NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Gasoline: Formulation Issues and Constraints

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HEI Workshop: Effect of Fuel Composition on PM

Chicago, IL December 8, 2016

Opportunities for today's AND tomorrow's fuel/engine systems

Co-Optimization of Fuels and Engines

better fuels. better vehicles. sooner.

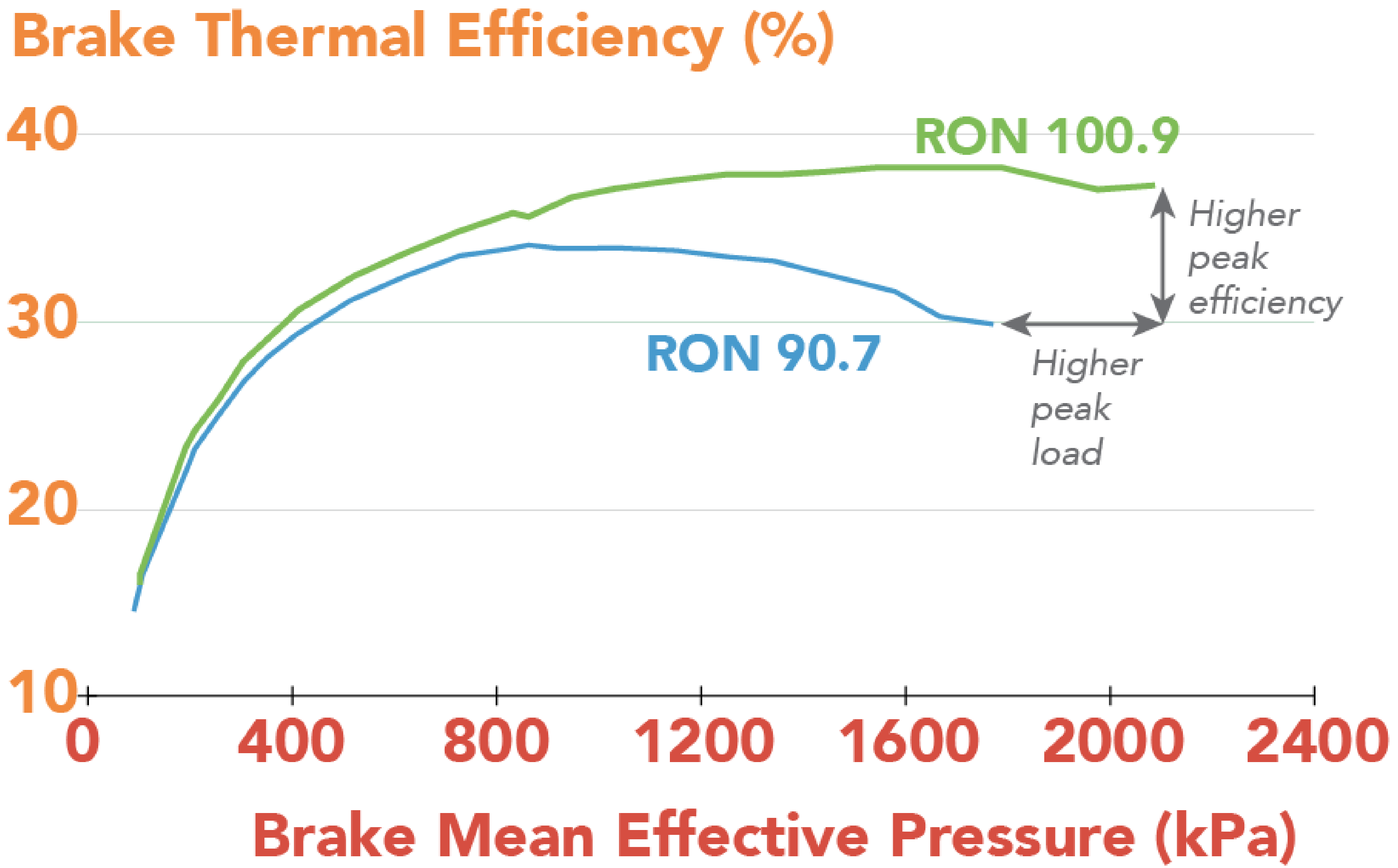
Draws on collaborative expertise of two DOE research offices, nine national laboratories, and numerous industry and academic partners.

