

Selection Criteria for Sustainable Fuels for High-Efficiency Spark-Ignition Engines with Examination of their Storage Stability, Impact on Engine Knock, and Fine Particle Emissions

Robert L. McCormick

Colorado State University, February 22, 2018

Team Members and Collaborators

Gina Fioroni, Matthew Ratcliff, Lisa Fouts, Earl Christensen, Jonathan Burton,
Petr Sindler, Peter St John, Seonah Kim

– *National Renewable Energy Laboratory*

Rob Paton, Bret Windom, Steve Burke, Brandon King

– *Colorado State University*

James E. Anderson

– *Ford Motor Company*

Scott Sluder, James Szybist

– *Oak Ridge National Laboratory*

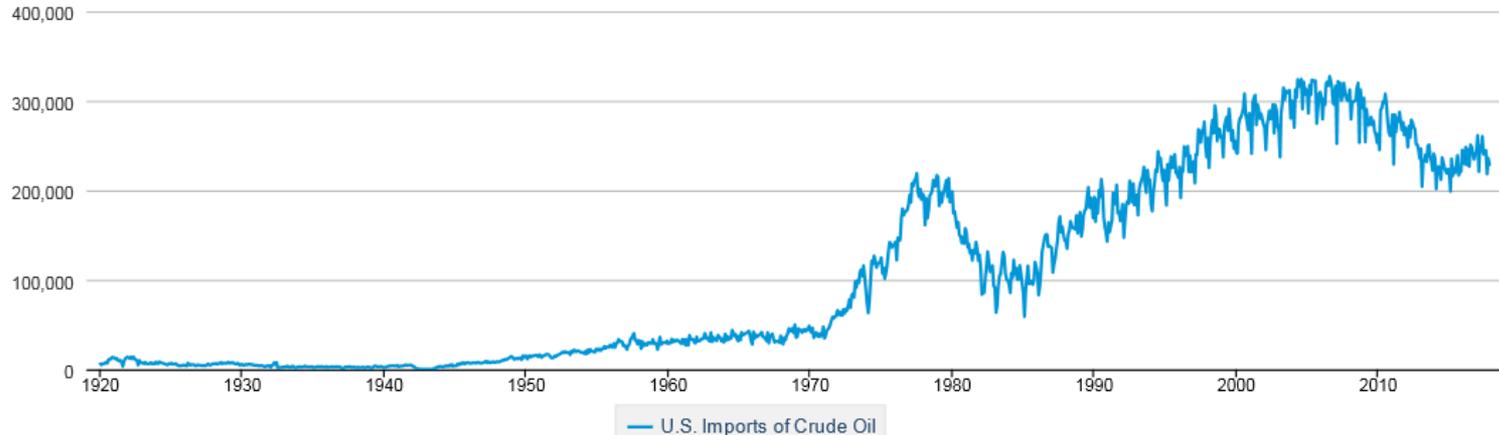
Drivers for Higher Efficiency in Transportation

- The US still imports as much or more petroleum as during the 1970s energy crisis – today it is about 25% of consumption
- This remains a national security issue and a threat to the US economy

U.S. Imports of Crude Oil

 Source: U.S. Energy Information Administration

Thousand Barrels



And in spite of
what some people
are saying.....

Anthropogenic carbon emissions are having a
dramatic effect on earth's climate



Record low sea ice

nasa.gov



Deglaciation

nasa.gov



Sea Level Rise

practicalaction.org/climate-change-image-gallery



Desertification

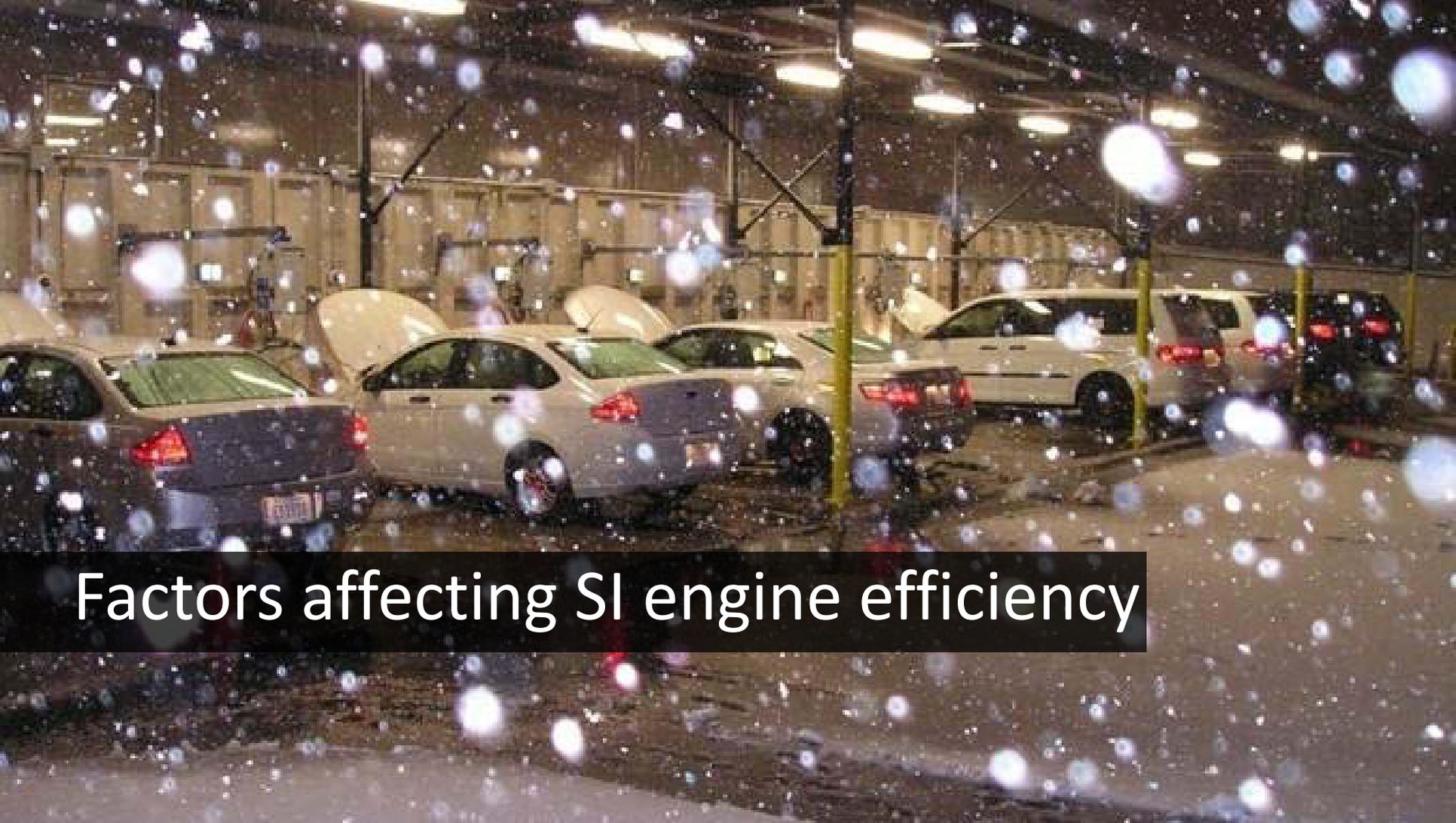
cnn.com

Goal: better
fuels and better
vehicles
sooner



Fuel and Engine Co-Optimization

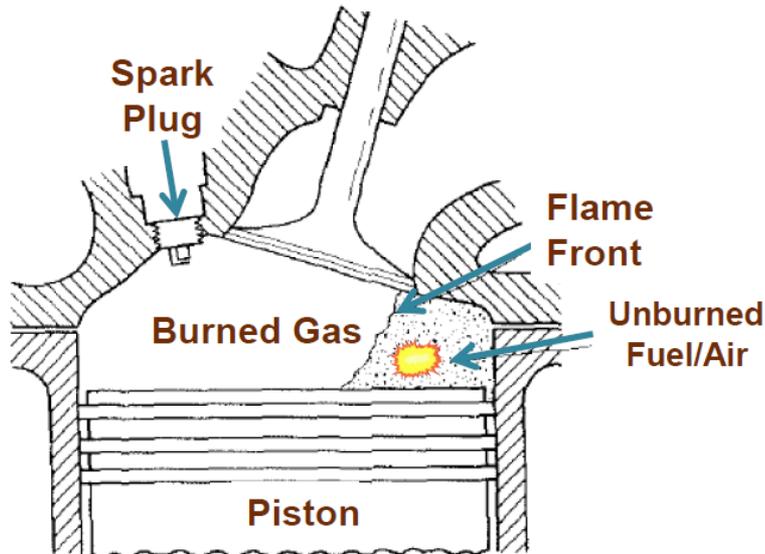
- What fuel properties maximize engine performance?
- How do engine parameters affect efficiency?
- What fuel /engine combinations are sustainable, affordable, scalable, and compatible?



Factors affecting SI engine efficiency

Engine Knock

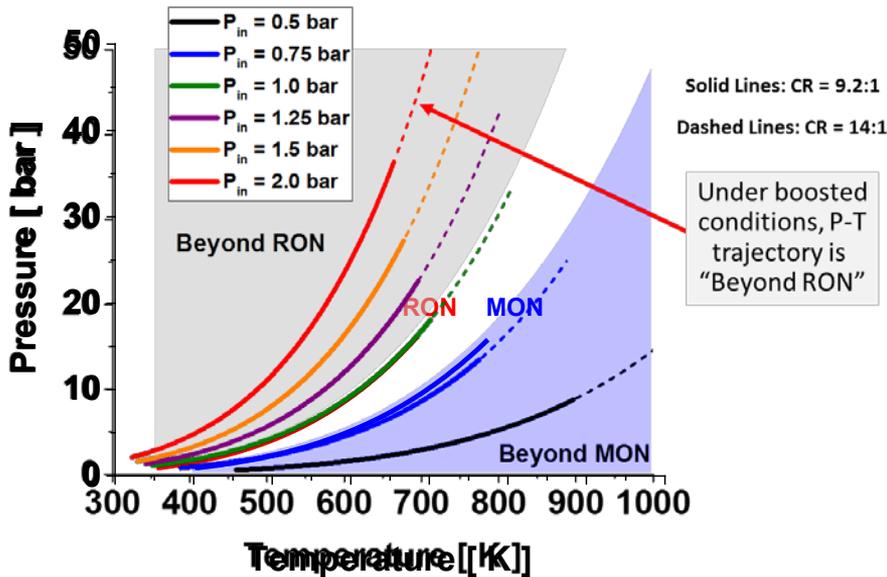
- Knock occurs when unburned fuel/air mixture auto-ignites
 - Essentially a small explosion in the engine
 - If severe can damage the engine
 - Higher octane number fuel is more resistant to auto-ignition



- *Modern engines sense the onset of knock and retard spark timing or limit load*
- *Spark timing retard (sparking later) reduces peak T and P – avoiding knock*
- *However this also reduces efficiency*
- *Engine knock with current fuels limits most high efficiency engine strategies*

Octane Index

- Two different octane numbers are measured in engine tests: Research and Motor
 - Different trajectories in P-T space
 - Comparison to reference fuel knock levels
- Pump octane, AKI = (RON + MON)/2 – older engines operated between RON and MON



