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Bioblendstocks that Enable High Efficiency Engine Designs

Robert L. McCormick

with Gina M. Fioroni, Matthew A. Ratcliff, Bradley T. Zigler, John Farrell

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Goal: better fuels and better vehicles **sooner**

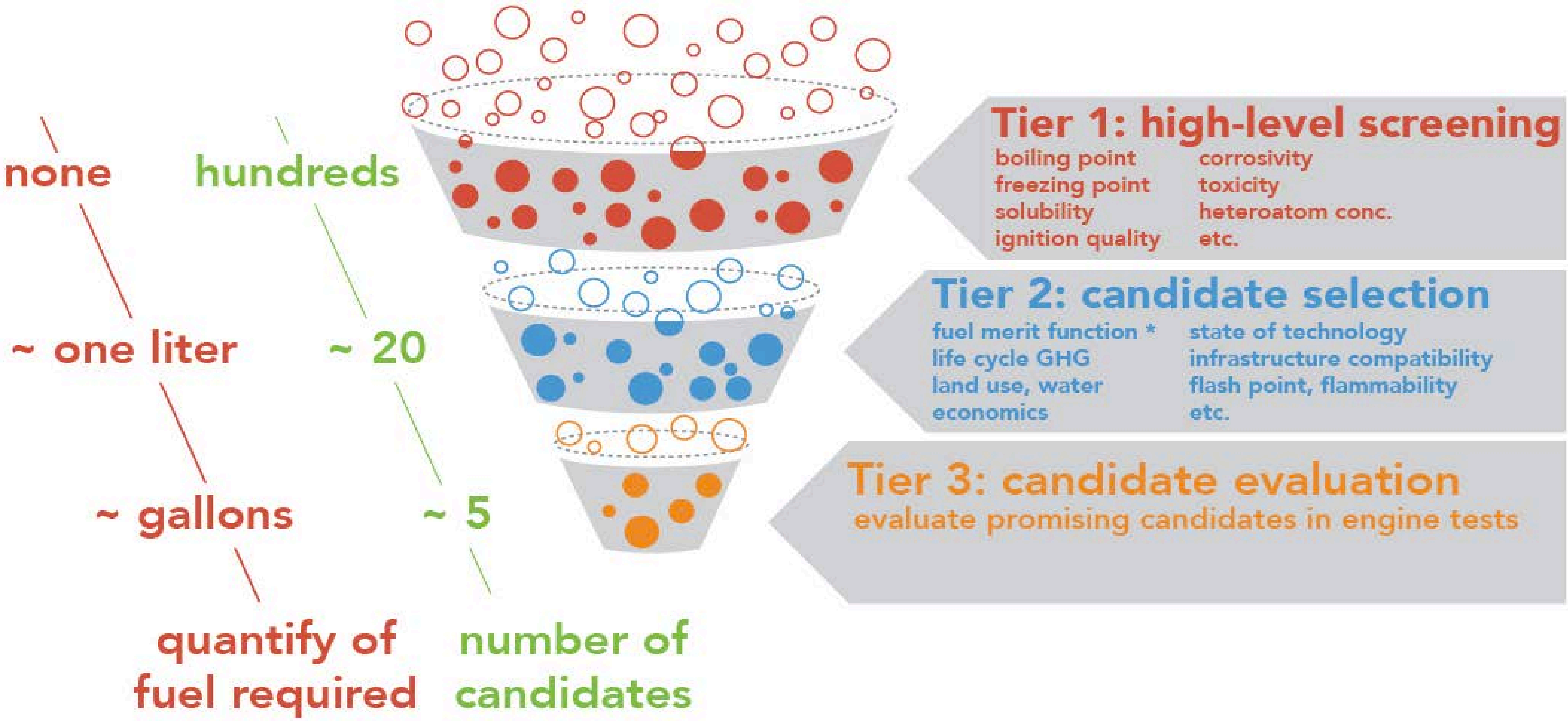
Fuel and Engine Co-Optimization

- What <u>fuel properties</u> maximize engine performance?
- How do <u>engine parameters</u> affect efficiency?
- What <u>fuel and engine combinations</u> are sustainable, affordable, and scalable?
- Are there fuel and engine combinations that are <u>optimal</u> – highest combined GHG reduction?

Spark-Ignition Engine Fuels

Strategies for achieving high efficiency SI combustion include higher compression ratio engines, and higher power density, turbocharged engines that enable smaller swept displacement volume (downsizing) and operation at lower engine speeds (downspeeding).

Fuel selection criteria ("decision funnel")