Co-Optima Project:

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

http://energy.gov/eere/bioenergy/co-optimization-fuels-engines

Current fuels constrain engine design

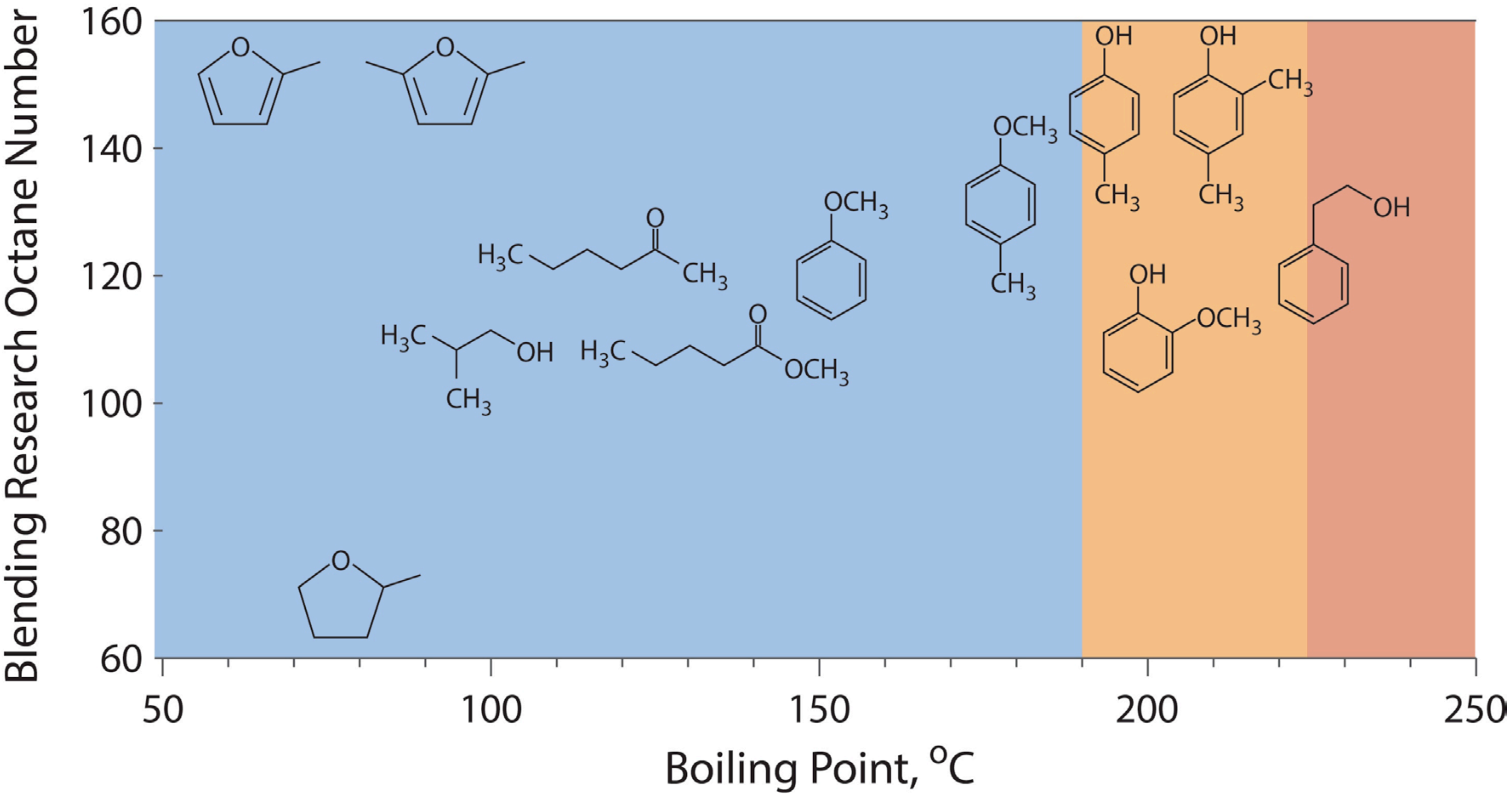


Engine: Ford Ecoboost 1.6L 4-cylinder, turbocharged, direct-injection, 10.1 CR source: C.S. Sluder, ORNL

What fuel properties do GDI engines want?