➤ Octane index concept

$$OI = (1-K) * RON + K * MON$$

$$OI = RON - K * S$$

$$S = RON - MON$$

➤ For RON test $K=0$, for MON test $K=1$

➤ $OI = AKI$ $K=0.5$

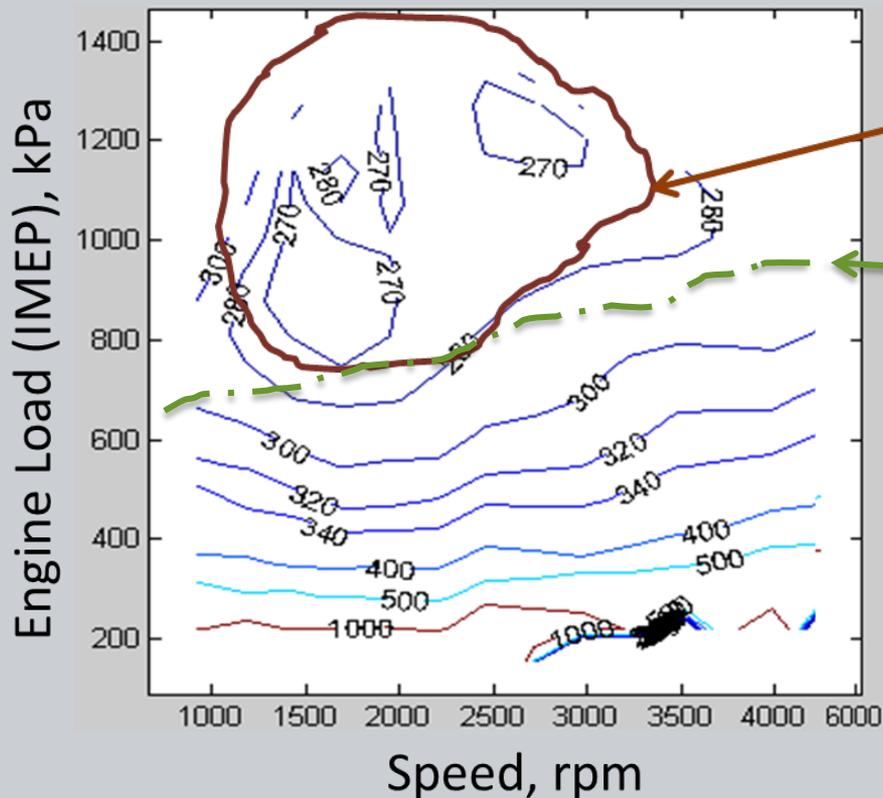
➤ For downsized-boosted engines $K < 0$

➤ Physical meaning of K ?

- An empirical parameter that characterizes location of P-T trajectory
- Defined by engine geometry and operating conditions – not a fuel property

Engine Operating Space

Contours are constant fuel consumption, g/kW-hr



Lowest fuel consumption at low-speed, high-load

Approximate knock limit for 87 AKI gasoline

2009 GM LNF 2.0L turbocharged direct injection gasoline engine
NREL, unpublished data

Factors limiting engine efficiency

Strategies to improve efficiency

Pumping loss at low to medium load

Downsize & Turbocharge ←
Downspeed ←
Direct injection ←
Cylinder deactivation ←
Exhaust gas recirculation ←

Friction

Downspeed ←

Low compression ratio and low knock resistance of the fuel

Increase compression ratio ←
Direct injection ←
Exhaust gas recirculation ←

← Pursued more aggressively with higher knock resistant fuel

← Lowers temperature, increasing knock resistance of fuel



Screening of potential SI engine biofuels

McCormick, R.L., Fioroni, G.M., Fouts, L., Christensen, E., Yanowitz, J., Polikarpov, E., Albrecht, K., Gaspar, D.J., Gladden, J., George, A. "Selection Criteria and Screening of Potential Biomass-Derived Streams as Fuel Blendstocks for Advanced Spark-Ignition Engines" *SAE Int. J. Fuels Lubr.* 10(2):2017, doi:10.4271/2017-01-0868

Co-Optima Initiative Tiered Screening Process



➤ *Critical properties for high efficiency SI engines: RON, S, and heat of vaporization (HOV)*

Screened over 400 potential bioblendstocks

Criteria

- Pure component
 - $T_M < -10^\circ\text{C}$ and $20^\circ\text{C} < T_B < 165^\circ\text{C}$
 - Solubility, corrosivity, toxicity, biodegradability, safe handling
 - **98 RON minimum**
- Blend with hydrocarbon blendstock
 - **RON>98, S>8**
 - RVP not greater than ethanol
 - Distillation, meets gasoline requirements, no greater effect than ethanol
 - Meets oxidation stability in blend

Representative bioblendstocks with desirable LDSI properties:

- Ethanol
 - 1-propanol
 - Isopropanol
 - Isobutanol
 - Diisobutylene (mixture of isomers)
 - Furan mixture (stability)
 - Cyclopentanone (stability)
 - Bioreformate (aromatics)
- } *High HOV*

Oxidative stability of alkyl furans

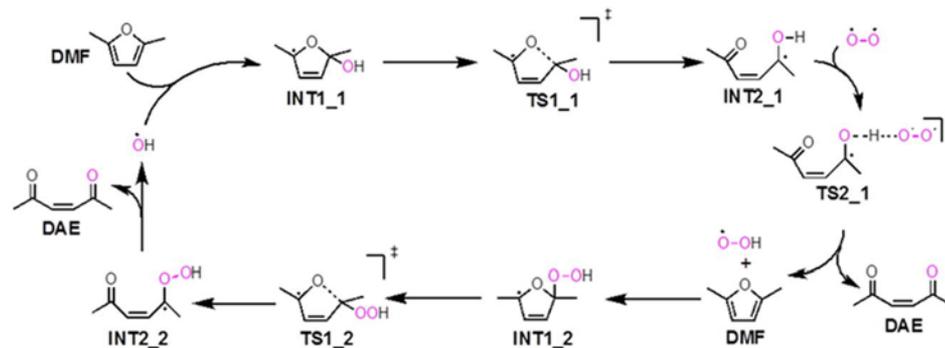
- Dimethylfuran and 2-methylfuran oxidize on standard gasoline stability test – and produce large amounts of gum
 - ASTM D525: 100°C/690 kPa O₂
 - 240 min minimum before break
- Mechanism is revealed using density functional theory calculations
- Can be slowed by antioxidant but requires high treat rate for 10 to 30 vol% furanic compound blends
- May preclude economical use as a gasoline blendstock



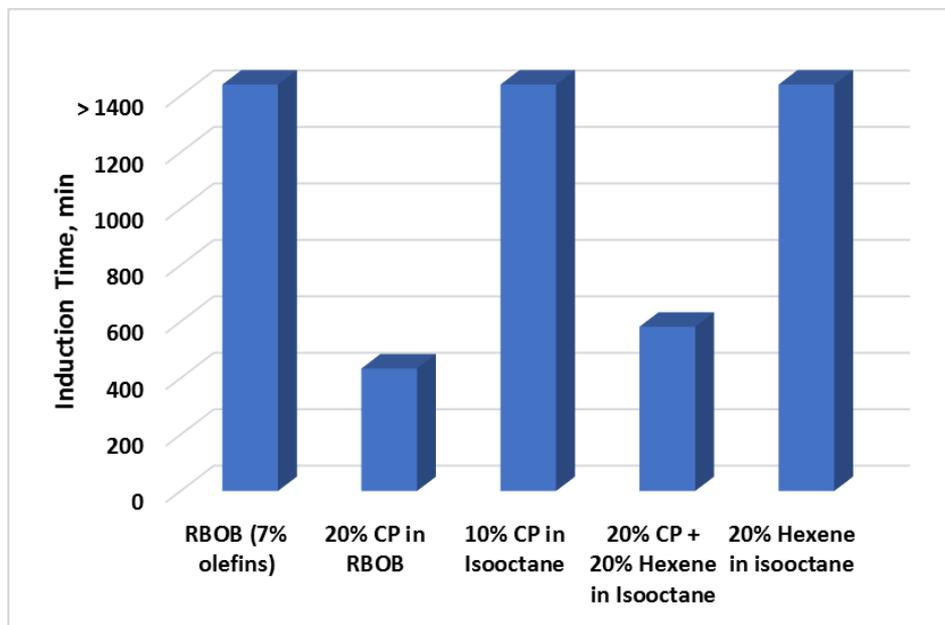
Furan

Ethylfuran

Methylfuran



Cyclopentanone Oxidation

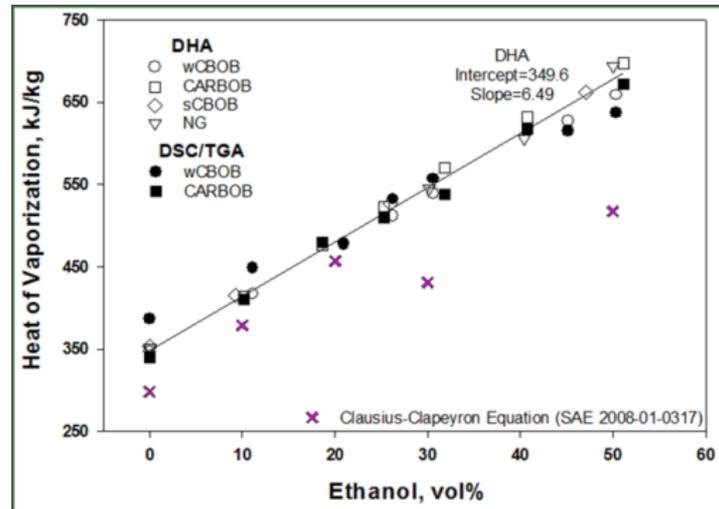


- Addition of cyclopentanone (CP) to commercial gasoline shows oxidation on the stability test
- However, there is no reaction in isooctane – requires the presence of an olefin
- Current work is focused on understanding the mechanism of this reaction and if it can be prevented

Heat of Vaporization Measurement for Full Boiling Range Gasolines

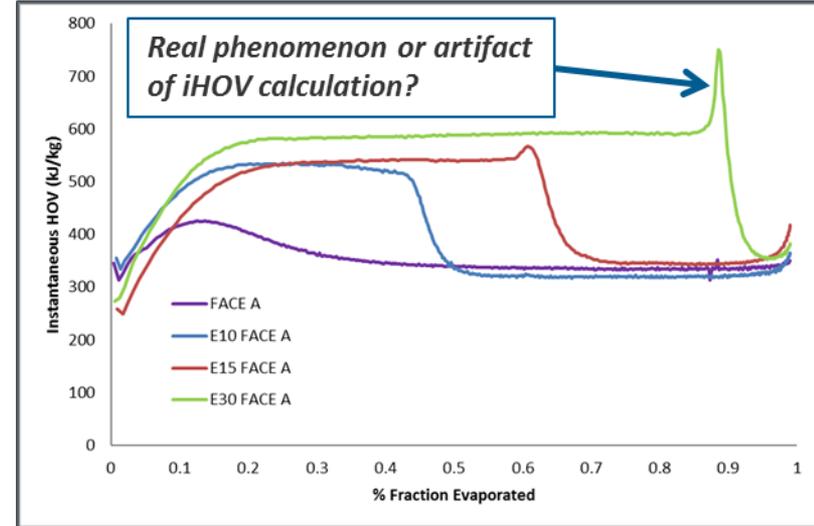
- Evaporative cooling of the fuel-air charge is a primary advantage of direct injection
 - Increasing the knock resistance of the by the equivalent of 5 ON units
- Heat of vaporization of the fuel is therefore an important property
- Two approaches have been developed:
 - Calculate from detailed hydrocarbon analysis (DHA)
 - Measure by DSC/TGA
- Good agreement between DHA and DSC/TGA