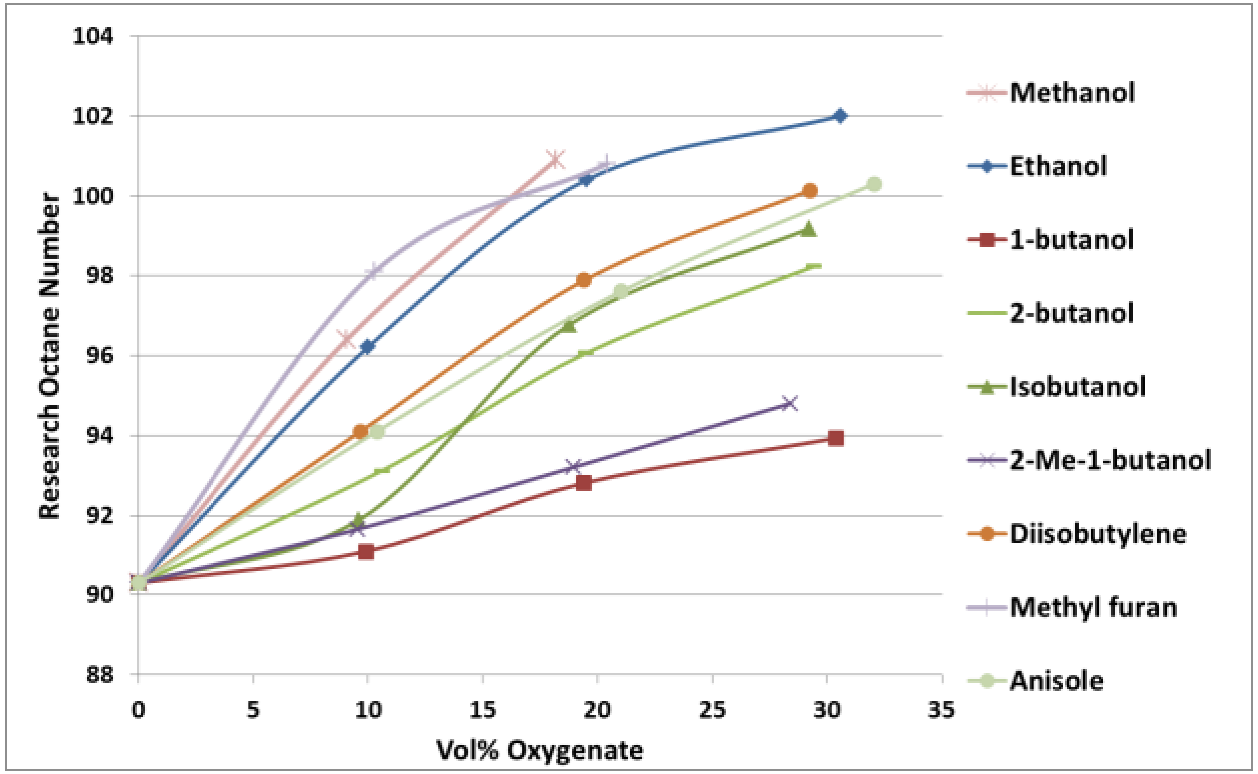
Example of 20 representative candidates

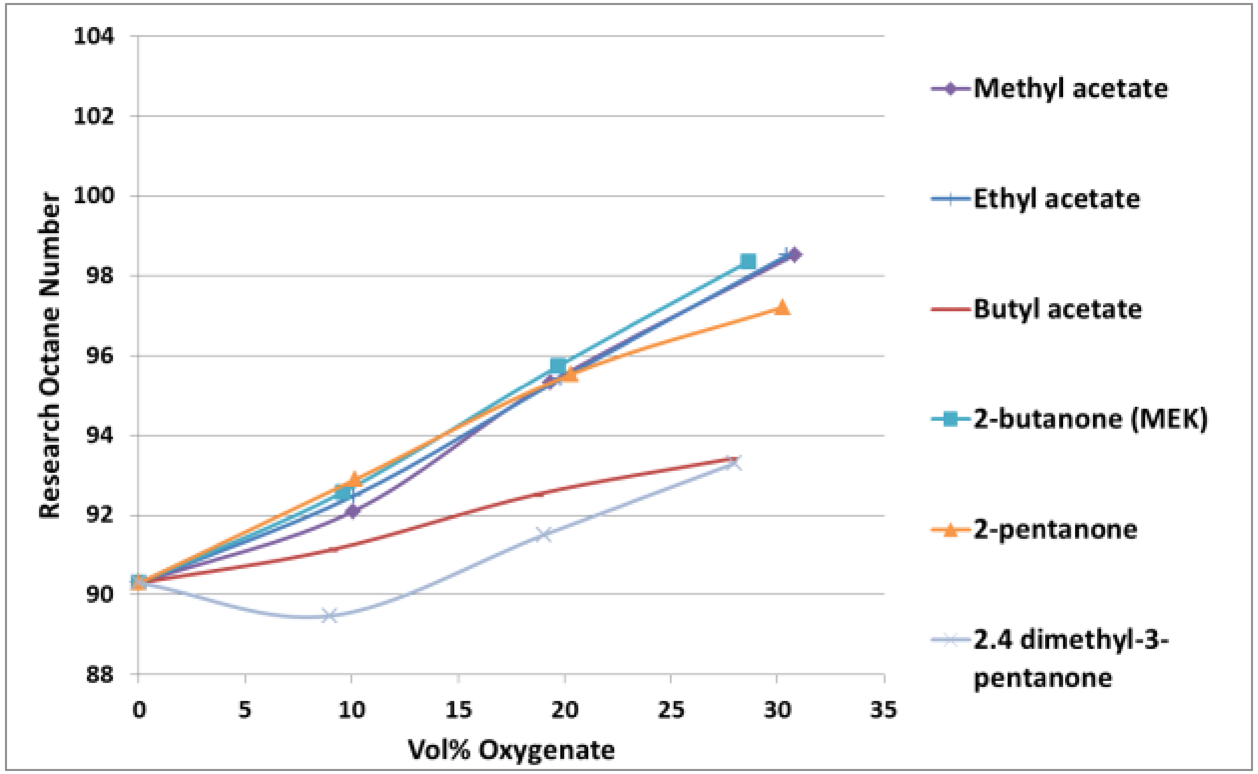
		RON	MON
0	Ethanol (Reference)	109	90
1	Methanol	109	89
2	1-butanol	98	85
3	2-butanol	107	93
4	Isobutanol	105	90
5	2-methyl-butanol	101	88.3
6	2-pentanol	99.4	90.8
7	2,5-dimethylfuran/2-methylfuran mixture	102	87
8	Acetic acid, methyl ester (methyl acetate)	>120	>120
9	Acetic acid, ethyl ester (ethyl acetate)	118	>120
10	Acetic acid, butyl ester (butyl acetate)	100.8	100

		RON	MON
11	Ketone mixture	99.4	99.6
12	Methylethylketone (2-butanone)	111	105.5
13	2-pentanone	105.7	103
14	2,2,3-trimethyl-butane	112	101
15	Isooctene	106	86.5
16	Vertifuel (60%+ aromatics)	105.7	90.6
17	Fractional condensation of sugars + upgrading		
18	Methanol-to-gasoline		
19	Catalytic fast pyrolysis		
20	Catalytic conversion of sugars	~110	

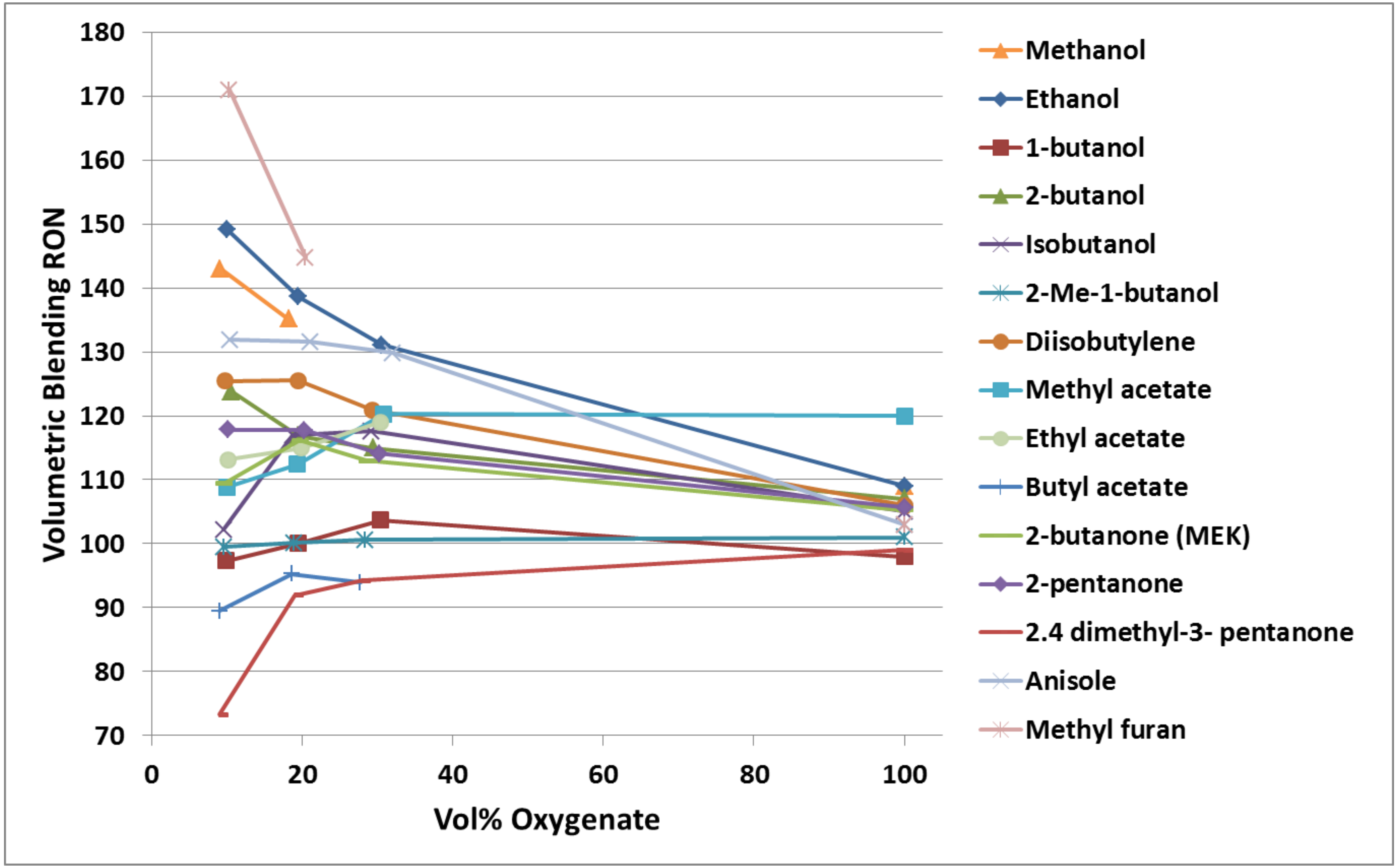
Blend Octane Numbers

Property	Result
Isooctane, vol%	55
n-Heptane, vol%	15
Toluene, vol%	25
1-Hexene, vol%	5
RON	90.3
MON	84.7
AKI	87.5





Blending Octane Numbers



- *Volumetric basis, given the BOB RON and blend RON, calculate the bRON of the bioblendstock*
- *Cautionary note: small experimental error in RON propagates into large error in bRON*

Octane Number Requirements

- Knock-limited spark advance correlates best with Octane Index:

  OI = RON – K S

- K is an engine property
  - Ranging from -0.5 to -1 or lower
  - Higher values at part load
  - Lower values at WOT for downsized/ downspeed/ boosted DI engines

