Ambient Composition Session

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Summary of the Ambient Composition Working Group Session

The focus of the ambient composition working group for the ECN1 Workshop was to examine the different methods of creating the thermodynamic state for the charge gas in experimental apparatuses including combustion vessels and constant pressure flow rigs in the Engine Combustion Network (ECN) under the 'Spray A' test condition. This was accomplished by comparing the different institutions ambient compositions and modeling their impact on autoignition of n-heptane as a diesel fuel surrogate. The slides presented at the workshop are provided, and a brief overview of the comparisons made with the key results outlined here.

First, the four preburn combustion vessels (Sandia, MTU, IFPEN, and Eindhoven) were compared in regards to preburn mixtures used which consist of varying levels of C_2H_2, C_2H_4, H_2, O_2, N_2 and Ar. This comparison was accomplished using a single-zone chemical kinetics model in Cantera interfaced with Matlab with the GRI 3.0 mechanism to compare minor species produced during the preburn and levels at injection. The different cool-down temperature histories of the vessels (heat transfer modeled as convective with a temperature trace being a quadratic exponential decay) were also modeled. The peak preburn temperature of Eindhoven is largest, followed by MTU, Sandia, and IFP. Although MTU and Sandia utilize the same preburn mixture, MTU uses a fan speed seven times that of Sandia which results in a higher peak temperature and a faster rate of cool down. MTU and IFP have similar cool-down rates, with Sandia having the longest cool-down time due to the low fan speed used. These differences (premixed gas mixture and cool-down rate) cause variations in minor species, NO is largest for Eindhoven, followed by MTU, Sandia and IFP due to the temperature trends from the preburn, but in all cases the levels at the time of diesel injection are more than 50 times less than equilibrium levels, with similar trends for NO_2. For OH, this species tracks the temperature-time trace and at injection IFP has the maximum OH (attributed to the largest level of H2 in the preburn mixture), followed by Eindhoven, MTU and Sandia, with these levels being one to two orders of magnitude less than equilibrium values. At equilibrium, for IFP NO in 3030 ppm and OH is 170 ppm, for MTU and Sandia NO is 5100 ppm and OH is 230 ppm, and for Eindhoven NO is 5250 ppm and OH is 240 ppm.

Additionally, for the conditions at injection the four preburn vessels major species (CO_2, H_2O, Ar, N_2, and O_2) were compared to the CMT and Caterpillar constant pressure flow rigs which use O_2 and N_2 to achieve the desired 15 percent oxygen conditions for 'Spray A'. Comparison included the major species levels and constant pressure specific heat capacities. Finally, the stoichiometric n-heptane ignition delay was determined using chemical kinetics modeling with a reduced mechanism to compare the influence of ambient compositions major species levels and the different minor species produced during the preburn on autoignition, relative to that of dry air and air plus ideal residuals to simulate EGR. Results showed that the preburn vessels, despite their respective differences in minor species at injection, did not significantly impact the ignition delay of n-heptane. More specifically, the vessel ignition delays were 4% shorter than ideal EGR and 83% longer than dry air. Comparing the preburn and constant pressure vessels major species at fuel injection, the specific heat capacities are similar (spanning 1.13 to 1.21 kJ/kg-K at 900 K), and the variation in ignition delay is within the modeling accuracy. More specifically, when considering major species only, IFP had the shortest ignition delay (0.65 ms), followed by CMT / Caterpillar at 0.69 ms, and the remaining preburn vessels of 0.72 ms. Again, the ignition delay was longer than that of dry air as expected due to the reduction in oxygen level at the 'Spray A' condition. There are however noticeable differences in the peak temperature of n-heptane ignition between the different vessels with the Nitrogen / Oxygen constant pressure flow rigs having a peak temperature at 45 K higher than the preburn vessels. Key conclusions are that despite the differences in preburn mixtures and ambient compositions, the ambient charge-gas compositions for the vessels considered show no significant differences in fuel ignition delay at the condition considered or mixture constant pressure specific heat capacity.