Chupka, G.M., Christensen, E., Fouts, L., Alleman, T.L., Ratcliff, M., McCormick, R.L. "Heat of Vaporization Measurements for Ethanol Blends Up To 50 Volume Percent in Several Hydrocarbon Blendstocks and Implications for Knock in SI Engines" *SAE Int. J. Fuels Lubr.* 8(2):251-263, 2015, doi:10.4271/2015-01-0763



Instantaneous Heat of Vaporization (iHOV)

- Instantaneous HOV: DSC-derived heat flow (J/s) divided by TGA-derived mass loss rate (g/s)
 - Constant T of 25°C
- FACE A gasoline (1% aromatics)
 - Show flattening of HOV at a high level that is sustained until ethanol evaporates
 - Ethanol paraffin azeotrope?
 - Note spike caused by mismatch in time response of DSC and TGA measurements during rapid transient
- Gasoline with more typical level of aromatics shows different behavior
- Using DSC/TGA/MS to investigate composition of evaporating gas





Biofuel Screening Summary

- Based on fuel properties a limited number of fuels were selected from over 400 proposed
- Poor oxidation stability was observed for alkyl furans and cyclopentanone
 - QM simulations revealed the mechanism of alkyl furan instability, additional research is required to resolve this issue
 - Cyclopentanone oxidation appears to require the presence of olefin, mechanism is being investigated now
- New methods developed for full boiling range HOV measurement, ongoing research on iHOV

A man in a dark blue lab coat and safety glasses is working on a complex engine test cell. The engine is surrounded by numerous hoses, wires, and sensors. A large, flexible metal hose is prominent in the foreground. The background shows a laboratory setting with a window and various pieces of equipment.

HOV effect on engine knock

Ratcliff, M., Burton, J., Sindler, P., Fouts, L., Fioroni, G.M., McCormick, R.L.
“Effects of Heat of Vaporization and Octane Sensitivity on Knock-Limited Spark Ignition Engine Performance” SAE Tech Pap 2018-01-0218.

Sluder, C.S., Szybist, J.P., Ratcliff, M., McCormick, R.L., Zigler, B.T. “Exploring the Relationship between Fuel Heat-of-Vaporization and Sensitivity” SAE *Int. J. Fuels Lubr.* 9(1):80-90, 2016, doi:10.4271/2016-01-0836.

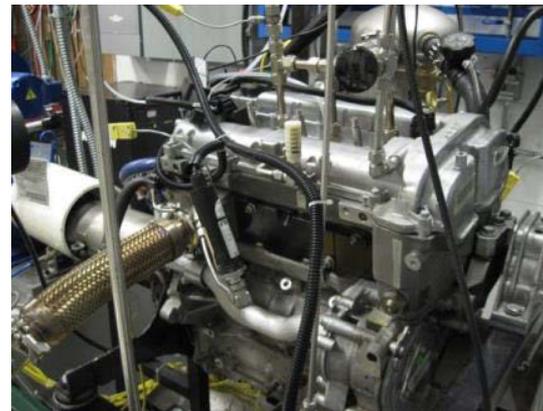
Motivation and background

- Evaporative cooling clearly produces increased fuel knock resistance in DI engines
 - For hydrocarbon fuel, increases effective ON by 5 units, allowing CR to be increased by 1 unit
- Studies also show additional cooling for high HOV ethanol blends
- Yet there are conflicting results on whether this results in additional increase in knock resistance
 - Octane sensitivity and HOV are covariant in some studies
 - Possibly because evaporative cooling is captured in the RON measurement?

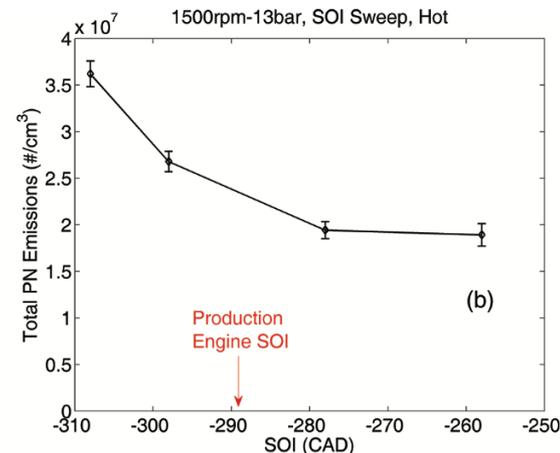
Engine Test Platform

GM LNF Engine Modified to Single Cylinder

- Direct injection with alternate upstream injector
- 75-hp AC dynamometer
- Independent control of fuel injection timing, spark timing, fuel pressure, etc.
- Combustion analysis (high speed cylinder pressure data)
- Critical flow orifice air system
- High-pressure fuel cart
- Emission measurement
 - CAI raw regulated emissions bench
 - TSI Fast Mobility Particle Sizer (FMPS) w/ Dekati diluter & thermodenuder for PN
 - AVL Micro-soot sensor and dilution system for PM mass



- *All experiments at 1500 RPM*
- *Start of injection at -280° aTDC, based on prior NREL study showing this minimized PN, a likely indicator of low fuel impingement (which can change K)*



Fuel Matrix

Fuel	RON	S	HOV (kJ/kg)	Oxygenate (vol%)	Oxygen (wt%)
Isooctane	100	0	303	0	0
TSF99.8	100.4	11.3	390	0	0
E20 + TRF88 (E20)	101.1	9.4	472	19.7	7.4
E40-TRF69 (E40)	99.2	12.2	595	39.4	14.0

- Fuels all nominally RON = 100
- High S fuels nominally S = 11, however some variation
- HOV ranges from 300 to 600 kJ/kg
- Knock limited load measured at a range of intake air temperatures for both direct injection and upstream fuel injection

Intake Valve Closing Temperature

- Intake valve closing temperature:

$$T_{IVC} = PV/nR$$

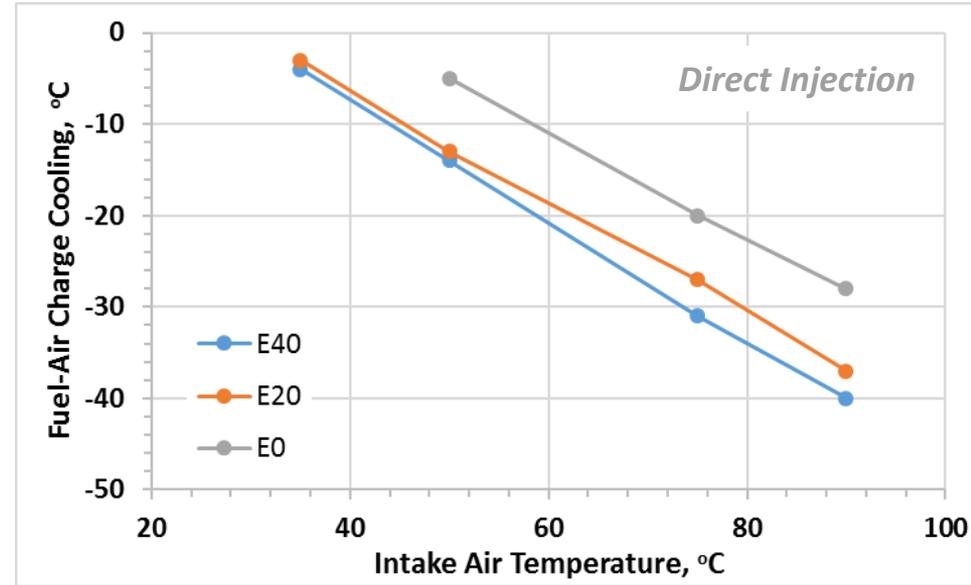
- Measured cylinder pressure
- Known volume at given crank angle
- Measured air and fuel mass flows

- T_{IVC} is how evaporative cooling is captured in P-T simulation

- Fuel-air charge cooling is:

$$T_{IVC} - T_{INTAKE}$$

- Greater cooling at higher T_{INTAKE}
- Significant additional cooling estimated for E20 vs E0, but only slightly more for E40

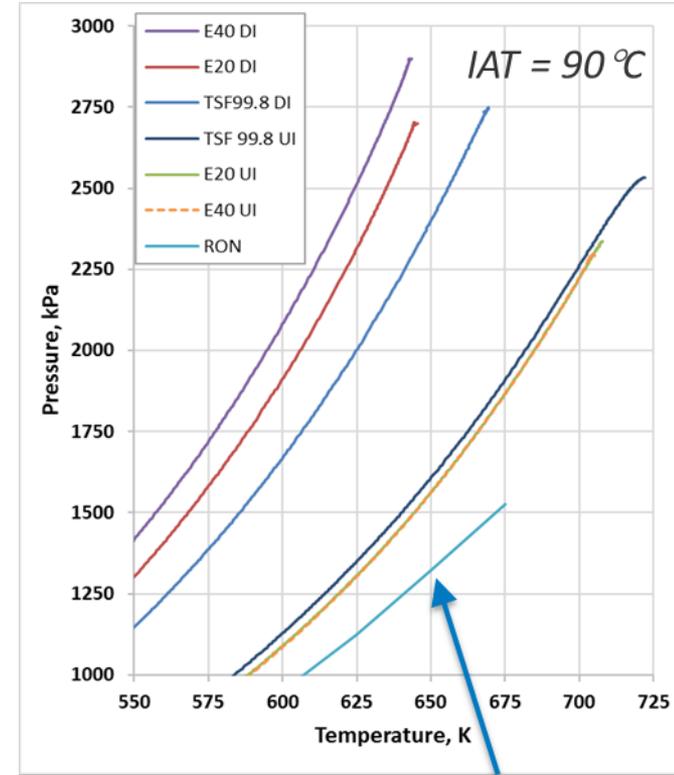


P-T Trajectories

- P-T trajectories generated from:
 - Measured cylinder pressure
 - Known volume at given crank angle
 - Intake valve closing temperature, $T_{IVC} = PV/nR$

$$T = \left(\frac{T_{IVC}}{P_{IVC} V_{IVC}} \right) P V$$

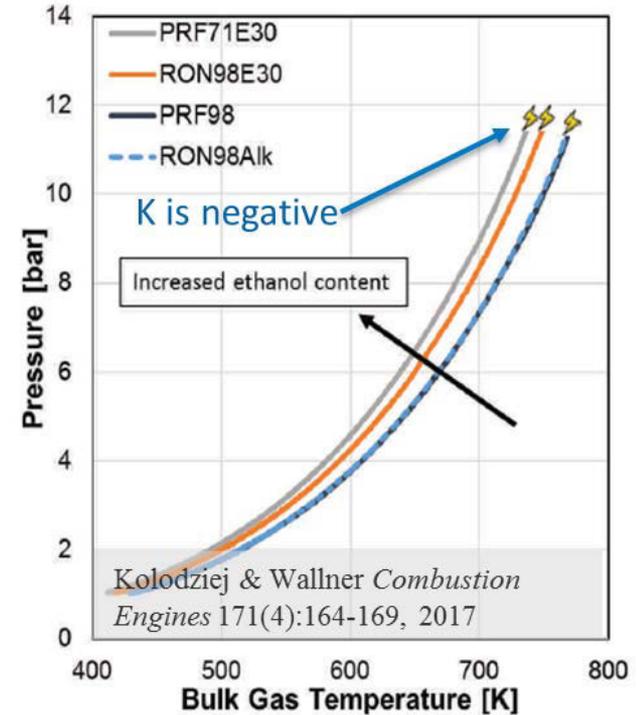
- P-T trajectories for all IAT sweep experiments were beyond RON
 - For UI, all fuels have the same trajectory – no HOV effect
 - For DI, fuels with higher HOV are further “beyond RON”
 - Even though T_{IVC} was not much lower for E40
- **Evaporative cooling reduces K in DI engines – it is not only a function of engine operating conditions**