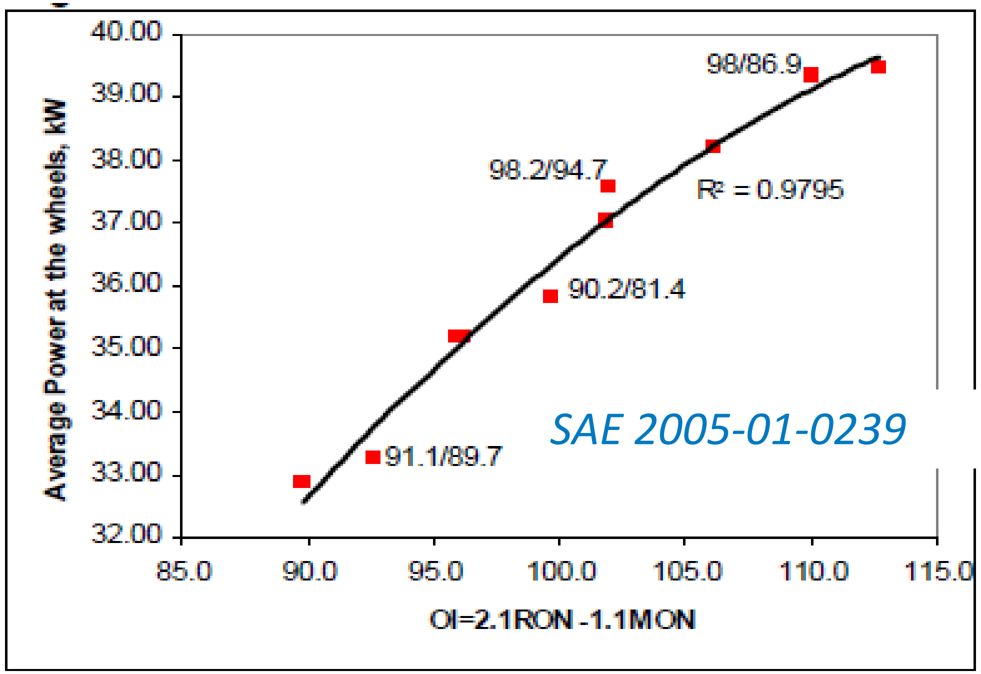
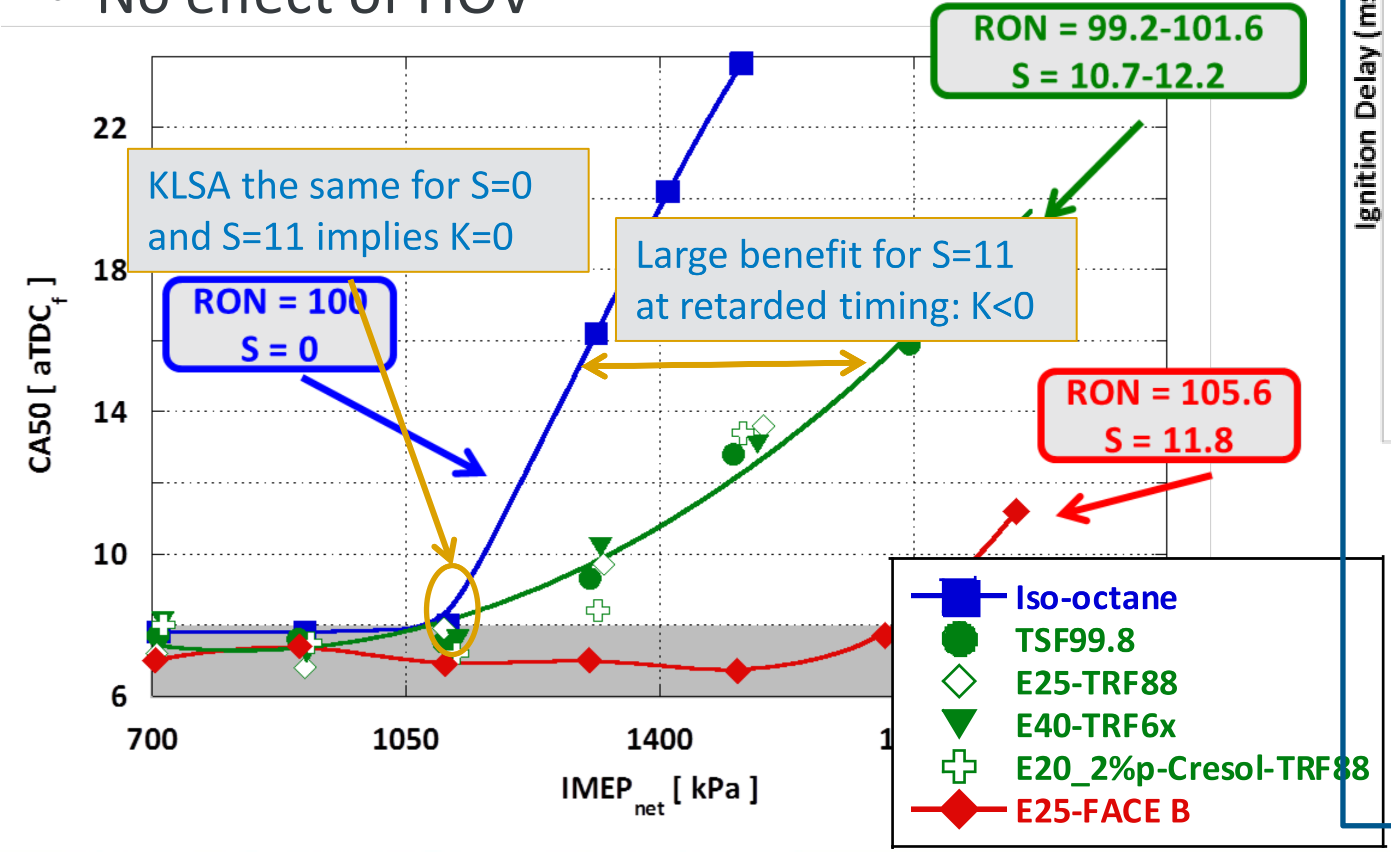


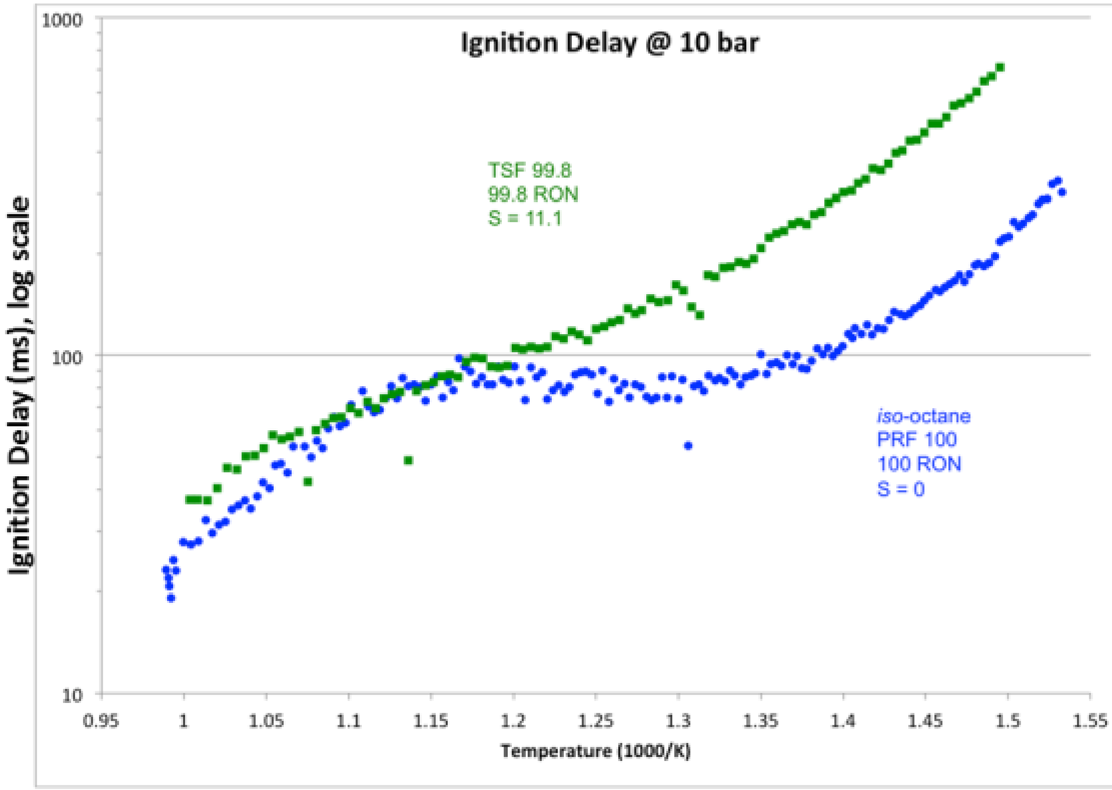
Fig.6c. Mean VTE vs OI = RON +1.08 S. Mercedes CLK1, 2 L

- Negative K implies
  - Knocking regime is outside that bracketed by the RON and MON tests
  - Temperature of the end-gas is lower for a given pressure

Significance of K (and HOV) at Retarded Phasing

- K=0 at KLSA - Single cylinder engine based on production DI engine (intake air 35°C)
- Large S effect at retarded timing (i.e. WOT) for RON = 100
- No effect of HOV

