility exists that new types of HC SCR lean NO_x devices, or entirely new catalyst systems can be employed to exploit the available reductants.

Summary and Conclusions

This report was intended to illustrate the variation in HC species that can exist in diesel engine exhaust when a variety of NO_x control methods are used. A set of appendices are included to give as much specific information on individual species as possible. Some specific conclusions are:

- The required increase in HCs for reduction of NO_x overwhelms the low concentrations of HC species that are present in conventional diesel engine exhaust
- Fuel composition as well as HC introduction strategy influences greatly the composition of the HCs in the exhaust
- A HC mix designed to simulate diesel exhaust for NO_x adsorber catalyst research will need to alternate between a baseline exhaust mix (lean operation) and high concentrations of CO, H₂, and fuel cracking products such as ethene and propene
- A HC mix designed to simulate diesel exhaust for lean NO_x catalyst research requires a constant mix much higher in HCs than lean diesel exhaust

- Engine strategies that reduce NO_x, such as HECC produce very different HC species and often much higher concentrations than conventional diesel exhaust

Because so many devices and strategies will likely use a finishing oxidation catalyst, the work presented here is by no means intended to describe tailpipe emissions, but rather the HC species that must work in concert with the aftertreatment to reduce NO_x.

Acknowledgements

This document summarizes much of the effort of past and current FEERC Staff. Their contributions were all critical to the creation of this report. The authors would like to thank the Coordinating Research Council for their support of this project. The Oak Ridge National Laboratory is operated for the Department of Energy under contract no. DE-AC05-00OR22725.

References

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- ¹ Sluder, C.S., Wagner, R.M., Lewis, S. A., and J. M. Storey, "Exhaust Chemistry of Low-NoDx, Low-PM Diesel Combustion," *SAE 2004-01-0114*. Society of Automotive Engineers. 2004.
- ² West, B.H., Thomas, J., Kass, M., Storey, J., Lewis, S. A. "NO_x Adsorber Regeneration Phenomena In Heavy Duty Applications - ORNL/ITEC CRADA," *Proceedings of the 9th Annual Diesel Engine Emissions Reduction Conference*, Newport, RI. 2003. Available online at <http://www.ornl.gov/deer/DEER2003/presentations.htm>
- ³ Farrauto, R.J.; Deeba, M.; Feeley, J.S. "Technical challenges in the development of lean-NO_x catalysts for mobile sources." *Motor Vehicles and the Environment - Demands of the Nineties and Beyond*, in Proceedings of the 27th International Symposium on Automotive Technology and Automation, Pergamon Press, 1994, p 39.
- ⁴ Hammerle, R.H., D.A. Ketcher, R.W. Horrocks, G. Lepperhoff, G. Häxthwohl, B. Läxers. "Emissions From Current Diesel Vehicles," *SAE 942043*. Society of Automotive Engineers. 1994.
- ⁵ Storey, J. M. E., Lewis, S.A., Domingo, N, and D.K. Irick, "Analysis of Semivolatile Organic Compounds in Diesel Exhaust Using a Novel Sorption and Extraction Method," *SAE 1999-01-3534*, Society of Automotive Engineers. 2004.
- ⁶ Wagner, R.M., Green, Jr., J.B., Edwards, K. D., Storey, J. M., and T.Q. Dam, "Simultaneous Low Engine-Out NO_x and Particulate Matter With Highly Diluted Diesel Combustion," *SAE 2003-01-0262*, Society of Automotive Engineers. 2003.
- ⁷ The Merck Index, 11th Edition, p.428. Merck & Co., Rahway, 1989.

Appendix A.1.

Average Concentrations over 10 regen cycles: rich for 3 sec, lean for 60 sec

FTIR data ppmC values	Concentrations in ppmC						Note: Aldehyde data is suspect due to carryover in sampling lines		
	CH4	C2H2	C2H4	C2H6	C3H6	13BU	H2CO	MECHO	CO
Post 80 Air:Fuel Ratio sweep	Methane	ethyne	ethene	ethane	propene	1,3Butadiene	Formaldehyde	acetaldehyde	CO
Engine Out, 46 scans, 10 spectra, engine out lean	EO Lean	2	4	16	0	4	3	13	7 190
Engine Out, 46 scans, 10 spectra, engine out 14.3:1 w/ cell scan	14.25:1	53	137	100	13	40	16	37	22 1071
Engine Out, 46 scans, 10 spectra, engine out 14:1 w/ cell scan	14:1	53	138	102	14	44	17	40	24 1064
Engine Out, 46 scans, 10 spectra, engine out 13.5:1 w/ cell scan	13.5:1	55	147	108	16	54	21	43	34 1119
Engine Out, 46 scans, 10 spectra, engine out 13:1 w/ cell scan	13:1	45	140	111	13	67	27	38	61 1078
no data	12:1	0	0	0	0	0	0	0	0 0