RON trajectory (Szybist & Splitter, C&F 2017)

Evaporative Cooling on the RON Test

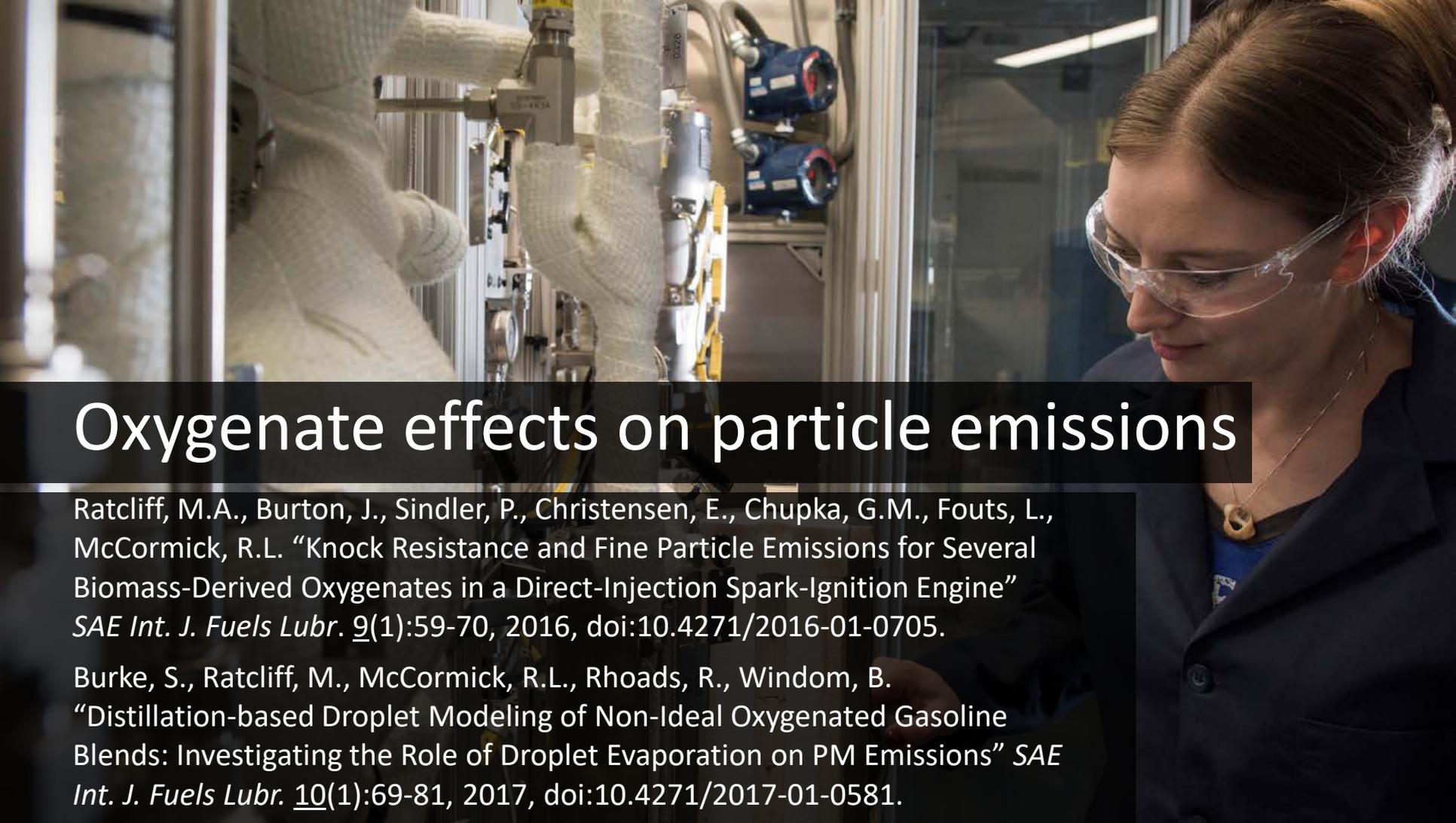
- Kolodziej and Wallner show ‘beyond RON’ P-T for RON measurements with E30
- For high HOV fuels, the requirement that $K=0$ for RON measurement is not satisfied
 - HOV effects may appear to be captured in the measurement if $K=0$ is assumed – when it’s not
 - K can be range from -0.2 to -0.4 for E40 to E85 blends





HOV Effect on Knock Limit Key Insights

- K is not a fuel property, but it is affected by the fuel HOV in DI engines and cannot be assumed constant with fuel
- $K \neq 0$ for RON tests with fuels having $HOV > HOV_{HYDROCARBON}$

A woman with brown hair tied back, wearing clear safety glasses and a dark blue lab coat, is looking down at a piece of equipment in a laboratory. In the background, a robotic arm with white protective sleeves is visible, along with various pipes and blue components of the machinery.

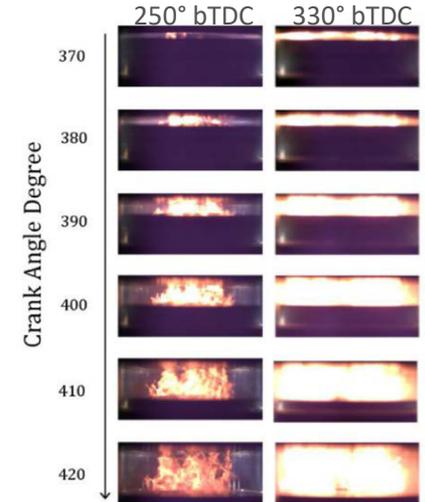
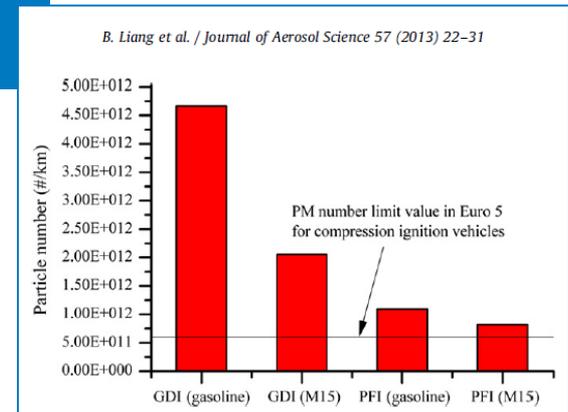
Oxygenate effects on particle emissions

Ratcliff, M.A., Burton, J., Sindler, P., Christensen, E., Chupka, G.M., Fouts, L., McCormick, R.L. "Knock Resistance and Fine Particle Emissions for Several Biomass-Derived Oxygenates in a Direct-Injection Spark-Ignition Engine" *SAE Int. J. Fuels Lubr.* 9(1):59-70, 2016, doi:10.4271/2016-01-0705.

Burke, S., Ratcliff, M., McCormick, R.L., Rhoads, R., Windom, B. "Distillation-based Droplet Modeling of Non-Ideal Oxygenated Gasoline Blends: Investigating the Role of Droplet Evaporation on PM Emissions" *SAE Int. J. Fuels Lubr.* 10(1):69-81, 2017, doi:10.4271/2017-01-0581.

Motivation and background

- Direct injection brings evaporative cooling, improved transient response, and is necessary for engine downsizing
 - Yet many studies show increased emissions of particles for DI
 - Fuel spray may impinge on cylinder wall or piston top
 - Low vapor pressure/high boiling components burn in diffusion flame
- *How is are fine particle emissions affected by fuel chemistry and properties?*



Particulate Matter Index (PMI)

Based on detailed hydrocarbon analysis of the base fuel and the quantity of added oxygenate:

$$PMI = \sum_{i=1}^n \left[\frac{(DBE_i + 1)}{\sqrt{VP(443K)_i}} \times Wt_i \right]$$

Tendency to form PM (points to $(DBE_i + 1)$)

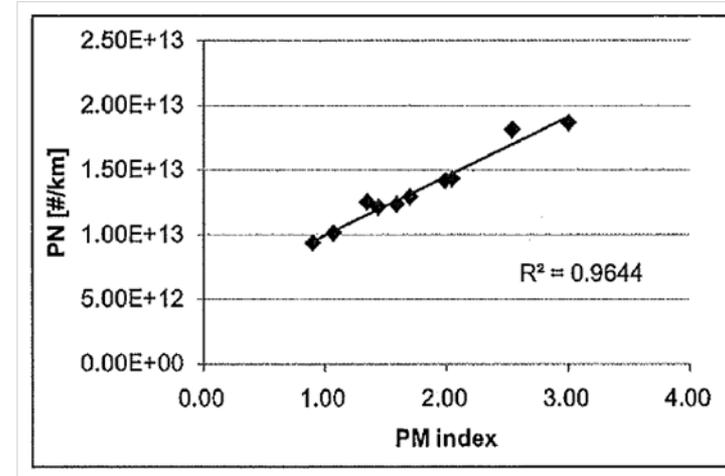
Driver to evaporate and mix with air (points to $\sqrt{VP(443K)_i}$)

Where-

$$DBE = (2C + 2 - H)/2$$

VP = Vapor pressure at 443K (170°C)

Wt_i = Weight fraction of compound

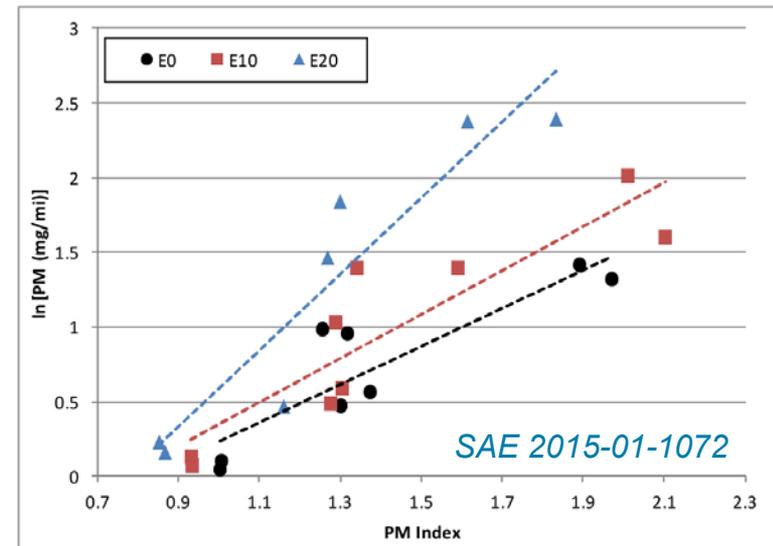


Aikawa, K., Sakurai, T. and Jetter, J.J. Development of a Predictive Model for Gasoline Vehicle Particulate Matter Emissions. SAE International 2010-01-2115.