Also discussed briefly was a recent *Energy and Fuels* journal publication with a goal of isolating and understanding chemical kinetics effects on the preburn process and autoignition of n-heptane fuel while including minor species and neglecting spray dynamics. The key conclusions can be found in the slides, with the main result being that the combustion vessel with the preburn procedure is an effective tool for studying spray combustion over a range of ambient conditions without concern over the reactive minor species produced by the preburn procedure. The citation is listed below for reference for further review.

Nesbitt, J.E., Johnson, S.E., Pickett, L.M., Siebers, D.L., Lee, S-Y., Naber, J.D., 'Minor Species Production from Lean Premixed Combustion and Their Impact on Autoignition of Diesel Surrogates,' *Energy and Fuels* 25 (3), pp. 926-936, 2011.

Discussion Issues & Questions

The key observation and conclusion from the above and the workshop is that there is no significant effect of ambient composition differences on the specific heat and autoignition delay of n-heptane as a diesel surrogate. There are however noticeable differences in the flame temperatures and the consequences of this are unknown. Further unknown is the potential differences in ignition or combustion duration as a result of these ambient environments. Questions were brought up on if the time-step used in the model influences the results (a consistent time-step was used in all of the modeling, however, there was no sensitivity study undertaken), the influence of other n-heptane stoichiometries in addition to the lambda one case studied here, and if the n-heptane mechanism used influences the results. These questions are continuously being addressed with additional modeling work.

Recommendations & Future Investigation

It is recommended that experimental testing is undertaken to characterize the differences in ambient gas composition between the vessels in regards to major and minor species levels and autoignition delay of the fuel. MTU has conducted some exhaust gas sampling, however this sampling was not in-situ, not in real-time in the vessel, nor under 'Spray-A' conditions. Sandia has tried some measurements of the exhaust gases but found that there are large levels of unburnt hydrocarbons due to the large amount of crevice volumes in the CV (think of the CV as a cube with 6 pistons (access ports) as the crevice volumes). Sampling directly in the CV is difficult but is something that would be useful experimentally and to also validate this simplified chemical kinetics preburn modeling.

The modeling used in this work involved a simplified single-zone model, and using a more detailed two-cell or multi-cell model would improve the accuracy and applicability of the modeling simulations. LLNL expressed some interest in looking into this, but this will be extremely complex to the differing vessel geometries.

Working Group Section: *Ambient Composition*

Leader: Jaclyn Nesbitt, Michigan Tech University
Dr. Jeffrey Naber, Dr. Seong-Young Lee

Contributing Institutions: Sandia, Eindhoven, CMT, Caterpillar, IFP, MTU

ECN1 – Workshop on Spray Combustion, Ventura, CA

May 13-14, 2011

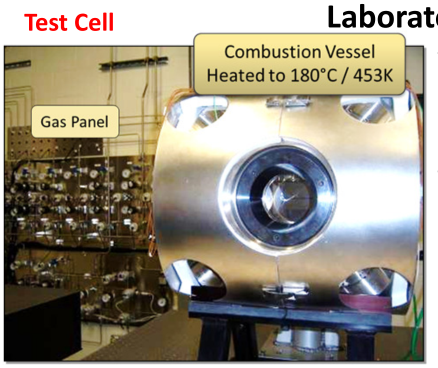
Outline

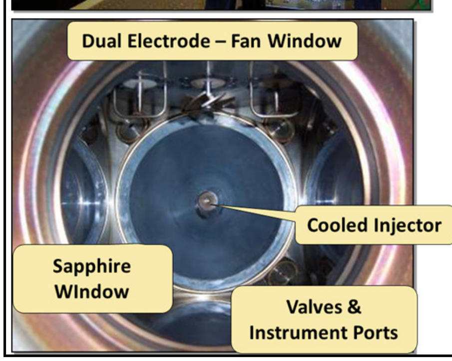
- Details of MTU Combustion Vessel
- Chemical kinetics reactor modeling of 'Spray A' 15% oxygen conditions for different institutions
  - Comparison of major species at injection for different vessels
  - Comparison of preburn environments
    - Cool-down & minor species generation
  - n-Heptane Ignition Delay
    - Influence of major species
    - Influence of prebrun
- Overview of Energy and Fuels Publication
  - Nesbitt, J.E., Johnson, S.E., Pickett, L.M., Siebers, D.L., Lee, S-Y., Naber, J.D., 'Minor Species Production from Lean Premixed Combustion and Their Impact on Autoignition of Diesel Surrogates', Energy Fuels 25 (3) pp 926-936, 2011.