DEM Air:Fuel Ratio sweep	Concentrations in ppmC						Note: Aldehyde data is suspect due to carryover in sampling lines		
	CH4	C2H2	C2H4	C2H6	C3H6	13BU	H2CO	MECHO	CO
Description:	Methane	ethyne	ethene	ethane	propene	1,3Butadiene	Formaldehyde	acetaldehyde	CO
Engine Out, 46 scans, 10 spectra, engine out lean	EO Lean	2	4	16	0	4	1	13	4 189.7
Engine Out, 46 scans, 10 spectra, engine out 14.25:1 w/ cell scan	14.25:1	32	48	41	0	10	1	10	6 1172
Engine Out, 46 scans, 10 spectra, engine out 14:1 w/ cell scan	14:1	40	60	43	0	11	2	16	6 1279
Engine Out, 46 scans, 10 spectra, engine out 13.5:1 w/ cell scan	13.5:1	48	74	46	0	11	1	18	5 1402
Engine Out, 46 scans, 10 spectra, engine out 13:1 w/ cell scan	13:1	53	83	48	0	11	2	21	5 1446
Engine Out, 46 scans, 10 spectra, engine out 12:1 w/ cell scan	12:1	77	126	62	0	12	2	27	5 1712

RPM	% Load	HC:NOx	ethane	ethylene	acetylene	propane	propylene	n-butane	isobutane	1,3 butadiene	1-butene	isobutylene	n-pentane	GC-MS Co 1-pentene
1900	100	none added	0	0	0	0	0	0	0	0	0	0	0	0
1900	90	none added	0	0	0	0	0	0	0	0	0	0	0	0
1900	80	none added	0	0	0	0	0	0	0	0	0	0	0	0
1900	60	none added	0	0	0	0	0	0	0	0	0	0	0	0
1900	40	none added	0	0	0	0	0	0	0	0	0	0	0	0
1900	20	none added	0	0	0	0	0	0	0	0	0	0	0	0
1900	0	none added	0	0	0	0	0	0	0	0	0	0	0	0
1900	100	3:1	1.70	88.82	1.75	0	37.90	0	0	9.04	8.67	5.43	0.00	3540.41
1900	80	3:1	0.00	16.96	0.52	0	7.88	0	0	2.59	1.66	1.42	0.00	1532.69
1900	60	3:1	0.00	9.88	1.10	0.51	4.12	0	0.24	0.00	0.74	0.99	0.00	171.54
1900	40	3:1	0.00	5.97	1.11	0	1.51	0	0	0.00	0.40	0.00	0.00	49.05
1900	20	3:1	0.00	9.07	1.94	0	1.63	0	0	0.41	0.53	0.00	0.00	#N/A
1900	0	none added	0.00	23.93	3.85	0	6.16	0	0	1.55	2.15	0.92	0.00	82.01
1900	100	6:1	4.37	217.59	4.56	0	91.96	0	0	25.43	23.24	13.85	0.00	20892.47
1900	80	6:1	3.04	53.48	1.79	0	25.76	0	0	9.37	4.55	4.28	0.00	2222.03
1900	60	6:1	0.00	6.95	0.00	0	2.85	0	0	1.18	0.60	0.87	0.00	23.41
1900	40	6:1	4.01	7.70	0.00	0	2.39	0	0	0.00	0.00	1.14	0.00	0.00
1900	20	6:1	3.67	8.76	1.90	0	2.10	0	0	0.00	0.00	0.00	0.00	0.00
1900	0	none added	3.85	16.59	3.09	0	3.67	0	0	1.66	1.04	0.00	0.00	#N/A
1900	100	8:1	8.86	501.92	9.77	1.05	168.29	0.52	0	50.17	46.16	27.76	0.00	19269.87
1900	80	8:1	6.25	114.71	0.00	0	51.73	0	0	20.42	9.60	9.20	0.00	8106.03
1900	60	8:1	0.00	20.55	2.77	0	7.03	0	0	3.17	1.50	4.35	0.00	1125.22
1900	40	8:1	0.00	11.07	1.49	0	2.63	0	0	0.94	0.94	3.04	0.00	0.00
1900	20	8:1	0.00	10.28	0.00	0	1.97	0	0	0.00	0.00	0.00	0.00	0.00
1900	100	3:1 in pipe	0	9.48758	0	0	4.935643	0	0	2.19149421	0	0	0	902.4958
1900	60	3:1 in pipe	0	2.50745	0	0	0	0	0	0	0.85385	0	0	131.8019