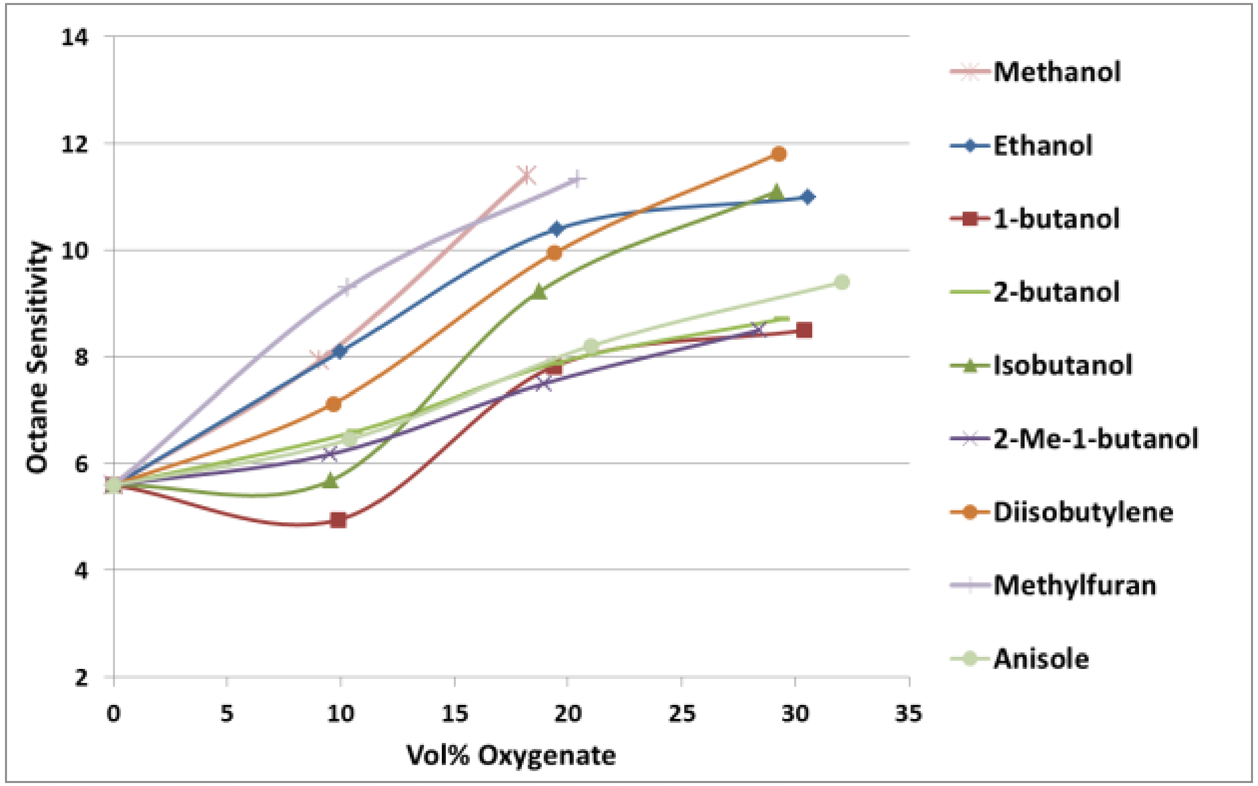


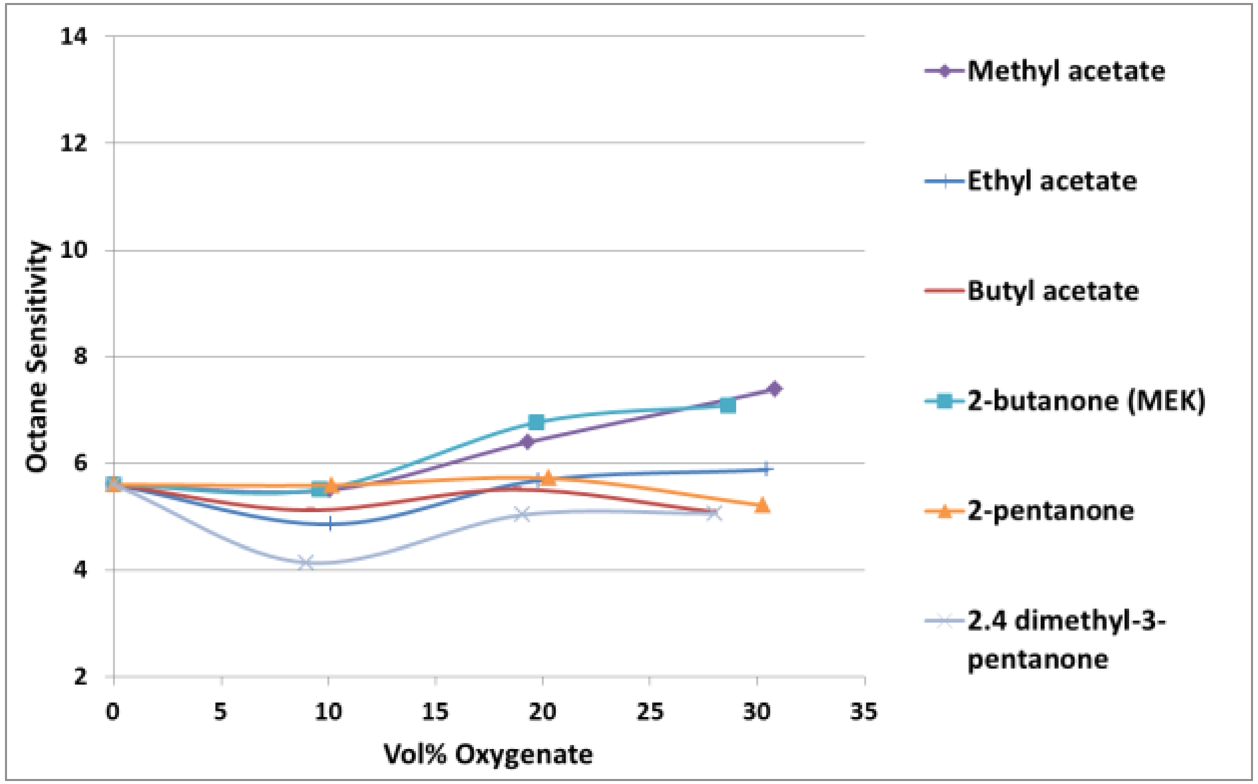


- S=0 fuel (isooctane) exhibits much shorter ID at low T “than expected”
- S=0 fuels exhibit LTHR or ITHR while S>>0 fuels do not

Octane Sensitivity

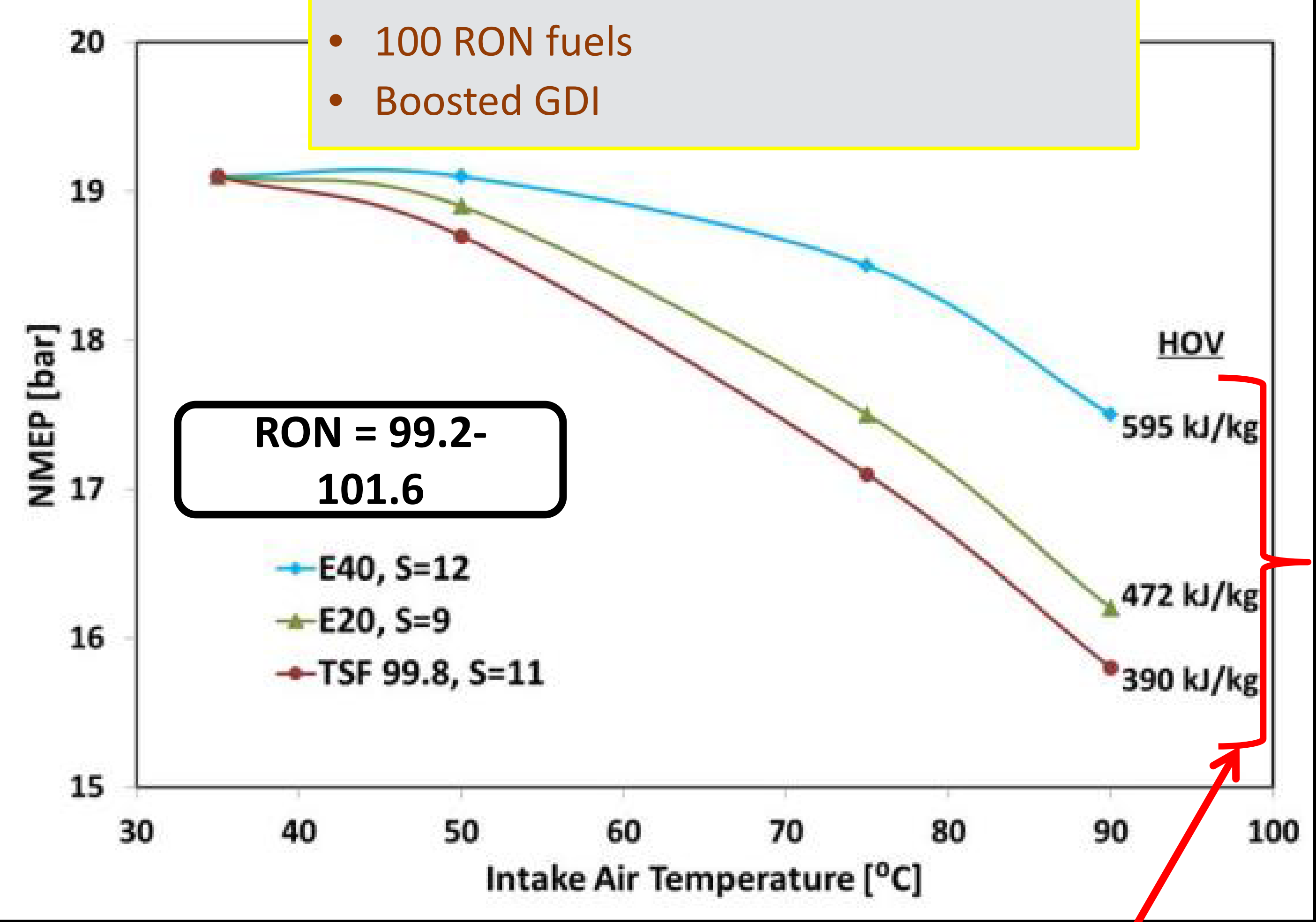
- Many auto makers are asking for S of 8 or higher
  - 8 is minimum requirement in proposed ASTM 100 RON fuel standard
  - Esters and ketones do not impart high S in this scenario
  - Could they be blended on top of an E10 to produce a high RON and high S fuel?