MTU Combustion Vessel Details

Laboratory Overview

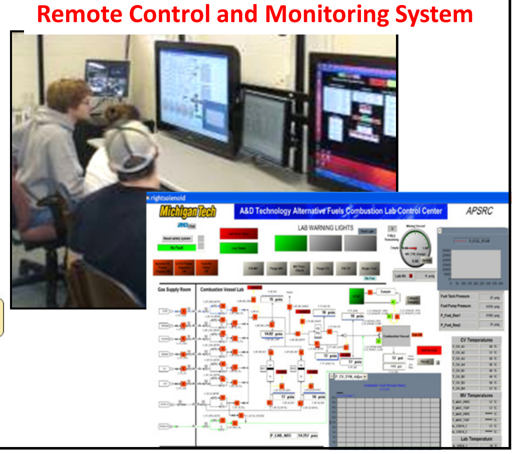
Test Cell



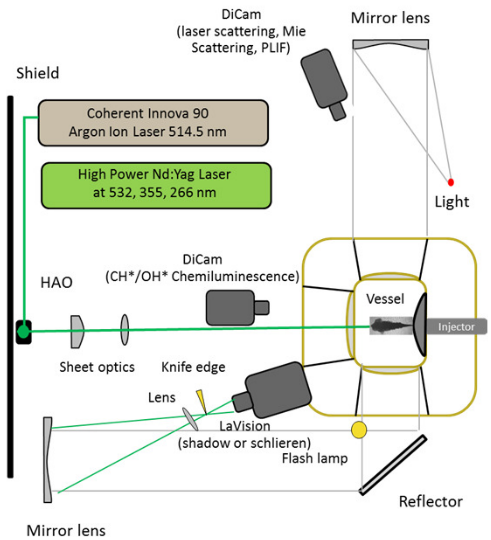


- **Injection Systems**
  - Diesel (4140 Bar) / GDI (200 Bar)
  - Piezo & Solenoid Injector Drivers
  - Cooled injector windows
- **Ignition Systems**
  - Generic automotive coil
  - Advanced ignition- dual-fan / spark plug

Remote Control and Monitoring System



Optical and Laser Diagnostics



Diagnostics

- Shadowgraph/Schlieren Imaging: Gas Phase
- Mie: Liquid phase (spray - droplet)
- TSI Phase Doppler Particle Analyzer (PDPA)– Droplet sizing
- Rayleigh: Gas phase, air-fuel mixture formation (ER), temperature
- PLIF: HCHO (cool flame)
- LII: Soot & PLIF: PAH
- Emissions: CH* & OH*

Cameras

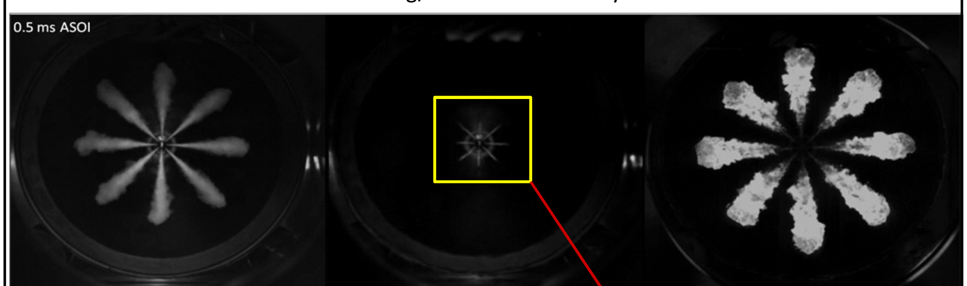
- PCO DiCam Pro Intensified Camera (ICCD),
- PCO SensiCam Unintensified Camera (CCD),
- LaVision UltraSpeedStar16: 1 million frame/sec