Aikawa, K., Jetter, J.J. Impact of Gasoline Composition on Particulate Matter Emissions from a Direct-Injection Engine: Applicability of the Particulate Matter Index. Int. J. Eng. Res. 15(3):298-306, 2013

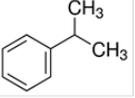
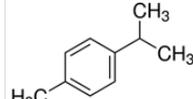
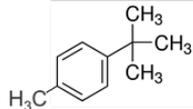
Does PMI Breakdown for Ethanol Blends?

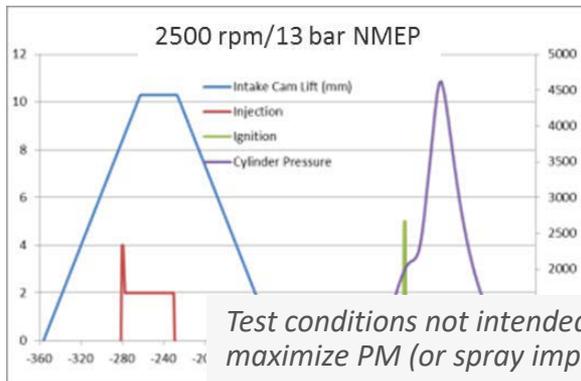
- High heat of vaporization – increased evaporative cooling may hinder evaporation of high boiling aromatics, increasing PM emissions
 - Alcohols only
 - Hypothesis in EPA EPAAct study which found ethanol increasing PM (PFI engines)



Fuel Matrix to Quantify HOV and Aromatics Effects

- Base fuel: FACE B gasoline (low boiling, low aromatics)
- Blending specific aromatics at 10 – 20 vol%
- Ethanol blended at 0 – 30 vol%
- Aromatic content constant with ethanol blending

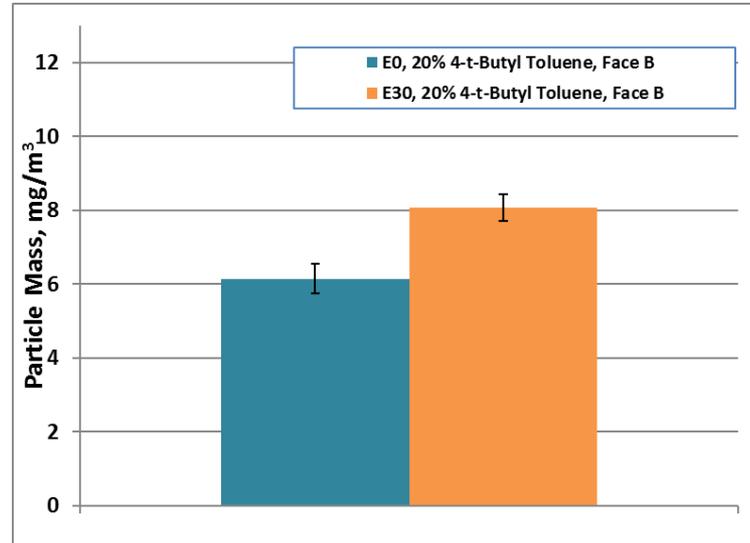
Component	Tb, °C	VP@443K, kPa	Yield Sooting Index (unified)	Structure
Cumene	153	152	187	
p-Cymene	177	85	330	
t-Butyl toluene	191	58	411	



- Factorial design intended to allow separation of ethanol (cooling) and aromatic dilution effects
- Goal to modify PMI to accommodate evaporative cooling

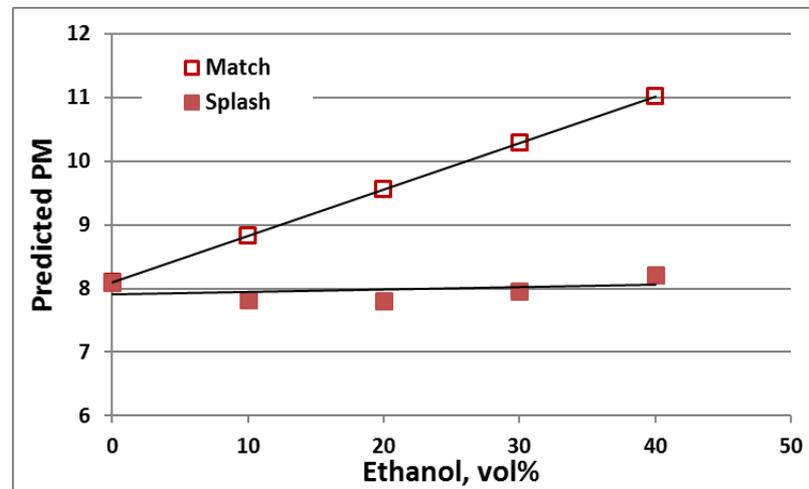
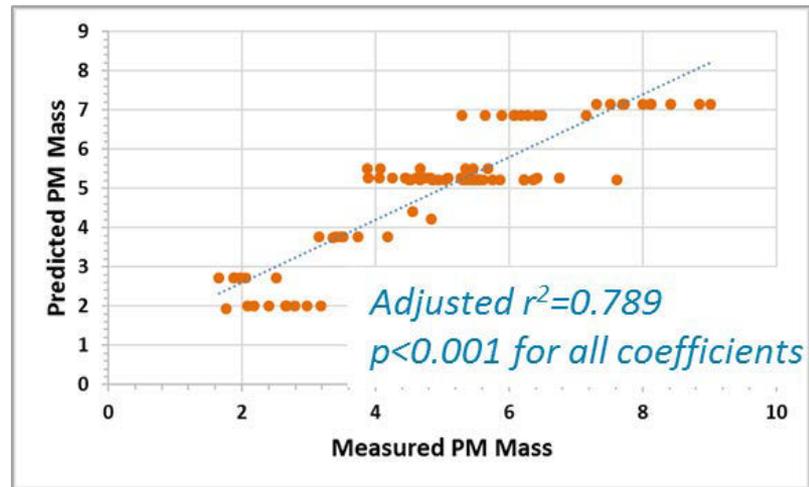
Engine Study Results – PM Mass Emissions

Comparison of E0 vs E30 at constant t-Butyl toluene content (vol%) shows ethanol (HOV) increasing PM



PM Study Analysis

- Linear regression model of factorial design
$$x_1 + x_2 * \{EtOH\% \} + x_3 * \{Aro\% \} + x_4 * \{Aro VP@443K \}$$
 - $X_2 (EtOH) = 0.044$
 - $X_3 (Aro) = 0.34$ ← *Much larger effect*
 - $X_4 (VP) = -0.031$
- Note large scatter in PM data
- Data intended to quantify competition between aromatic dilution and HOV effects for ethanol blending
- Use of model equation indicates that splash blending (ethanol dilutes aromatics) would eliminate PM effect



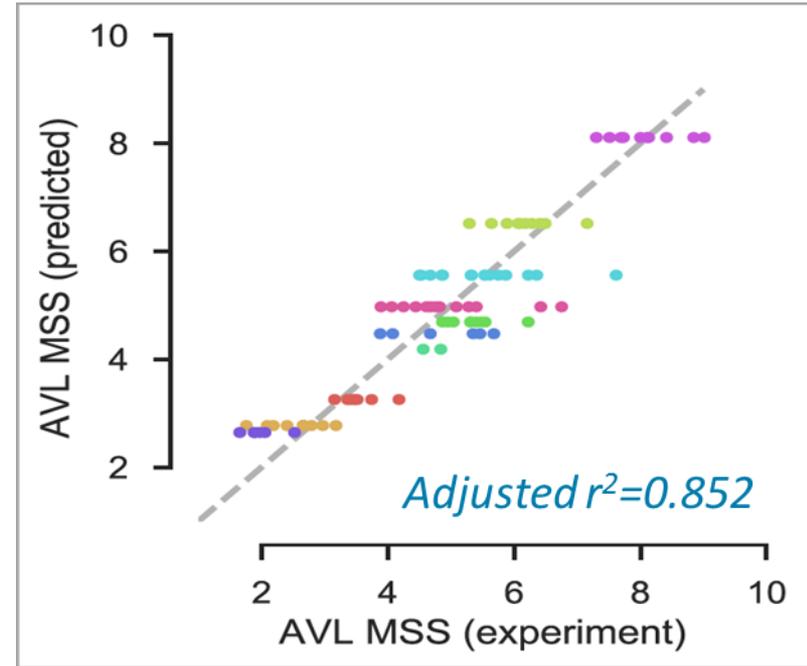
Improved Models

- Combinations of variables capture effect interactions
- Regularized regression approach reveals improved model

$$x1 + x2 * \left\{ \frac{EtOH\% * Aro\%}{Aro\ VP@443K} \right\} + x3 * \left\{ \frac{Aro\ YSI * Aro\%}{Aro\ MW} \right\}$$

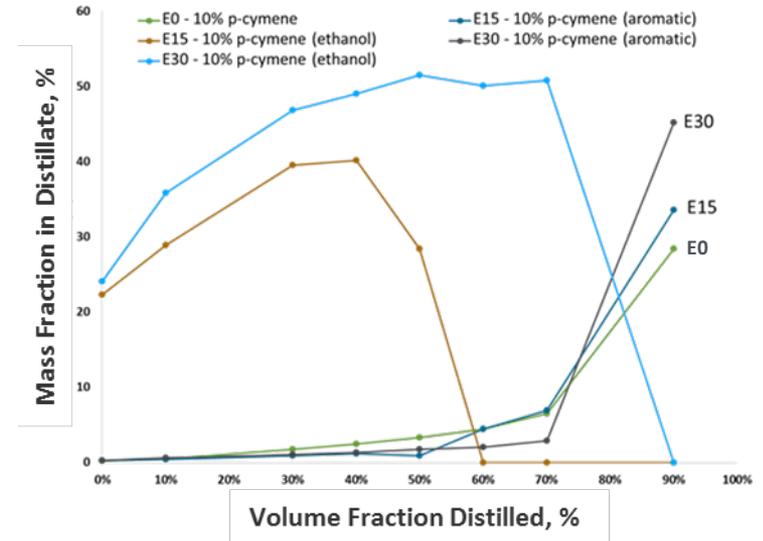
- Expansion of analysis to literature data suggests modification to PMI:

$$\log PM \sim a \rho + b T_{70} + c \sum_i^n \frac{YSI_i \Delta H_{vap,i}}{P_{vap,i} (443K)} x_i$$