RPM	% Load	HC:NOx	Compounds (ppb)											
			hexane	benzene	1-heptene	heptane	toluene	octane	ethylbenzene	o-xylene	nonene	nonane	decane	undecene
1900	100	none added	0	0	0	0	0	0	0	0	0	0	0	0
1900	90	none added	0	0	0	0	0	0	0	0	0	0	0	0
1900	80	none added	0	0	0	0	0	0	0	0	0	0	0	0
1900	60	none added	0	0	0	0	0	0	0	0	0	0	0	0
1900	40	none added	0	0	0	0	0	0	0	0	0	0	0	0
1900	20	none added	0	0	0	0	0	0	0	0	0	0	0	0
1900	0	none added	0	0	0	0	0	0	0	0	0	0	0	0
1900	100	3:1	79.96	2608.09	3593.15	1396.77	2642.12	270.51	660.10	942.52	3215.46	435.53	668.61	1987.12
1900	80	3:1	75.98	340.44	1184.95	141.73	580.06	363.81	295.14	483.62	1306.22	584.44	968.71	1263.85
1900	60	3:1	62.11	124.22	99.08	141.96	338.65	207.03	220.34	696.51	442.16	465.82	727.57	875.45
1900	40	3:1	40.13	84.72	14.86	65.40	151.60	206.60	133.77	243.75	54.99	286.86	526.15	478.59
1900	20	3:1	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
1900	0	none added	19.68	236.17	39.36	0.00	141.05	31.71	30.62	115.90	92.94	73.26	101.69	75.44
1900	100	6:1	125.57	3267.97	5011.42	1954.34	3338.80	313.92	819.41	1019.03	3852.34	785.60	1427.93	3448.27
1900	80	6:1	109.20	535.58	2067.77	214.92	1126.62	483.58	615.31	908.23	2223.77	1261.81	2504.55	285.99
1900	60	6:1	70.23	151.27	268.32	147.67	370.97	448.40	324.15	587.07	619.48	732.93	1449.66	172.88
1900	40	6:1	45.53	81.58	144.18	140.39	314.92	314.92	275.08	901.14	58.81	825.25	1557.55	942.88
1900	20	6:1	16.97	111.26	56.57	62.23	101.83	167.83	152.74	279.08	414.85	499.71	997.54	109.37
1900	0	none added	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
1900	100	8:1	207.34	8124.95	10274.35	3644.57	7562.17	807.47	2096.59	2632.33	7461.71	1553.13	2374.77	8307.82
1900	80	8:1	185.39	1065.61	4164.81	399.07	2213.31	1218.45	1236.85	1839.71	4133.68	2288.31	4149.25	5909.70
1900	60	8:1	150.51	301.01	712.40	270.91	933.14	685.16	619.23	1079.35	1003.38	1443.43	2706.25	2025.39
1900	40	8:1	84.48	209.70	125.22	202.16	525.01	562.73	442.03	754.33	710.57	1265.76	2554.15	1045.49
1900	20	8:1	38.52	144.83	47.76	75.50	171.02	212.62	208.00	322.01	206.46	570.07	1255.70	1440.58
1900	100	3:1 in pipe	29.799	102.169	178.7963	97.9123	159.64	344.821	236.2665805	287.351	338.436	559.803	1136.63	849.2826
1900	60	3:1 in pipe	18.18	59.0836	106.805	52.2663	63.6285	77.2632	136.3468115	290.873	86.353	340.867	631.74	465.8516