Laser and Light Sources

- 5 W Argon-Ion Laser
- High power Nd:Yag laser
- Short-pulsed high-power flashlamp

Diesel Spray Imaging

Liquid Phase – Back Scattering Imaging
High Pressure Common Rail Injector – 8 Holes; 2000 Bar Injection Pressure
34.8 kg/m^3 Ambient Density

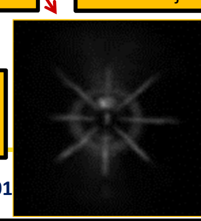


NonVaporizing Spray – 373 K N_2 1.0 ms Injection Duration

Vaporizing Spray – 1200 K 0% O_2 1.0 ms Injection Duration

Combusting Spray – 1200 K 21% O_2 0.6 ms Injection Duration

Zoomed-In View
Vaporizing Spray - 1200 K 0% O_2
1.0 ms Injection Duration



Comparing 'Spray A' Ambient Compositions

Goals & Objectives

- **Goal:**
  - Examine test facilities charge gas composition impact on autoignition in comparison to those in an engine through kinetics modeling.
- **Objectives:**
  - Compare major species at injection
  - Compare preburn environments – cool-downs and minor species produced
    - Sandia / MTU / IFP / Eindhoven
  - Compare n-heptane ignition delay under 'Spray A' conditions
    1. Consider major species at fuel injection
    2. Preburn minor species effects

MAJOR SPECIES COMPARISON AT INJECTION

'Spray A' Ambient Environment Comparison – Post Preburn

		'Spray A' Environment (Post preburn) – Volume %					
Institution	Ambient Composition Method	O2 (%)	N2 (%)	CO2 (%)	H2O (%)	Argon (%)	Mixture Specific Heat (at 900 K) (kJ/kg-K)
Sandia	Preburn, Premixed	15.0	75.1	6.2	3.6	--	1.16
MTU	Preburn, Premixed	15.0	75.1	6.2	3.6	---	1.16
IFP	Preburn, Seq. Fill	15.0	71.7	1.7	11.6	---	1.21
Eindhoven	Preburn, Seq. Fill	15.0	71.2	6.4	3.2	4.2	1.13
CMT	Flow Rig	15.0	85.0	--	--	--	1.13
Caterpillar	Flow Rig	15.0	85.0	--	--	--	1.13
Ideal EGR – 38.3% (CO2, H2O)	--	15.0	77.7	3.8	3.5	--	1.16
Dry Air	--	21.0	78.1	--	--	0.9	1.12
Modified Preburn HCR (Match Diesel R = 1.85)*	--	15.0	75.3	6.1	3.6	--	1.16

*Johnson, S.; Nesbitt, J.; Lee, S.-Y.; Naber, J. D. Journal of KONES, Powertrain and Transport 2009, 16 (2), P2-00-2.