Distillation and droplet evaporation simulations

- Our results do not prove that evaporative cooling increases PM – cause and effect not established
- Advanced distillation curve data were acquired by Burke and Windom for use as input to droplet evaporation simulations
- Distillation shows suppression of aromatic evaporation to higher temperatures if ethanol is present
- PM emission impact may be a combination of cooling and non-ideal VLE effects



Burke, S., et al., SAE 2018-01-0361



PMI Modification Summary

- Ethanol blending appears to cause increased PM for high boiling aromatics under some conditions – if aromatics are not diluted by the ethanol
 - Regression model predicts that if aromatics are diluted by ethanol, PM will not increase
- This might be caused by higher evaporative cooling, non-ideal vapor-liquid equilibrium effects, or both
- Preliminary modification to PMI incorporating HOV/ethanol effects developed

FY18-FY19 Research

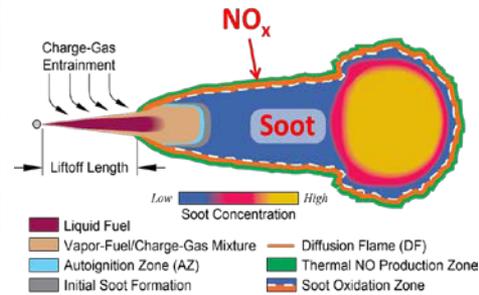
Focus on autoignition and PM precursor formation mechanisms, finish SI knock and PM study, and expand to diesel, mixed-mode, and gasoline compression ignition combustion



Flow reactor studies of autoignition and PM precursor formation



Engine combustion studies with representative LDSI blendstocks



Develop screening criteria for diesel, gasoline compression ignition blendstocks



Set up new research SCE with 300 bar capability for advanced combustion studies

This research was conducted as part of the Co-Optimization of Fuels & Engines (Co-Optima) project sponsored by the U.S. Department of Energy – Office of Energy Efficiency and Renewable Energy, Bioenergy Technologies and Vehicle Technologies Offices.

Thank you

www.nrel.gov

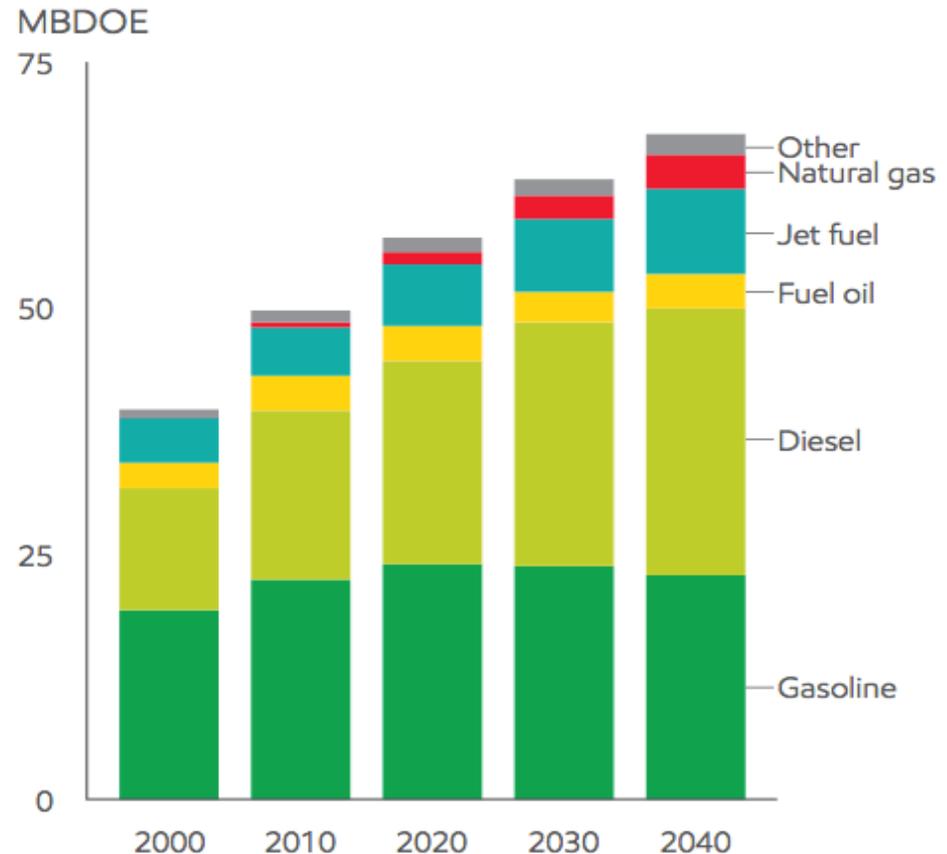
robert.mccormick@nrel.gov

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.



Global transportation demand by fuel

- Gasoline demand peaks in 2020-2030 and then declines
- Demand for distillate (diesel + jet) continues to increase
- Decades will pass before full electric cars dominate market
 - Battery range
 - Sustainable generation buildout
- Can gasoline powered cars be dramatically more efficient?



ExxonMobil Outlook for Energy, 2017
<http://corporate.exxonmobil.com/en/energy/energy-outlook>

Why are SI engines more efficient at low-speed and high load?

Work, W (or power) from an engine:

W_{gross} = theoretical output of the engine

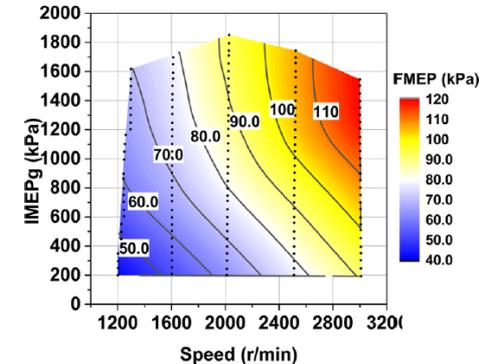
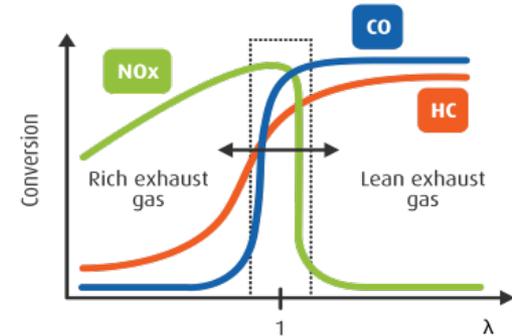
$$W_{brake} \text{ (or } W_{net}) = W_{gross} - W_{pump} - W_{friction}$$

W_{pump} is the thermodynamic cost of moving air into and out of the cylinder

- Higher at low to medium loads because of throttling
- Engine constrained to use stoichiometric amount of air for exhaust catalyst functionality

$W_{friction}$ is the cost of getting work out of the engine

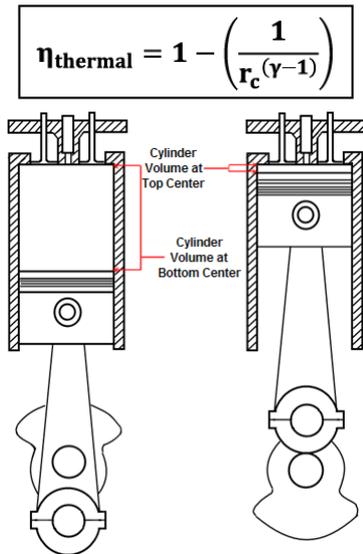
- Contact friction, alternator, fuel pump, belts, etc.
- Increases with engine speed



Strategies to improve efficiency

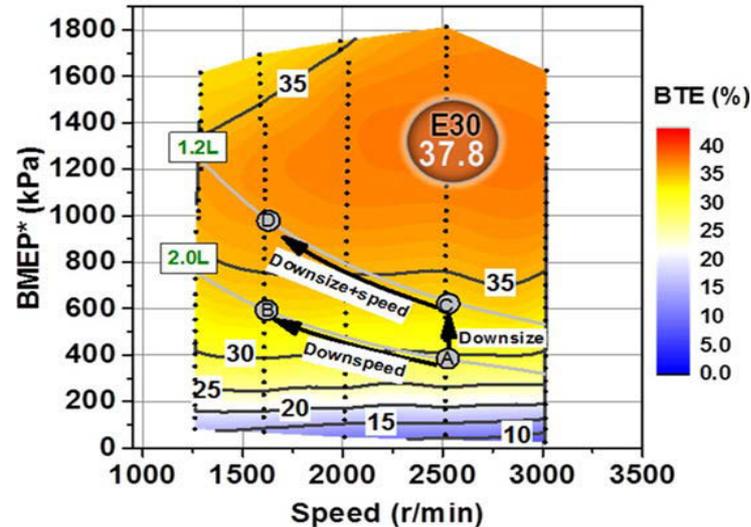
Engines are poorly efficient at light and medium loads, and at high speeds. They are knock limited at high load.

Increase Compression Ratio

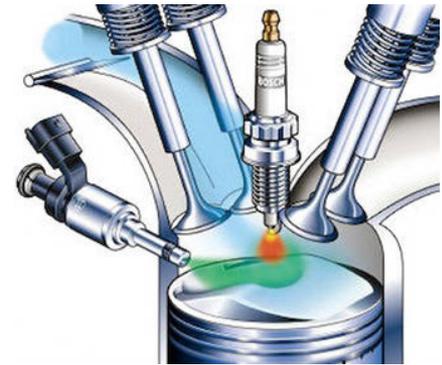


Downspeed

Downsize/turbo



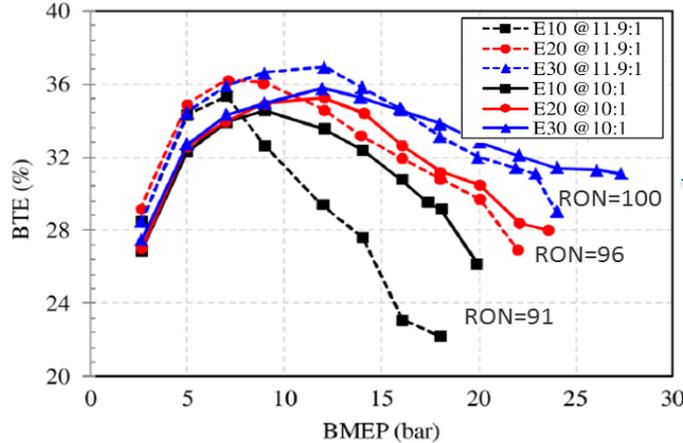
Direct Injection



- Fuel evaporative cooling
- Volumetric efficiency
- Power density
- Knock resistance

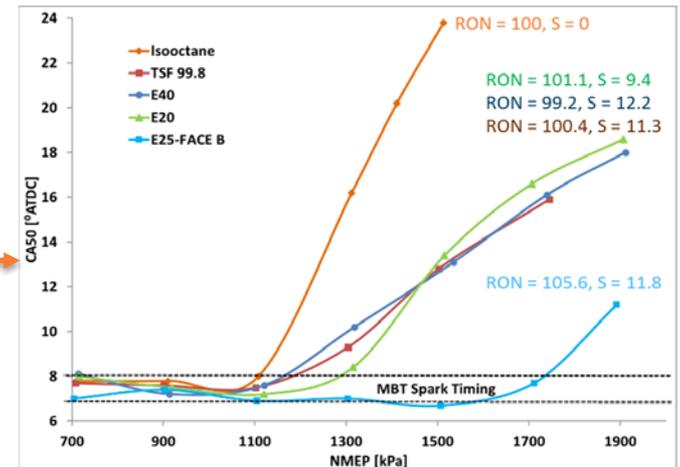
Illustration of load, CR, and octane effects