RPM	% Load	HC:NOx	Empore Extraction Compounds (ppb)						
			undecane	dodecane	Napthalene	Tridecane	Tetradecane	Pentadecane	Hexadecane
1900	100	none added	0	0	13.25	11.08	12.53	15.04	16.41
1900	90	none added	0	0	#N/A	#N/A	#N/A	#N/A	#N/A
1900	80	none added	0	0	4.96	40.85	53.92	48.59	47.83
1900	60	none added	0	0	#N/A	#N/A	#N/A	#N/A	#N/A
1900	40	none added	0	0	#N/A	#N/A	#N/A	#N/A	#N/A
1900	20	none added	0	0	4.77	67.82	98.74	104.44	100.75
1900	0	none added	0	0	12.17	92.83	149.83	137.41	139.81
1900	100	3:1	1105.85	2591.08	1978.72	2272.62	2220.55	1728.37	1334.33
1900	80	3:1	1857.06	4660.91	903.51	7871.27	11319.80	6879.82	5422.81
1900	60	3:1	1453.66	4210.14	897.56	13279.58	16215.44	10076.62	6865.69
1900	40	3:1	1046.36	3130.15	340.40	8011.23	15476.74	12962.89	8275.14
1900	20	3:1	#N/A	#N/A	143.21	2308.14	2628.18	2081.85	2337.24
1900	0	none added	99.50	417.68	118.70	664.57	1104.30	1022.52	1301.51
1900	100	6:1	2598.28	5270.61	4172.85	5332.65	6959.47	4352.20	2861.41
1900	80	6:1	5218.83	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
1900	60	6:1	2879.51	5222.38	754.00	15852.34	27094.67	14077.93	5779.29
1900	40	6:1	3739.25	#N/A	615.89	18598.61	12851.38	7509.80	3566.76
1900	20	6:1	2594.72	9441.70	173.02	3866.45	4109.55	4353.54	2364.18
1900	0	none added	#N/A	#N/A	308.30	1092.81	1567.50	2408.96	1638.74
1900	100	8:1	4170.10	#N/A	31595.69	8195.04	7862.10	4771.48	2467.41
1900	80	8:1	7023.43	#N/A	1302.43	18763.12	#N/A	39796.28	5209.67
1900	60	8:1	4922.28	#N/A	725.22	13549.61	95086.63	17364.46	4566.46
1900	40	8:1	4975.53	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
1900	20	8:1	2663.92	7030.35	347.00	9150.48	22067.78	10322.60	3064.12
1900	100	3:1 in pipe	2047.643698	5383.047	548.07997	13818.57	23261.5681	17744.08914	48899.6952
1900	60	3:1 in pipe	1268.025347	3570.014	328.49396	8963.406	10222.8815	7892.814075	9628.60605

Appendix A.2. (cont.)

RPM	Load %	HC:NOx	ethane (ppm)	ethylene (ppm)	acetylene (ppm)	propane (ppm)	propylene (ppm)	isobutane (ppm)	1,3 butadiene (ppm)	1-butene (ppm)	isobutylene (ppm)	n-pentane (ppm)
3000	100	none added	0	2.89855	0	0	0.605714	0	0	0	0	0
3000	90	none added	0	2.67558	0	0	0.590381	0	0	0	0	0
3000	80	none added	0	2.71531	0	0	0	0	0	0	0	0
3000	60	none added	0	1.76087	0	0	0	0	0	0	0	0
3000	40	none added	0	2.70195	0	0	0.753989	0	0	0	0	0
3000	20	none added	0	23.1753	3.429605	0	7.227325	0	1.896774187	2.19635	0.839331	0
3000	100	3:1	1.0252	52.3582	1.71913	0	13.83945	0	2.29072859	3.13416	1.0545791	0
3000	80	3:1	0	68.5199	2.260213	0	22.20644	0	3.131845834	6.98023	2.804874	0
3000	60	3:1	0	36.6357	1.084551	0	16.44714	0	4.707550209	0	1.4722387	0
3000	40	3:1	0	25.3977	4.255791	0	8.705398	0	2.537245071	1.53281	1.1847925	0
3000	20	3:1	0	19.1255	3.254187	0	4.204624	0	1.447111221	1.64755	0.6899276	0
3000	0	none added	2.2793	78.9273	8.134616	0	26.06395	0	7.995097784	8.22354	3.7528628	0