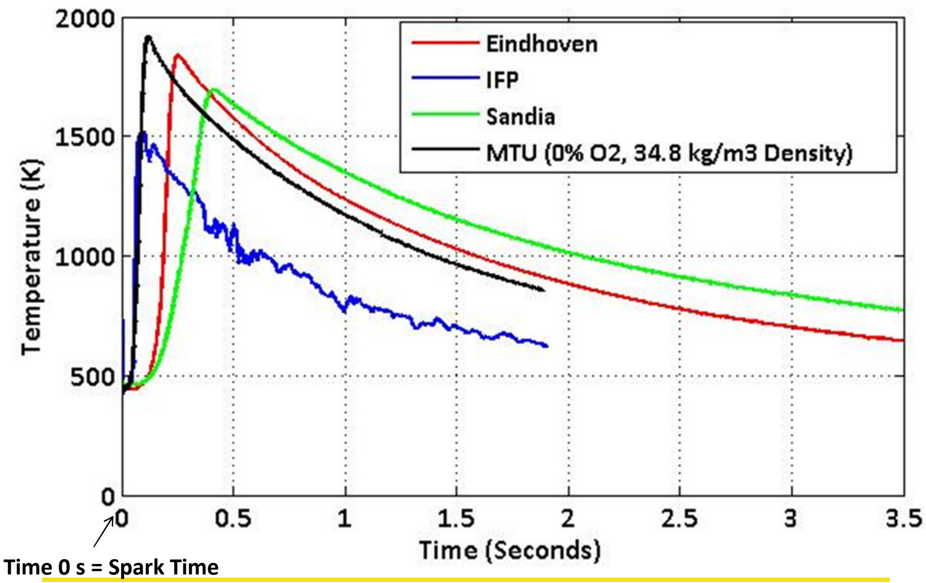
COMPARISON OF PREBURN ENVIRONMENTS

'Spray A' Ambient Composition Environment Comparison – Preburn Mixture

		Preburn Mixture Comparison (Volume %)						
Institution	**Ambient Composition Method**	**C2H2 (%)**	**C2H4 (%)**	**H2 (%)**	**O2 (%)**	**N2 (%)**	**Argon (%)**	**$T_{adiabatic}$ (U,V) (K)**
Sandia	Preburn, Premixed	3.06	--	0.50	22.63	73.82	--	1927
MTU	Preburn, Premixed	3.06	--	0.50	22.63	73.82	--	1933
IFP	Preburn, Sequential Fill	--	0.816	9.39	21.43	68.36	--	1772
Eindhoven	Preburn, Sequential Fill	3.15	--	--	22.64	70.07	4.14	1946

Adiabatic flame temperature calculated for initial temperature and pressure to match core density of 'Spray A' of 22.8 kg/m^3

Comparison Experimental Preburn Data



Chemical Kinetics Preburn Modeling Diagram

Software: Engineering Equation Solver (EES) & Cantera integrated into Mathworks Matlab

Initial Conditions Definition

Initial Conditions
(T, P, Mole fractions of C_2H_2, C_2H_4, H_2, N_2, O_2, Ar)

→

Extent of Reaction Calculation
Equate internal energies to elevate temperature
(T, P, Mole fractions of C_2H_2, H_2, N_2, O_2, CO_2, H_2O, Ar)

↓

Premixed Combustion & Cool-Down

Mechanism: Detailed GRI-Mech 3.0, 53 species, 325 elementary reactions

Constant-Volume Reactor

→

Output
- Mole factions of 53 Species
- T_{Target}
- P_{Target}

Cool-Down Curve Fitting

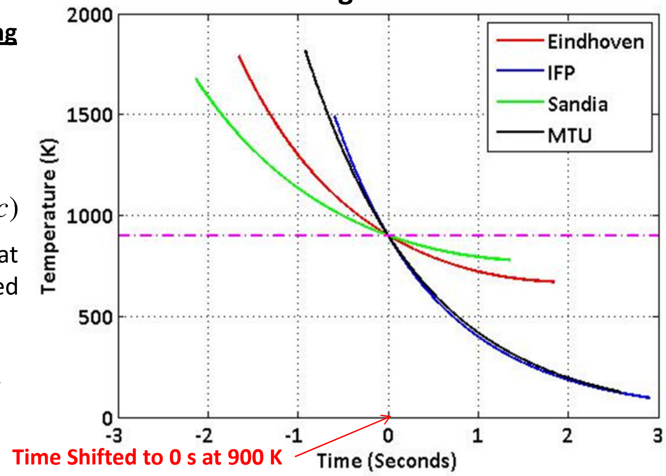
Heat Transfer Modeling

- Curve fit exponential decay function to experimental data (constants a, b, c):