Impact of HOV on Knock Limited Load at Elevated Intake Temperatures

- Knock-limited load at CA50 = 20.5° ATDC
- 100 RON fuels
- Boosted GDI



At intake air T above 50°C, HOV can have a significant impact on achievable load at knock limit, i.e. HOV imparts additional knock resistance

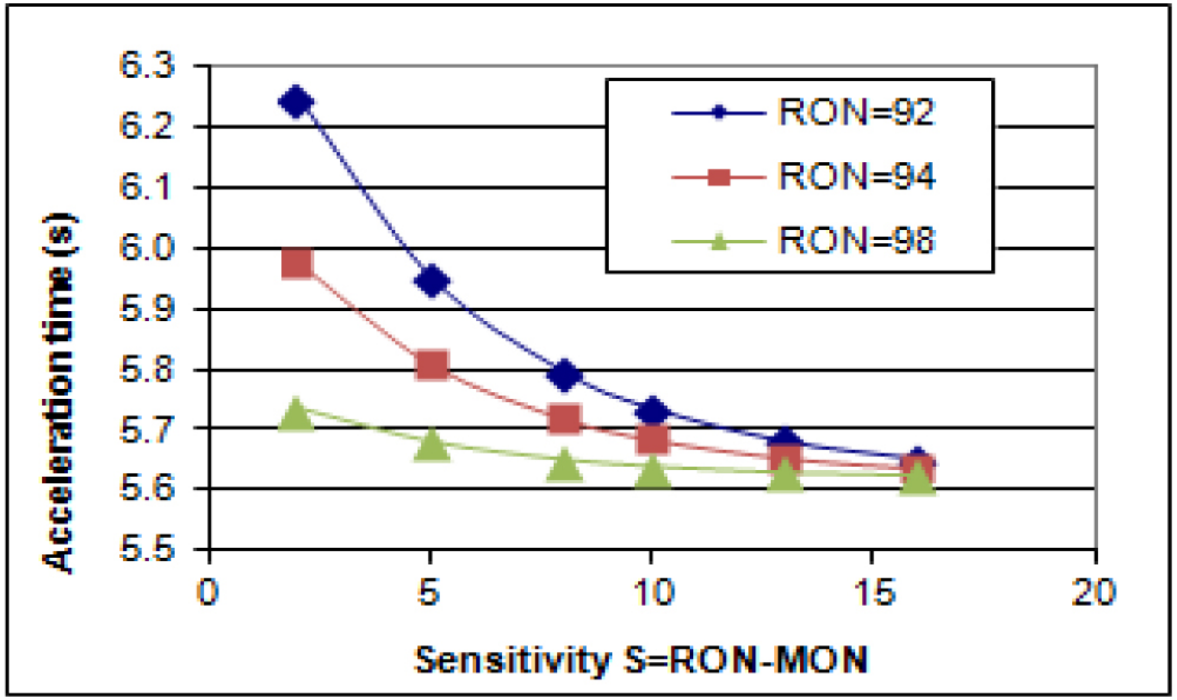
Fuels with fixed RON and S with varying HoV

SI Summary

- Critical properties for enabling high efficiency SI combustion include:
  - RON
  - Octane Sensitivity
  - HOV
  - Flame speed/dilution tolerance

- Uncertainties
  - Are we so far beyond RON that a new antiknock metric or octane number test is needed?
  - What about lean/dilute conditions? Are other fuel properties important?
  - Does the OI=RON – KS paradigm apply to highly boosted engines?

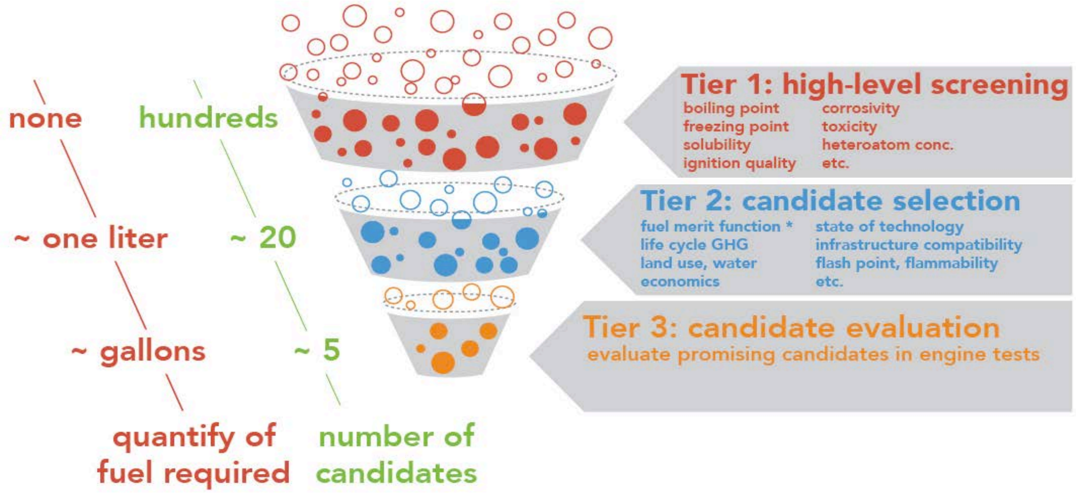
- SAE 2014-01-1216 (Shell and GM)
  - For K = -0.75 at WOT (current production car)
  - S has less effect as RON increases
- Other recent presentations at high boost



Compression-Ignition Engine Fuels
Diesel Combustion

Diesel Combustion

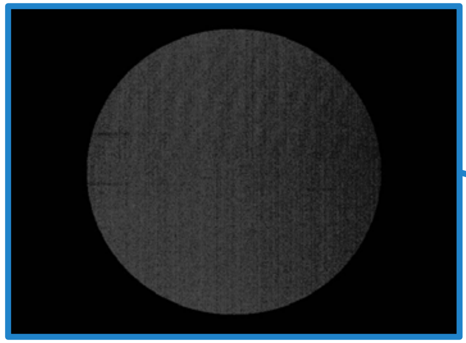
- Inherently very efficient – but pollutant emissions are relatively high
  - High monetary cost for emission control
  - Some energy penalty for emission control
- Research focused on:
  - Efficiency improvement (friction, VCR,…)
  - Reducing PM and NOx to reduce ECS cost, complexity, and energy penalty
    - Sandia LLFC (Mueller, Gehmlich)
    - Late-cycle soot oxidation in cylinder (Andersson)
    - Are there opportunities for fuel to enable LLFC or soot oxidation?
- Potential for carbon reductions from low-net carbon fuels

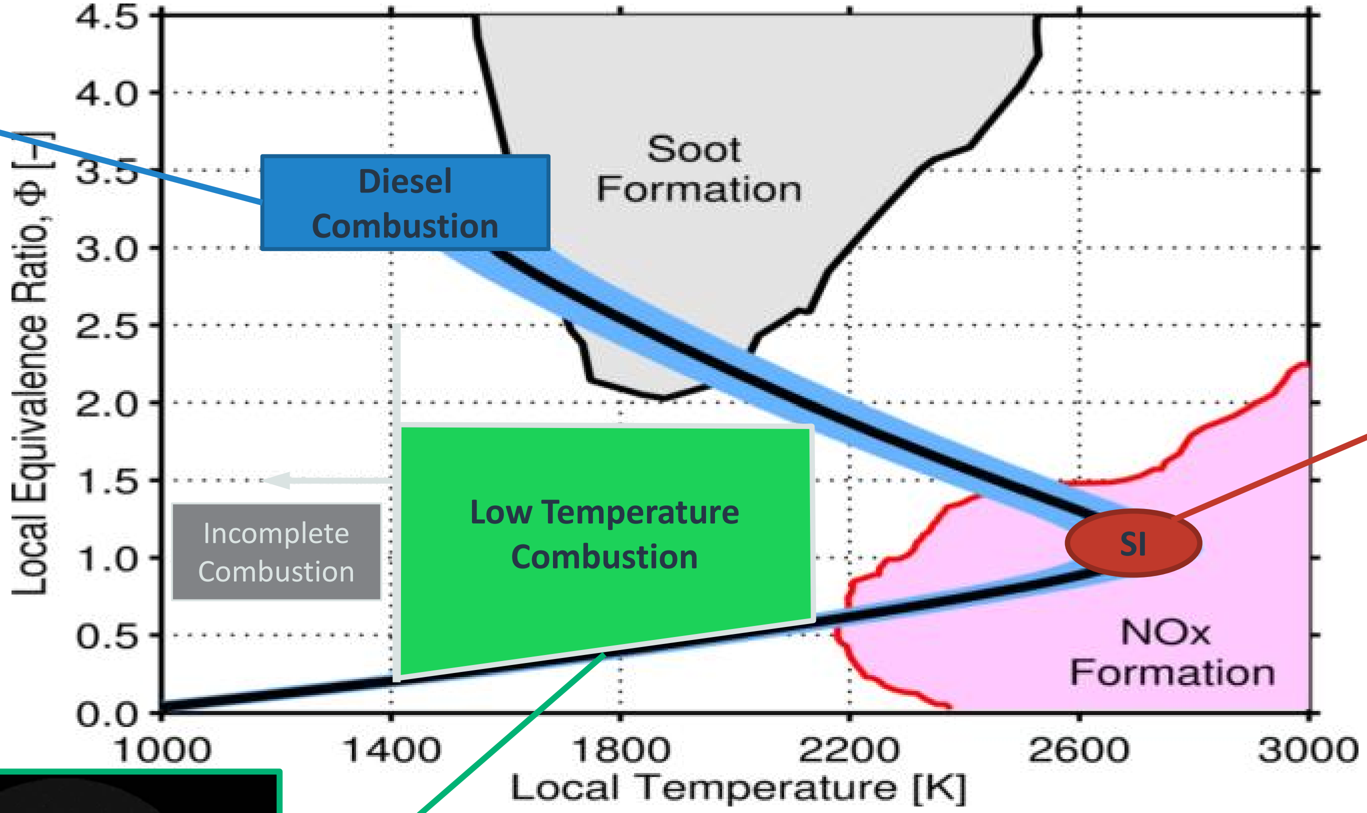


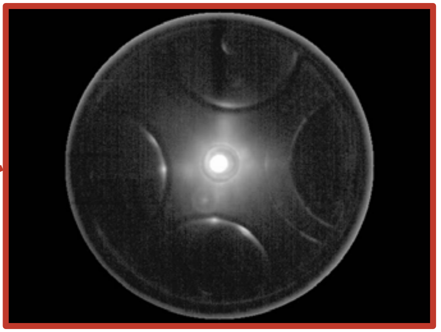
1. Cetane number (CN) required > 40 (> 55 if possible)
2. Headspace in a fuel storage tank will not be explosive
3. Melting point below -10 °C, and lower than -40 °C if possible
4. Soluble in low-aromatic base fuel to -10 °C
5. Blends are water tolerant
6. Normal/final boiling point below 350 °C
7. Toxicity lower and biodegradability similar to current fuels
8. Corrosivity equal to or lower than those of current fuels
9. No heteroatoms beyond oxygen and possibly nitrogen (i.e., very low metals, S, P, etc.)
10. Oxidative stability equal to or better than those of current fuels
11. Lower heating value at least 25 MJ/kg
12. Compatibility with commercially available elastomers
13. Viscosity between ~0.5 and 5.0 cSt at 40 °C
14. No strong odor