RPM	Load %	HC:NOx	GC-MS Compounds (ppb)														
			1-pentene (ppb)	hexane (ppb)	benzene (ppb)	1-heptene (ppb)	heptane (ppb)	toluene (ppb)	octane (ppb)	ethylbenzene (ppb)	o-xylene (ppb)	nonene (ppb)	nonane (ppb)	decane (ppb)	undecene (ppb)		
3000	100	none added	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
3000	90	none added	30.82729	10.276	80.4935	0	46.2409	0	46.241	0	0	0	0	17.126	27.402	0	0
3000	80	none added	58.10384	0	36.9752	38.73589	10.5643	0	0	5.282167043	0	0	5.2822	0	0	0	0
3000	60	none added	74.65053	0	21.3287	30.21569	0	8.887	0	0	0	0	0	0	0	0	31.99309
3000	40	none added	0	0	52.3462	75.02949	0	12.214	0	8.724358974	0	3.4897	5.2346	15.704	12.2141	0	0
3000	20	none added	147.8406	20.849	881.357	266.3025	24.6401	350.65	40.751	37.9078341	93.8219	159.21	71.077	139.31	303.2627	0	0
3000	100	3:1	459.5377	0	1886.36	167.2416	61.7739	548.43	27.12	108.4810325	122.041	7.5334	0	34.654	0	0	0
3000	80	3:1	567.2489	18.245	774.577	286.9417	51.4173	344.99	59.71	111.1277113	267.038	134.35	11.61	64.686	348.3107	0	0
3000	60	3:1	272.9238	21.547	256.764	398.6124	174.168	150.83	17.956	104.1419737	145.44	228.04	89.778	143.64	317.8126	0	0
3000	40	3:1	222.2566	0	177.432	177.4318	42.9572	63.502	65.37	136.3423123	168.093	102.72	13.074	108.33	283.8908	0	0
3000	20	3:1	0	9.7637	302.674	72.25122	29.291	72.251	11.716	68.34574607	158.172	121.07	41.007	64.44	101.5423	0	0
3000	0	none added	1430.244	86.292	1375.16	866.592	510.408	914.33	223.99	370.872	501.228	829.87	378.22	583.85	1121.796	0	0

RPM	Load %	HC:NOx	undecane dodecane		Empore Extraction Compounds (ppb)				
			(ppb)	(ppb)	Napthalene (ppb)	Tridecane (ppb)	Tetradecane (ppb)	Pentadecane (ppb)	Hexadecane (ppb)
3000	100	none added	0	0	4.0101202	3.63954	5.87038408	5.978367731	4.63102623
3000	90	none added	15.41365	0	0.4721939	0	3.57316842	5.412610159	16.3012595
3000	80	none added	0	0	5.7276103	7.99972	9.99873998	10.48666102	13.6180945
3000	60	none added	0	94.20186	0.8572271	4.376944	9.72371615	8.321641274	12.495175
3000	40	none added	31.40769	90.73333	4.4794169	34.39994	51.8049696	57.93544233	61.237554
3000	20	none added	258.721	569.5652	0	0	0	0	0
3000	100	3:1	10.54677	120.5345	264.19337	34.75745	63.821478	85.21774327	64.6479432
3000	80	3:1	21.56209	202.352	653.08691	283.9983	232.371745	239.0332422	138.382188
3000	60	3:1	91.57311	637.4207	262.02297	703.492	879.115005	596.6242466	452.761578
3000	40	3:1	85.91433	423.9686	223.86005	623.4574	566.380357	560.7188644	426.345067
3000	20	3:1	64.44027	412.0272	340.88641	816.5391	904.790998	785.3702894	608.627641
3000	0	none added	796.824	2695.248	1530.5201	4657.459	5729.34872	4345.192549	2513.50507

		GC-MS Compounds (ppb)												
		1-pentene	hexane	benzene	1-heptene	heptane	toluene	octane	ethylbenzene	o-xylene	nonene	nonane	decane	undecene
		(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
Initial	bag 9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
during scope	bag 34	0.00	36.77	46.80	0.00	0.00	13.37	0.00	5.57	7.80	0.00	0.00	18.94	0.00
during scope	bag39	35.02	0.00	28.32	13.41	14.16	5.22	2.98	0.00	5.96	0.00	5.96	11.92	10.43
during 3:1	bag47	0.00	0.00	14.90	11.71	0.00	7.45	3.19	8.51	7.45	0.00	0.00	4.26	5.32
during 6:1	bag 56	0.00	0.00	5.75	0.00	0.00	7.19	0.00	4.31	2.88	0.00	0.00	1.44	17.25
during 6:1	bag 64	0.00	2.79	13.93	0.00	0.00	12.54	0.00	4.18	5.57	18.11	0.00	12.54	0.00
during 8:1	bag 71	0.00	0.00	58.80	40.23	30.95	3.09	0.00	0.00	4.64	0.00	0.00	15.47	0.00
during 8:1	bag 78	235.00	0.00	72.31	54.23	21.69	16.27	0.00	25.31	61.46	0.00	19.88	39.77	106.65