$$T(t) = \exp(at^2 + bt + c)$$

- Assume convective heat transfer, constant varied to match exp. data

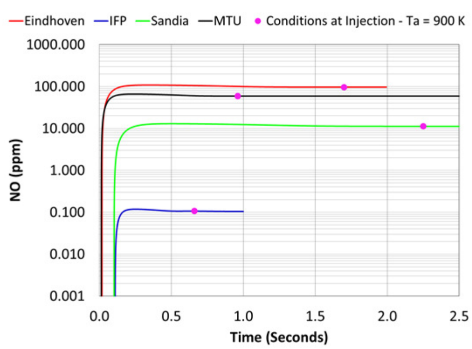
$$Q = Constant \frac{dT(t)}{dt}$$



Institution	Time Constant Cool Down Decay (s)	Fan Speed (RPM)	Location
Sandia	6.5	1000	Upper Corner (opposite injector)
MTU	1.3	7000	Top Window
IFP	1.2	3140	Upper Corner (near injector)
Eindhoven	3.5	1890	Lower Corner

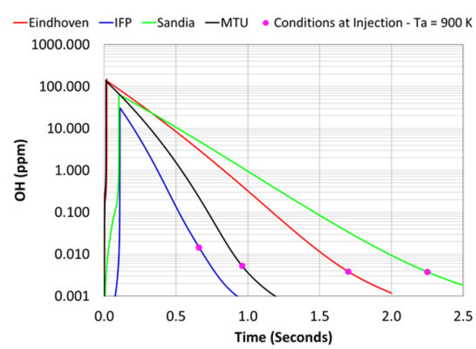
Preburn Modeling Results: NO and OH Time Traces

NO – Time Trace



- **At injection, Eindhoven maximum NO (Highest peak temp preburn), IFP minimum NO**
- **NO below equilibrium (IFP: 3000ppm, Sandia/MTU/Eindhoven > 5000ppm)**

OH – Time Trace



- **At injection, IFP maximum OH, Sandia minimum OH**
- **OH levels below equilibrium (180 ppm IFP, 240 ppm Sandia / MTU / Eindhoven)**

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Preburn Modeling Results– Conditions at 900 K for Fuel Injection

	Sandia	MTU	IFP	Eindhoven
Time (S) Relative to Peak Cool-Down Temp	2.15	0.95	0.55	1.68
Pressure (MPa)	5.81	5.82	6.13	5.71
NO (PPM)	11.24	59.14	0.11	**96.72**
NO2 (PPM)	2.47	9.64	0.02	**16.66**
OH (PPB)	3.78	5.24	**14.34**	3.87

N-HEPTANE IGNITION DELAY COMPARISON

Fuel Autoignition Modeling – n-Heptane

Input
- **Species Mole Fractions**
  - 53 GRI Species (Preburn)
  - Major Species (H2O, CO2, N2, O2, Ar)
- Mix stoichiometrically with n-heptane fuel
- T_{target} = 900 K (Spray A)
- P_{target} = ~6 MPa (Spray A)

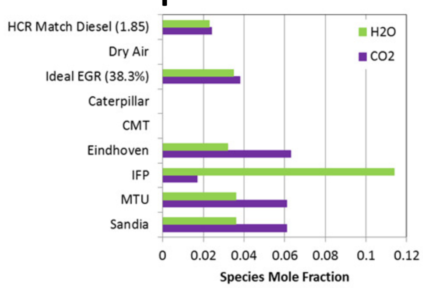
Ignition Modeling

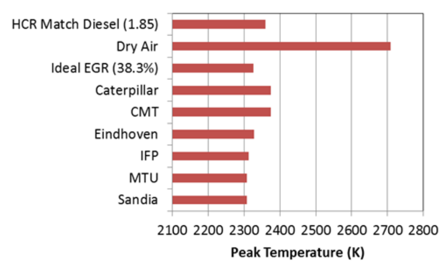
Mechanism: Reduced, 179 species, 823 reversible reactions, modified from LLNL to include NO and NO_2 (from GRI-Mech 3.0)