Jung, H., Leone, T., Shelby, M., Anderson, J. et al., *SAE Int. J. Engines* 6(1):2013, doi:10.4271/2013-01-1321



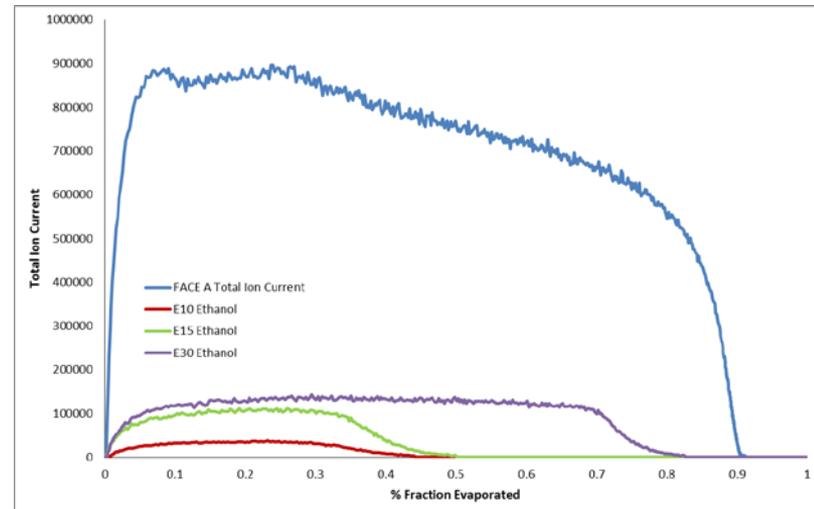
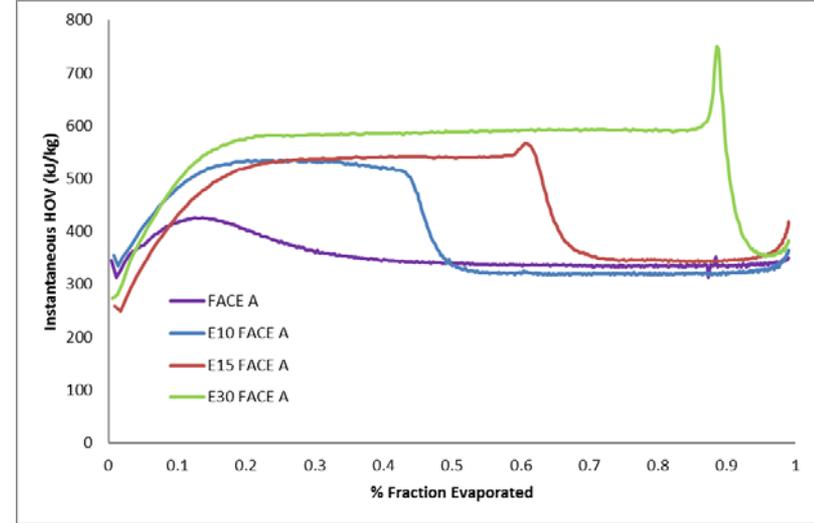
- Even a moderate increase in load steeply increases brake thermal efficiency
- Increasing compression increases BTE at low loads, but is dramatically limited for the low RON fuel
- Increasing CR actually reduces efficiency at higher loads because the engine is knock limited

- Most efficient combustion phasing is MBT (maximum advance for best torque)
- Fuels with the same RON show different behavior with increased load
- Higher S (lower MON) is better for downsized boosted engines ($S = RON - MON$)



Coupling of Mass Spectrometer to DSC/TGA

- Coupled a high resolution mass spectrometer to the DSC/TGA
- Confirms higher ethanol content during plateau
- Next step is to examine co-evaporating species
- Approximate molar ethanol fraction can be calculated from HOV on plateau:
 - 0.45-0.5 for E10
 - 0.5-0.55 for E15
 - 0.6-0.65 for E30
 - In the range of binary azeotropes between ethanol and typical gasoline hydrocarbons

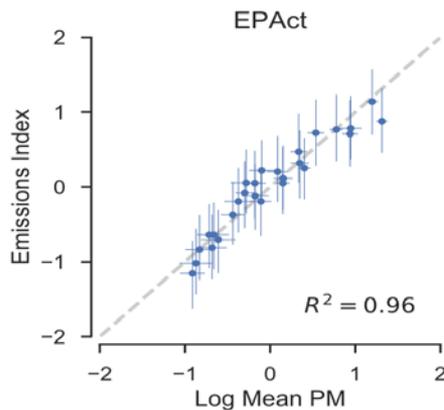
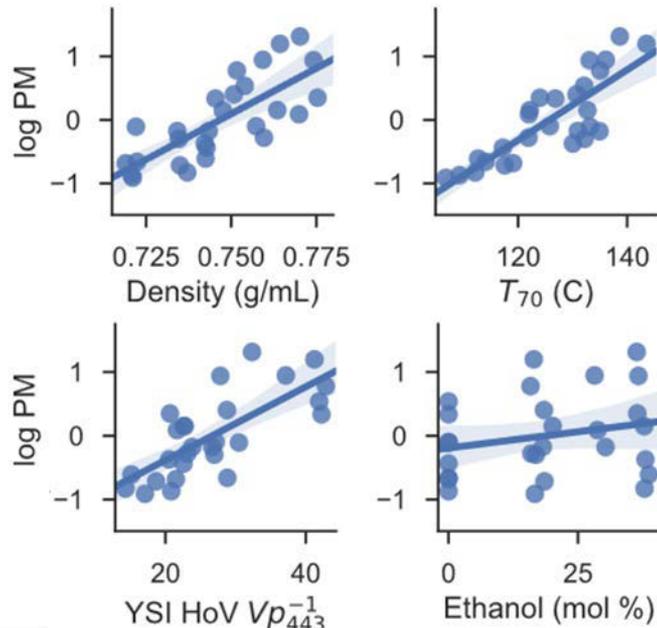


Re-Analysis of EPA Act Study Data

- Analysis of EPA Act study data (SAE 2015-01-1072)
 - Found ethanol caused PM emissions increase
 - Highly controversial
- Our re-analysis based on regularized regression (data determines factors that are important) shows a modification to PMI is a better fit:

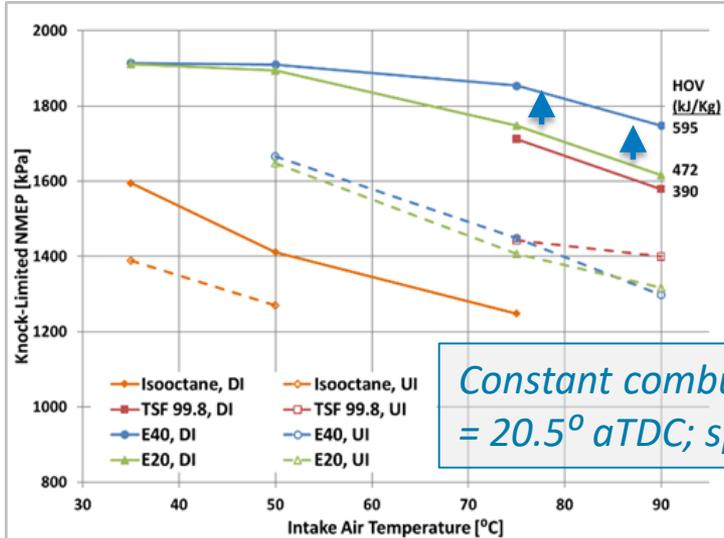
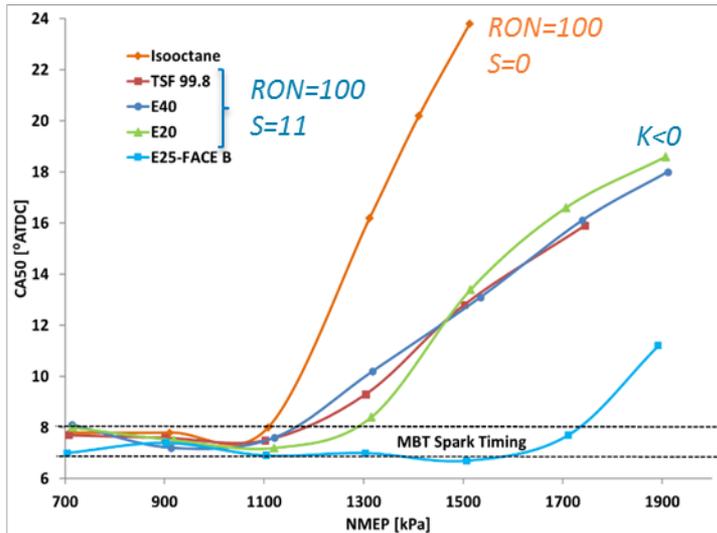
$$\log \text{PM} \sim a \rho + b T_{70} + c \sum_i^n \frac{\text{YSI}_i \Delta H_{\text{vap},i}}{P_{\text{vap},i} (443K)} x_i$$

- Utilized DHA of the 27 gasolines studied
- 15 cars, 2008 model year (port fuel injection)



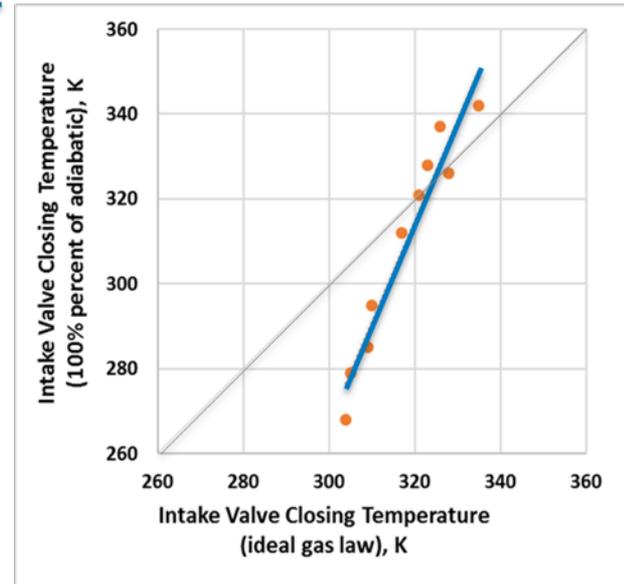
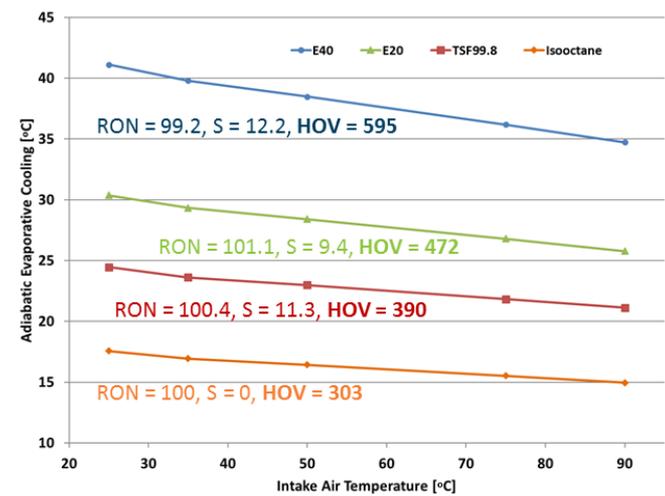
Experiments to differentiate HOV and S effects on knock-limited performance

- Matched RON and S fuels with varying HOV produced similar knock-limited performance in load sweeps at intake air temperature (IAT) = 50°C
 - Consistent with concept that HOV is a thermal contributor to S
- Note high S fuels achieved much higher knock limited load indicating that K in the octane index equation is negative, even at the highest IAT
- E40 produced higher knock-limited loads at IATs > 50°C despite similar RON and S. Why?