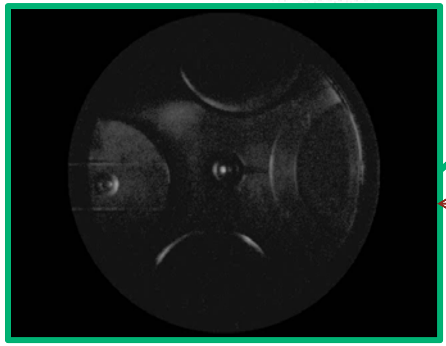
Compression-Ignition Engine Fuels
Low-Temperature Combustion

Fuel Properties that Maximize Benefits of Various Combustion Strategies





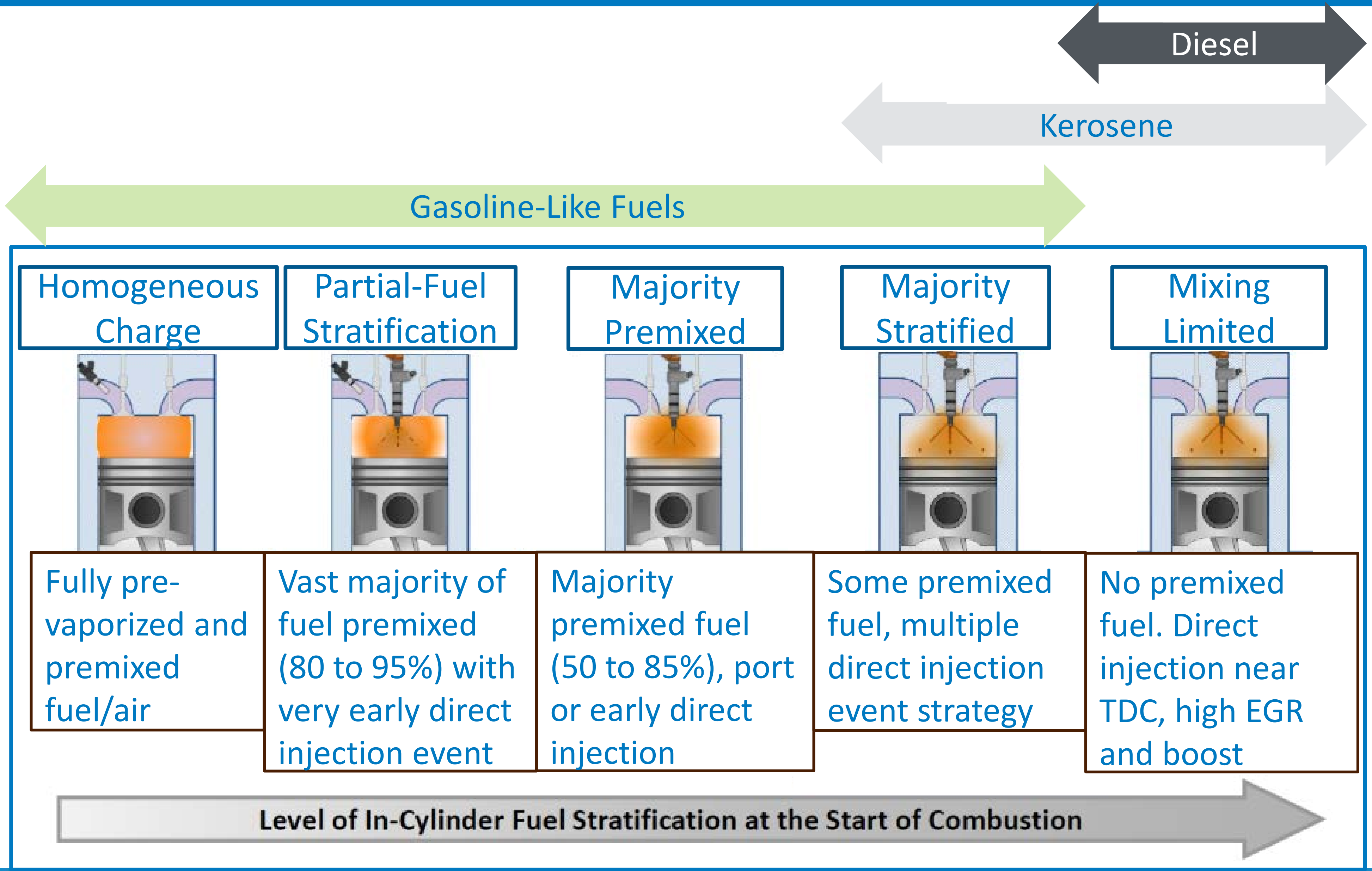




Vision of diesel-like efficiency (or better) with low emissions

Source: Combustion movies courtesy of Dr. Mark Musculus at Sandia National Laboratories

LTC Strategies Classified by Fuel Stratification



List of Critical Fuel Properties for LTC

- Volatility – must be compatible with combustion strategy being pursued

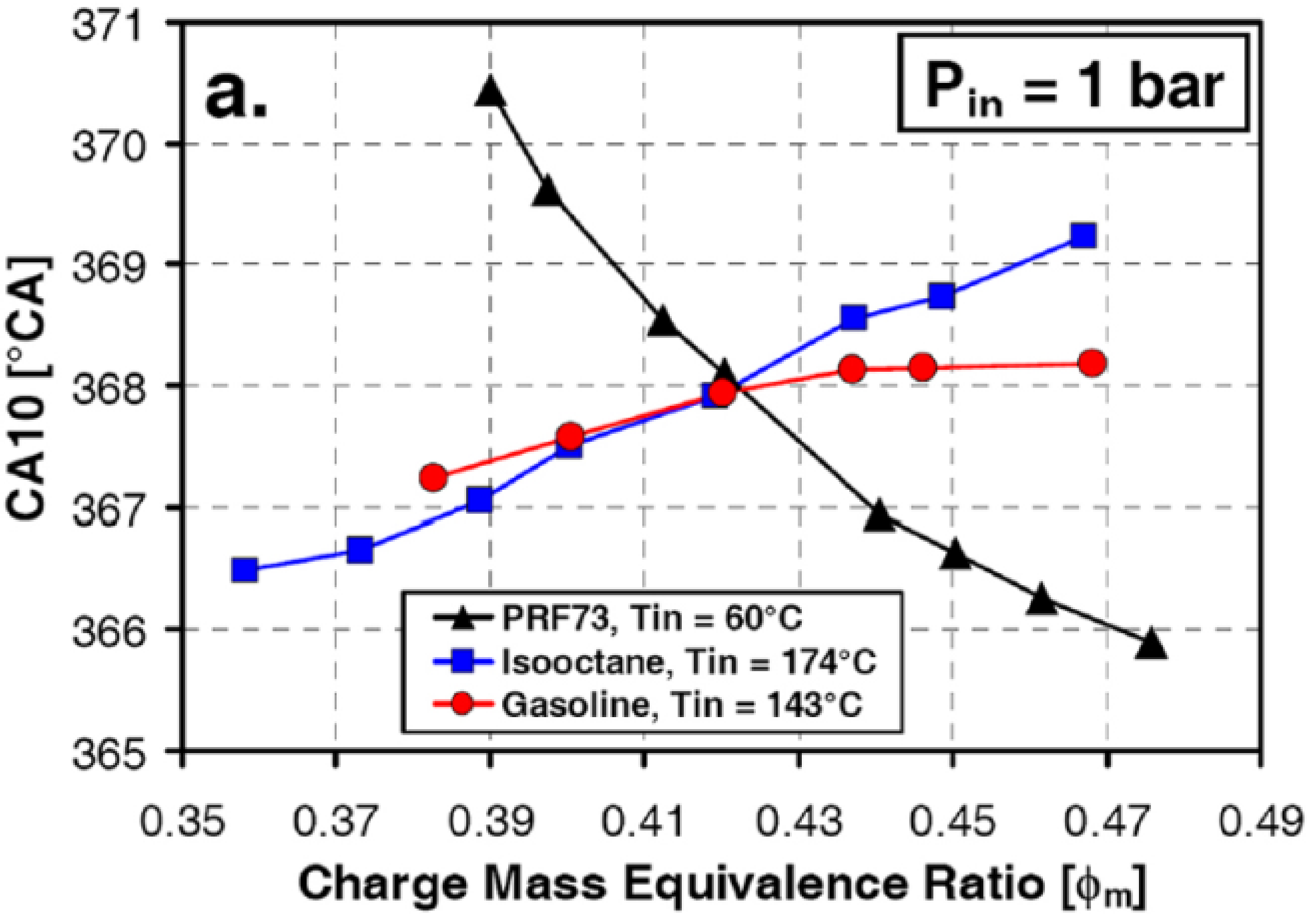
List of ~~Critical~~ Interesting Fuel Properties for LTC

- Range of fuels investigated by experiment or simulation is not that large
  - Engine combustion researchers find that almost any fuel can be burned
- Can barriers to commercialization of LTC engines be reduced by fuels with optimal properties?
- Maybe. The following properties seem interesting:
- Volatility (vapor pressure, T10, T50, T90)
- RON, MON, CN or some autoignition metric
  - LTHR, ITHR or lack of these
  - New metric for lean, boosted conditions?
- Phi-sensitivity
- Flame speed/dilution tolerance
- Heat of vaporization?