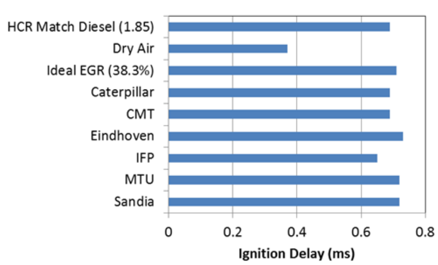
Constant Pressure Perfectly Stirred Reactor, Constant pressure / enthalpy conditions

Output
- N-Heptane ignition delay

Ignition Delay – Major Species Ambient Composition Comparison - Stoichiometric n-Heptane Mixture







Insignificant differences (within modeling accuracy) in ignition delay for different ambient environments.

Autoignition Modeling Results – Influence of Preburn

	Sandia	MTU	IFP	Eindhoven	Air Plus Ideal Residuals (38.3%) – 15% O2	Dry Air
n-Heptane Ignition Delay (ms)	0.69	0.66	0.68	0.67	0.71	0.37
Peak Temperature (K)	2302	2302	2307	2320	2326	2707

- n-Heptane ignition delay at spray A conditions (900 K)
- No variation in ignition delay as result of preburn
- CV ignition delay 4% shorter than ideal EGR (15% O_2)
- CV ignition delay 83% longer than dry air (21% O_2)

Conclusions

- **Major Species Comparison**
  - Similar specific heats
- **Preburn Comparison**
  - Peak Temperature, NO and NO2 at Injection: Eindhoven , MTU > Sandia > IFP
  - OH at Injection: IFP > MTU > Eindhoven > Sandia
- **Ignition Delay Comparison**
  - Major Species Consideration: no significant variation in n-heptane ignition delay.
  - Preburn Consideration: no variation in ignition delay due to minor species from preburn
    - CV Ignition delay 4% shorter than Ideal EGR (15% O2)
    - CV Ignition Delay 83% longer than dry air

Minor Species Production from Lean Premixed Combustion and Their Impact on Autoignition of Diesel Surrogates

Energy and Fuels Volume 25, Issue 3, pp. 926-936

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Brief Overview: Goals and Main Conclusions

- **Goal: Isolate and understand chemical kinetics effect on preburn process and autoignition of n-heptane fuel while including minor species, and neglecting spray dynamics**
- **Conclusions:**
  - Preburn -- Most significant minor species formed is NO, OH tracks equilibrium, range of NO produced in CV is not outside that representative of CI engines.
  - Minor species of NOx and OH from preburn shorten ignition delay by 3% relative to air, and increase it by 6% relative to air plus residuals at 1000 K. Impact is comparatively insignificant due to accuracy of modeling simulations
  - NO largest impact on ignition: ignition delay ↓ 10% for 10X increase in NO (120 ppm)
  - CV useful for simulating heavy EGR-- CV ignition delay reduced by maximum 7% for given percent O2 relative to ideal EGR with no minor species
  - Change in minor species mole fraction – minimal influence on ignition delay, rather, dominating trend is increase in oxygen yielding reduction in ignition delay
- **Combustion vessel with preburn procedure is effective to study spray combustion over various ambient conditions without concern over reactive minor species produced by preburn.**

Summary, Recommendations & Further Investigation Required

- **Summary / Recommendations**
  - No significant effect of ambient composition differences on specific heat and ignition delay.
  - Although preburn mixtures and cool-down histories are different which yield differing minor species, this does not yield any significant impact on autoignition of n-heptane as a diesel surrogate.
- **Further Investigation Required / Guidelines**
  - Consequences of differences in flame temperature due to different compositions.
  - Experimental measurement of exhaust gas and species to validate modeling and further compare the vessels
    - If differences are significant relative to what was predicted by the model, further assessment of the mixtures used will need to be undertaken to standardize the preburn mixture to ensure consistencies for spray and combustion studies.