Intake Valve Closing Temperature

- Three approaches to determining T_{ivc}
 - $T_{ivc} = IAT$ - assumed for UI experiments (no evap cooling)
 - Ideal Gas Law: $T_{ivc} = PV/nR$ from measured air and fuel mass flows for DI
 - Estimate T_{ivc} from fuel HOV and combustion stoichiometry for DI (adiabatic, maximum possible cooling effect)
 - $$\Delta T_{ad} = \left(\frac{m_{fuel} * HOV}{(m_{fuel} + m_{air}) * Cp_{mixture}} \right)$$
- Points above parity line are at highest IAT, colder than adiabatic case
 - Likely errors in fuel mass flow and assumed zero residual gases
- Lowest points are from lowest IAT cases, indicating less effective evaporative cooling
- Steep slope of data is consistent with hypothesis that the fraction of T_{ad} increases with IAT
 - i.e., faster DI fuel evaporation lessens opportunities for heat transfer



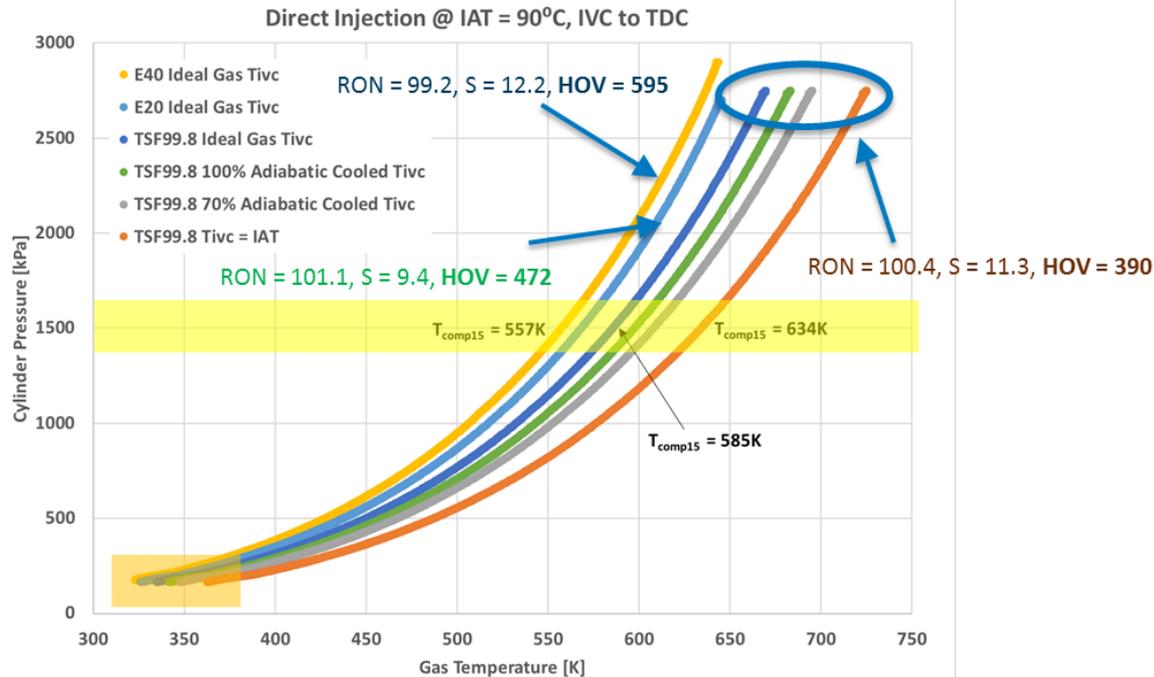
In-cylinder temperatures and K

- K estimated using Kalghatgi equation:

$$K = 0.0049(T_{comp15}) - 0.135\lambda - 3.67$$
- Compressing gas temperatures pinned to intake valve closing temperature (T_{ivc}):

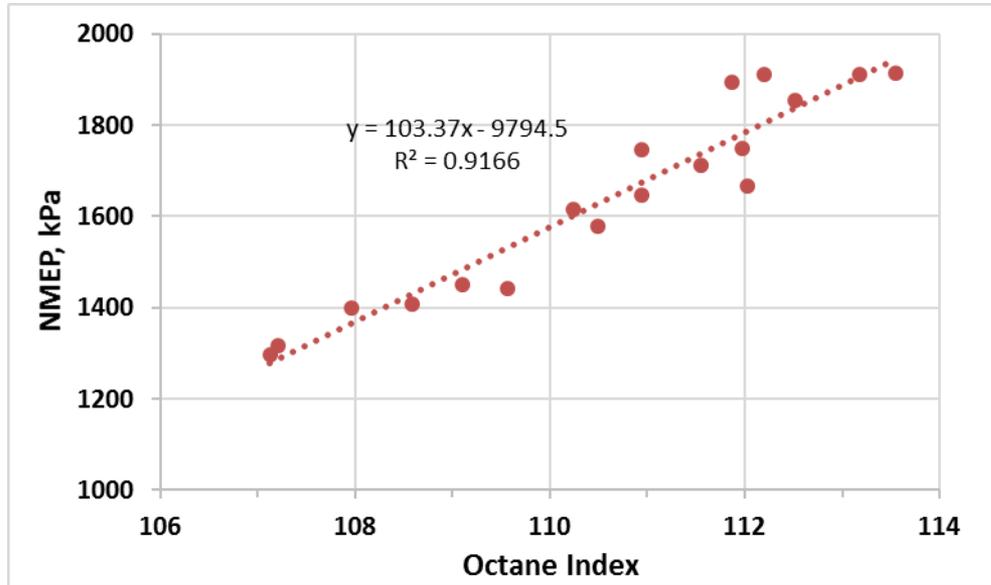
$$T = \left(\frac{T_{ivc}}{P_{ivc} \times V_{ivc}} \right) \times P \times V$$

- T_{ivc} and consequently T_{comp15} and then K are affected by evaporative cooling



K and Octane Index

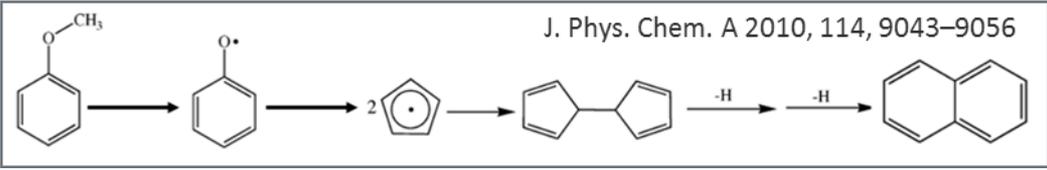
- K s derived from ideal gas based T_{ivc} yield OI values with good correlation to knock-limited loads
- $K = 0.0049(T_{comp15}) - 0.135\lambda - 3.67$



- *Octane index describes fuel knock resistance well*
- *How is HOV affecting K and S ?*
- *To some extent HOV is captured in RON, increasing S – however HOV also impacts K*
- *Because IVCT is affected by K , and IVCT is affected by HOV, K is changed by a fuel property for DI engines*
- *Generally not recognized in studies that focus only on hydrocarbon fuels*

Does PMI Breakdown for Oxygenates?

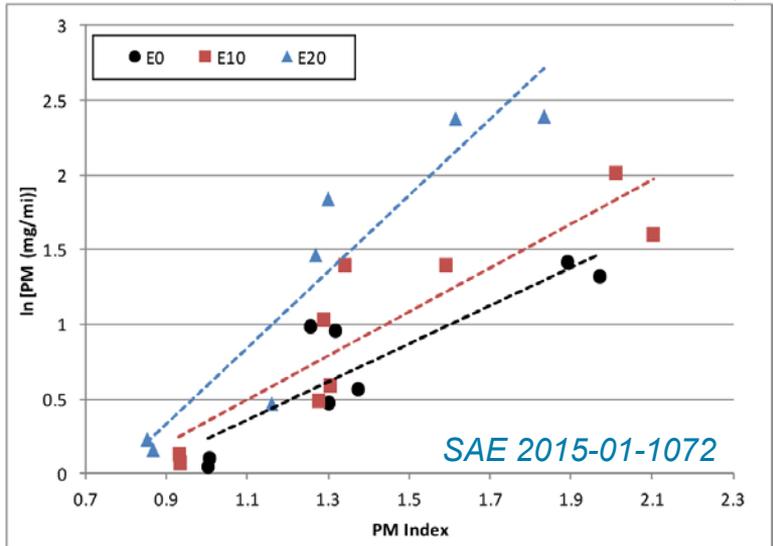
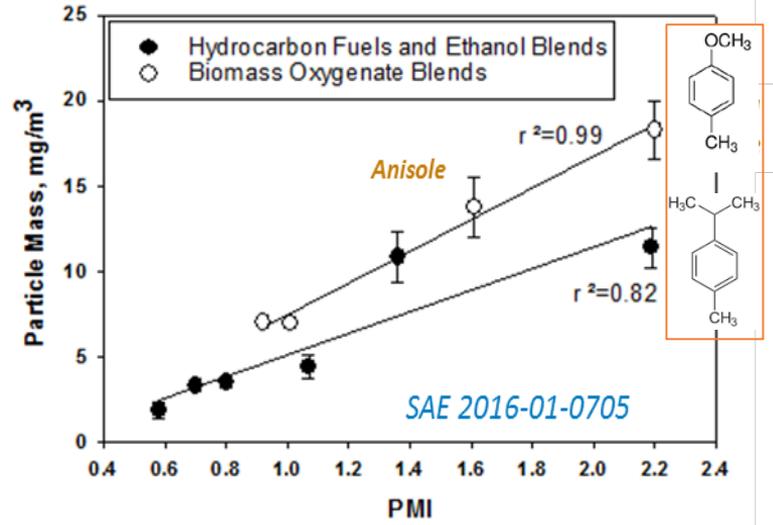
1. Some oxygenates having a low energy path to soot precursors, for example:

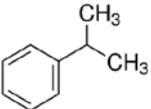
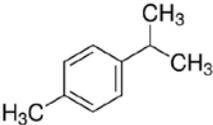


Also secondary alcohols and certain esters

2. High heat of vaporization – increased evaporative cooling may hinder evaporation of high boiling aromatics, increasing PM emissions

- Alcohols only
- Hypothesis in EPA EAct study which found ethanol increasing PM (PFI engines)



Component	Tb, °C	VP@443K, kPa	Yield Sooting Index (unified)	Structure
Cumene	153	152	187	
p-Cymene	177	85	330	
t-Butyl toluene	191	58	411	