Gasoline-Like Fuels - ϕ-Sensitivity and Partial Fuel Stratification

- Some fuels show high degree of ignition delay sensitivity to equivalence ratio
  - Faster ignition under more fuel rich conditions
- Fuels that exhibit LTHR or ITHR exhibit phi-sensitivity
  - Fuels with low octane sensitivity
  - Fuels without LTHR/ITHR at 1 bar intake pressure can show at higher pressures
- Has been used to create phi-stratification for reducing ringing and increasing achievable load

Dec et al., SAE 2011-01-0897



Comments on Fuel Properties and LTC

- Researchers have successfully burned broad range of fuels in various LTC modes
- In many cases non-fuel factors (injection pressure, SOI, …) seem more important than fuel properties
  - But fuel properties have been used to advantage in some studies (i.e. PFS)
- What fuel will work may be very dependent on hardware and strategy
- Makes it very difficult to do a simple screening based on fuel properties as has been done for SI and (soon) for diesel
- Probably leads us to pick the fuel we want to use:
  - High RON, high S fuel for boosted, downspeed SI engine
  - Naphtha-type fuel with ON about 70

Thank you!

robert.mccormick@nrel.gov

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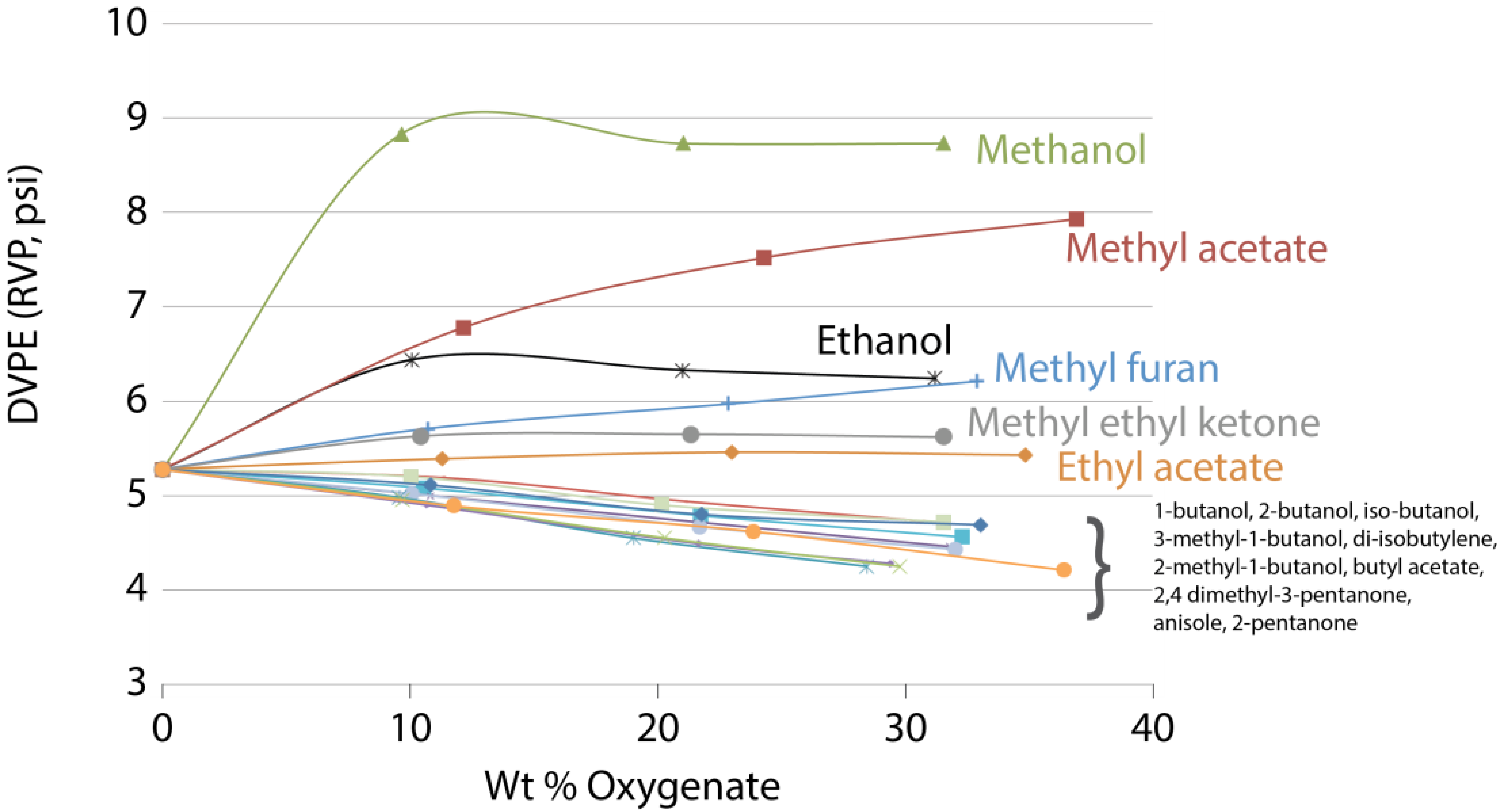
Impact of key blending properties



Fine Particle Emissions: Particulate Matter Index (PMI)

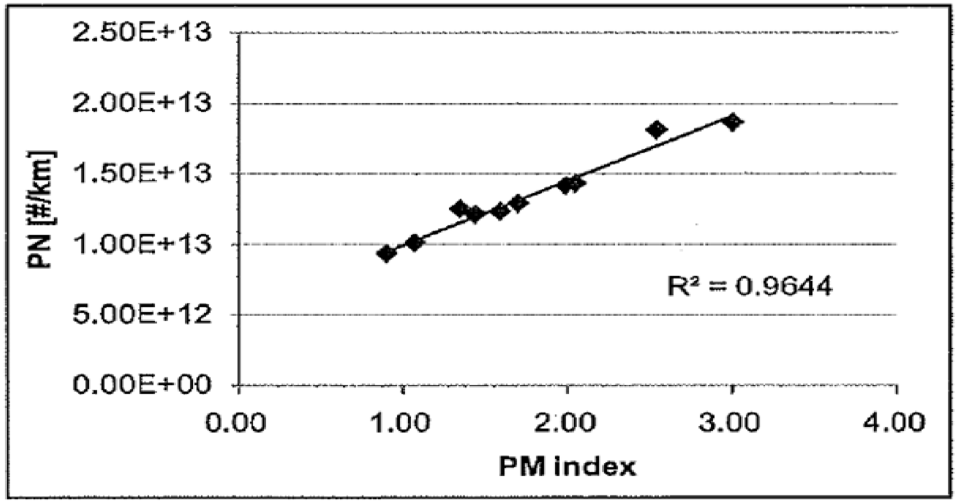
Based on detailed hydrocarbon analysis of the base fuel and the quantity of added oxygenate

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

Tendency to form soot — (DBE_i)

Driver to evaporate and mix with air — $VP(443K)$

Where-
$DBE = (2C + 2 - H)/2$
Wt_i = *Weight fraction of compound*
VP = *Vapor pressure at 443K (170°C)*