		Empore Extraction Compounds (ppb)						
		undecane	dodecane	Napthalene	Tridecane	Tetradecane	Pentadecane	Hexadecane
		(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
Initial	bag 9	0.00	0.00	0.70	27.33	40.21	38.53	36.39
during scope	bag 34	18.94	94.71	0.00	0.00	0.00	#N/A	0.00
during scope	bag39	20.87	76.01	0.00	0.00	0.00	#N/A	0.00
during 3:1	bag47	6.39	12.77	6.05	177.23	201.62	210.52	278.04
during 6:1	bag 56	10.06	104.94	18.32	101.04	115.62	117.61	88.05
during 6:1	bag 64	15.32	39.00	39.74	415.89	319.99	229.89	184.78
during 8:1	bag 71	26.30	119.14	6.58	80.91	72.12	54.42	99.50
during 8:1	bag 78	43.38	303.69	102.61	272.32	289.08	485.03	665.42

	Speed	Torque	Power	EGR	SOI ATDC	Pentene	Benzene	1-Heptene	Toluene	octane	1-Nonene	Nonane
	RPM	ft-lb	HP	(%)	(degrees)	ppm (mass)	ppm (mass)	ppm (mass)	ppm (mass)	ppm (mass)	ppm (mass)	ppm (mass)
Approach 1	1500	25.13867	7.178586	22.2	-2	2.48	9.22	1.76	3.93	0.38	0.42	0.68
Approach 1	1500.004	24.45676	6.987942	34.9	-2	0.42	2.83	0.30	0.90	0.10	0.00	0.00
Approach 1	1500	23.84321	6.822222	40.2	-2	0.95	4.18	0.63	1.48	0.17	0.04	0.24
Approach 1	1500.008	24.04802	6.862162	44.3	-2							
Approach 1	1499.992	22.03264	6.303326	46.3	-2	2.10	9.00	1.65	2.80	0.53	0.21	0.62
Approach 1	1500.002	21.00894	6	48.8	-2	2.74	11.89	1.51	3.98	0.40	0.41	0.94
Approach 1	1500.008	18.69397	5.33659	54.0	-2	4.34	14.31	2.37	5.56	0.48	0.59	0.83
Approach 1	1500.01	16.51123	4.717672	56.0	-2	5.68	14.57	5.20	6.57	0.52	0.44	0.93
						NO Data						
Approach 2	1500	25.33202	7.238462	22.3	-2	0.35	3.88	0.25	1.16	0.08	0.00	0.00
Approach 2	1500	24.77484	7.081497	44.1	-2	0.66	3.76	0.27	0.93	0.00	0.00	0.00
Approach 2	1499.998	24.16736	6.9079	43.4	0	0.97	4.06	0.39	1.17	0.08	0.00	0.00
Approach 2	1499.998	22.29938	6.36632	43.5	2	1.78	7.06	1.58	2.35	0.19	0.00	0.07
Approach 2	1500.002	18.90021	5.400416	43.2	4	4.83	10.78	2.29	3.12	0.18	0.09	0.14

	Decane ppm (mass)	1-Undecene ppm (mass)	Undecane ppm (mass)	Dodecane ppm (mass)	Tridecane ppm (mass)	Formaldehyde ppm mass	Acetaldehyde ppm mass	Acrolein ppm mass	Propionaldehyde ppm mass	Benzaldehyde ppm mass
Approach 1	1.36	1.21	2.29	2.19	1.83	11.92	6.07	0.00	2.43	2.49
Approach 1	0.12	0.36	0.45	0.53	0.35	6.15	2.99	1.08	1.06	1.13
Approach 1	0.36	0.60	0.67	0.50	0.21	0.69	0.33	1.12	1.08	1.15
Approach 1						0.82	0.37	1.31	1.16	1.21
Approach 1	0.66	0.92	1.13	0.88	7.33	0.84	0.39	1.37	1.20	1.33
Approach 1	1.03	1.21	1.40	1.21	7.12	1.25	0.57	1.61	1.60	1.83
Approach 1	1.15	1.34	1.57	1.32	2.30	35.85	8.96	3.53	2.46	3.23
Approach 1	1.18	1.38	1.74	1.44	5.55	45.05	13.48	5.75	3.53	2.87
Approach 2	0.08	0.48	0.64	0.89	7.35	No Data				
Approach 2	0.02	0.31	0.48	0.64	7.19	6.40	2.72	0.00	0.00	0.64
Approach 2	0.08	0.41	0.47	0.67	7.35	7.92	3.40	0.00	0.00	0.81
Approach 2	0.20	0.46	0.58	0.71	8.39	8.73	3.88	1.13	0.00	0.97
Approach 2	0.20	0.49	0.59	0.69	7.48	15.28	7.32	2.07	0.00	1.27