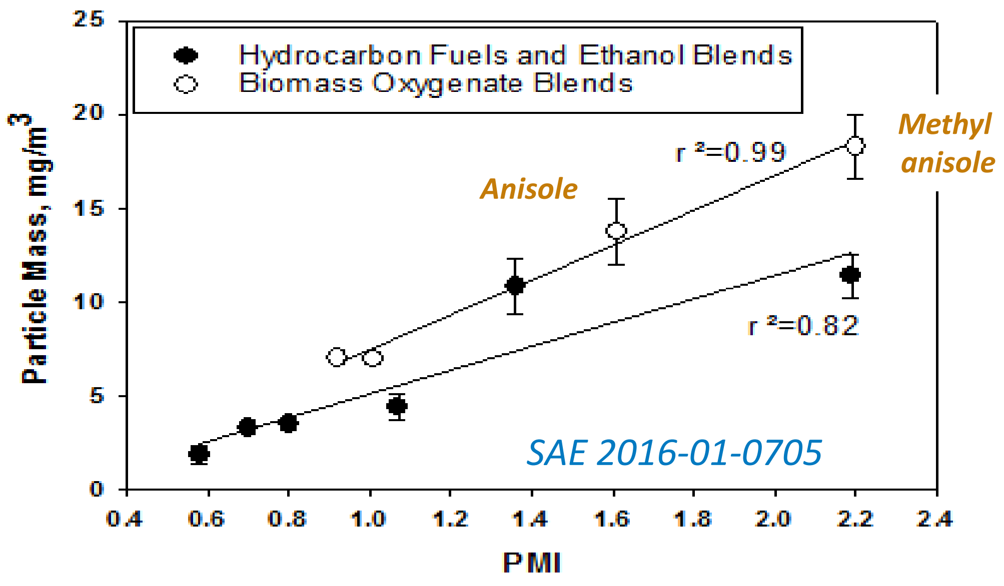


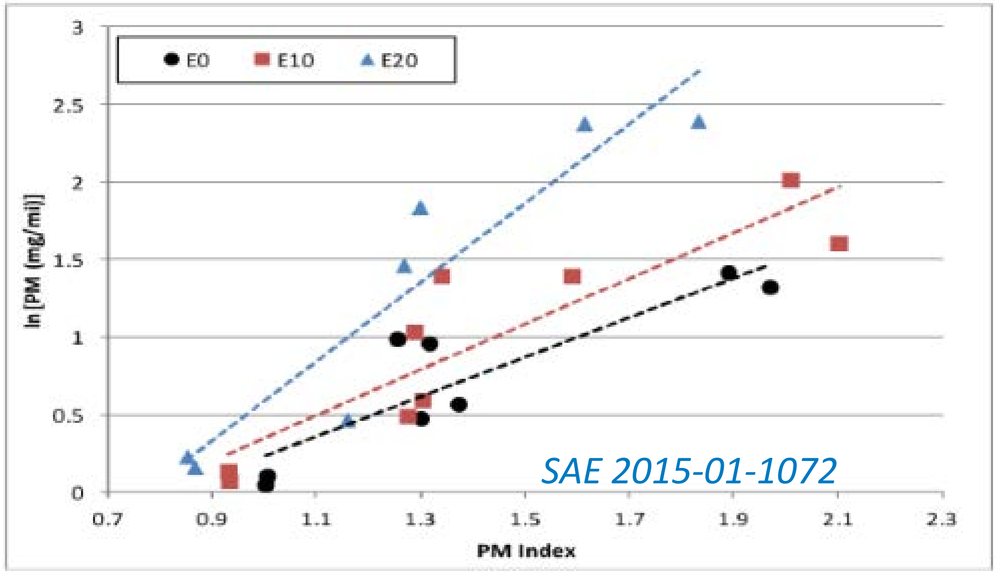
GDI engine equipped cars, FTP-75 bag 1

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

Does PMI Breakdown for Oxygenates?

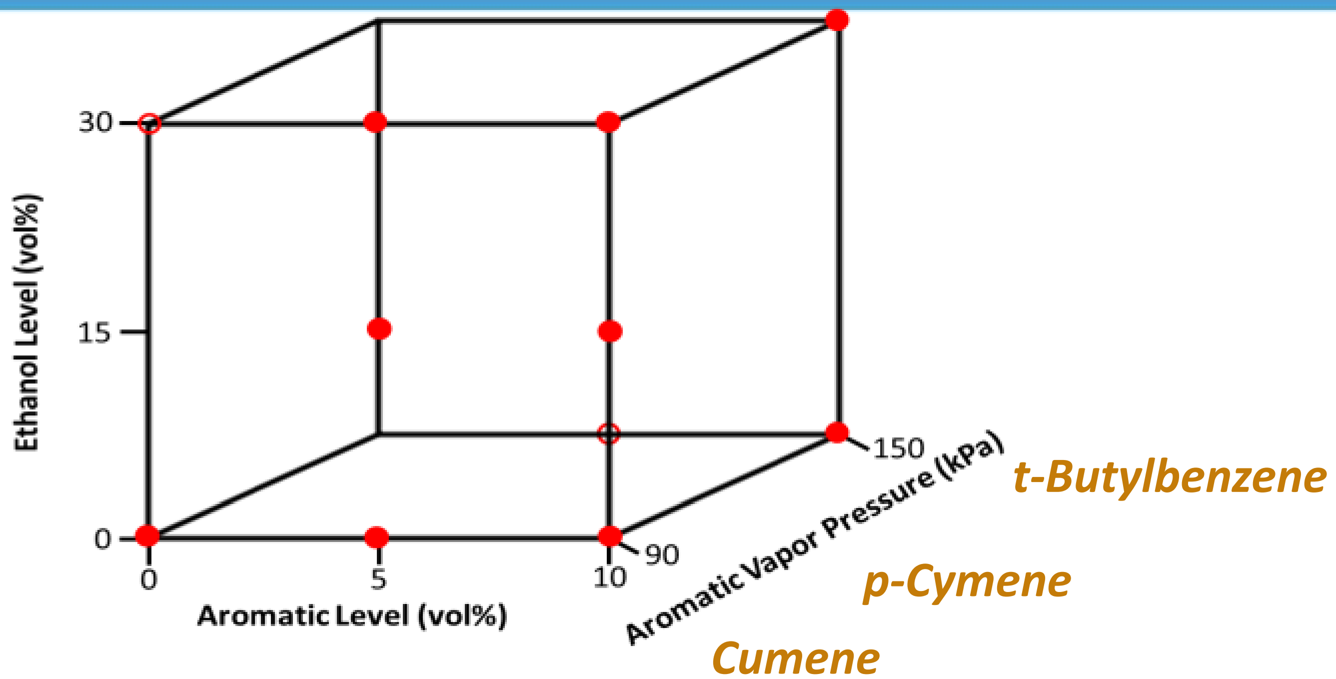
- Studies of oxygenate soot formation tendency and soot precursor formation suggest that:
  - o Anisole forms cyclopentadienyl radical which couples to naphthalene (*J. Phys. Chem. A* 2010, 114, 9043–9056)
  - o Secondary alcohol dehydration to alkene (*Environ Sci Technol*, 2011, 45 (6), pp 2498–2503)
  - o 2,5-DMF decomposition to olefinic carbonyls and radicals (Djokic, M., et al, *Proc Comb Inst*, 2013, 34 251–258)
- High heat of vaporization may lower effective vapor pressure of high boiling aromatics, increasing PM emissions

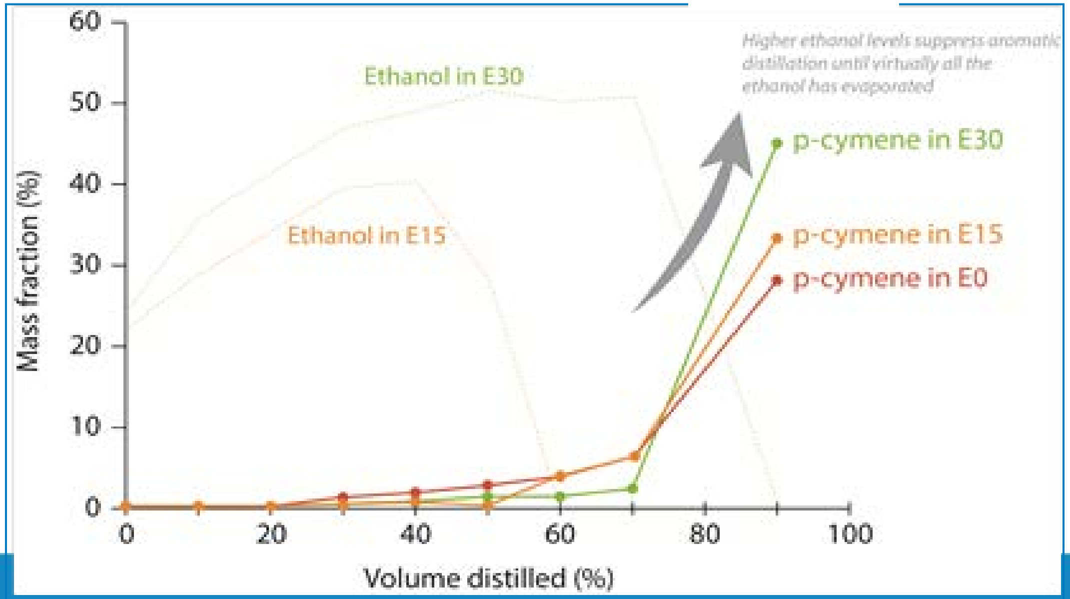




Ethanol HOV Effect on PM?

- Study outline
  - o Develop fuel test matrix
  - o Detailed fuel properties including advanced distillation
  - o SCE engine PM/PN emissions
- Demonstrate that ethanol suppresses evaporation of aromatics
- SCE engine tests ongoing





Multiple Compression Ignition Strategies – Multiple Fuels?

Will new fuels with different chemistry yield new opportunities?

Gasoline-Like

Diesel-Like

what is the underlying kinetic cause for autoignition phi-sensitivity?

what about RCCI?

Advanced SI Fuel

- High value of K (2)
- High RON
- High S
- High HOV
- Current volatility
- Dilution tolerance?
- Phi-sensitivity?

GCI Fuel

- Low value of K?
- Lower RON
- Low S?
- HOV?
- Volatility?
- Dilution tolerance?
- Phi-sensitivity?

Partially Premixed Fuel

- High CN?
- HOV?
- Lower T90 < 288C
- Oxygenates?
- Dilution tolerance?
- Phi-sensitivity?

Diesel Fuel

- Mixing limited combustion
- High CN (upper limit?)
- HOV?
- Current diesel volatility
- Oxygenates for LLFC?

are mixture preparation, cold start and vapor lock the same for SI and GCI?

are RON and MON good metrics for GCI?