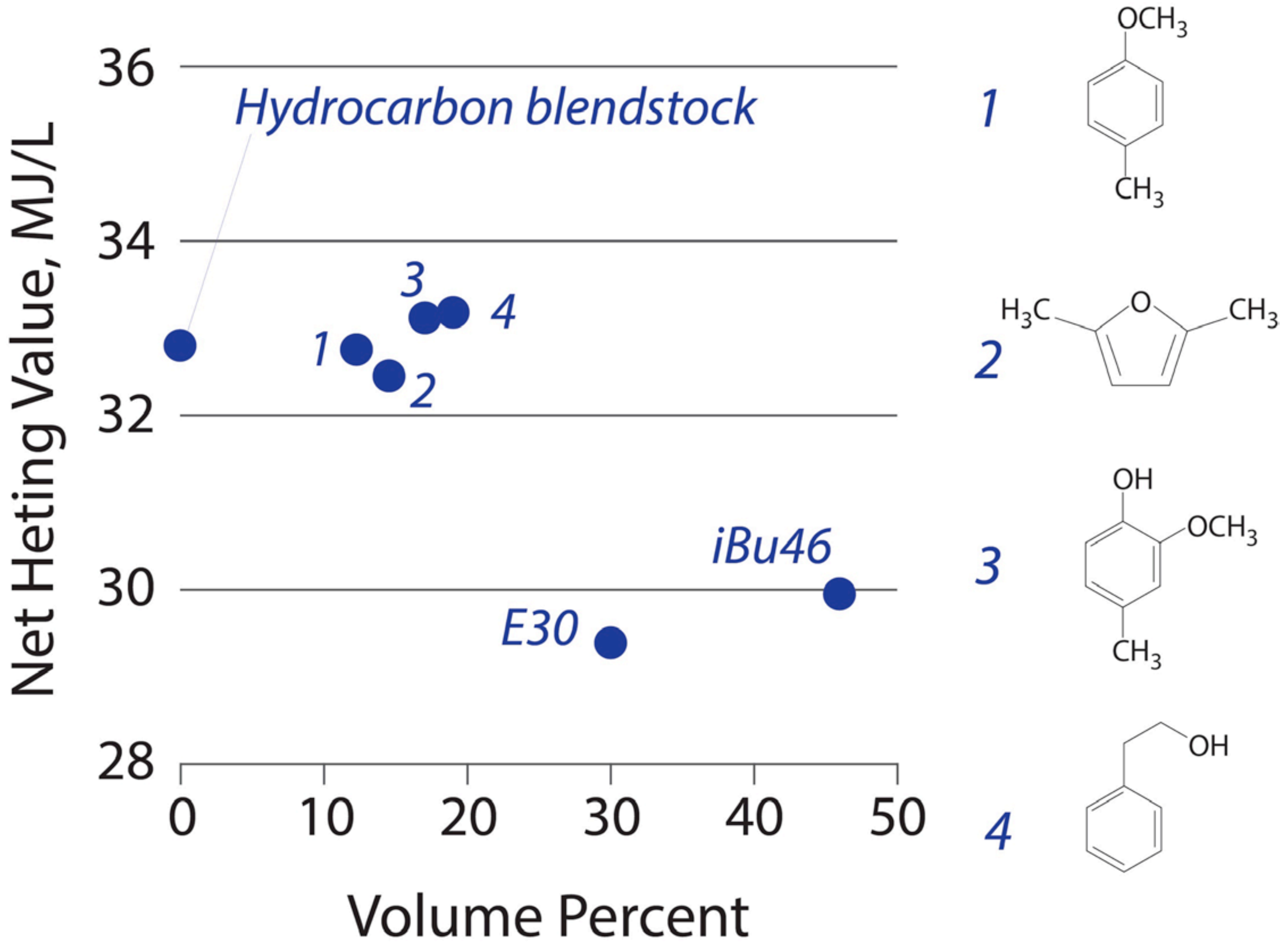
RON
viscosity
heating value
flame speed
volatility
flammability limits
sensitivity
diffusivity
smoke point
cloud point
MON
soot precursor formation
bulk modulus of compressibility
heat of vaporization
cetane number
PMI
sulfur level
T50
C/H ratio
flame stretch
heat of combustion
strain sensitivity
density
specific heat ratio
Wobbe index
ignition limits
T10
naphthene level
flash point
T70
Markstein length
surface tension
olefin level
oxygenate level
exergy destruction
laminar burning velocity
drivability index
energy density
T90
aromatics level

Biomass can provide fuels with advantageous properties



Biomass can provide fuels with advantageous properties

- Higher mass and energy density than ethanol
- High RON
- Heat of vaporization (mass basis) similar to gasoline
- Equivalent effective RON to E30 attained at much lower blend level, with negligible effect on volumetric energy content



An overview of how fuel properties impact particulate formation

Premixed vs non-premixed (diffusion) flames

Premixed: gas stove, homogeneous gasoline engine, etc

Non-premixed (diffusion): candle, pool fire, SIDI piston-top fire, diesel combustion, etc

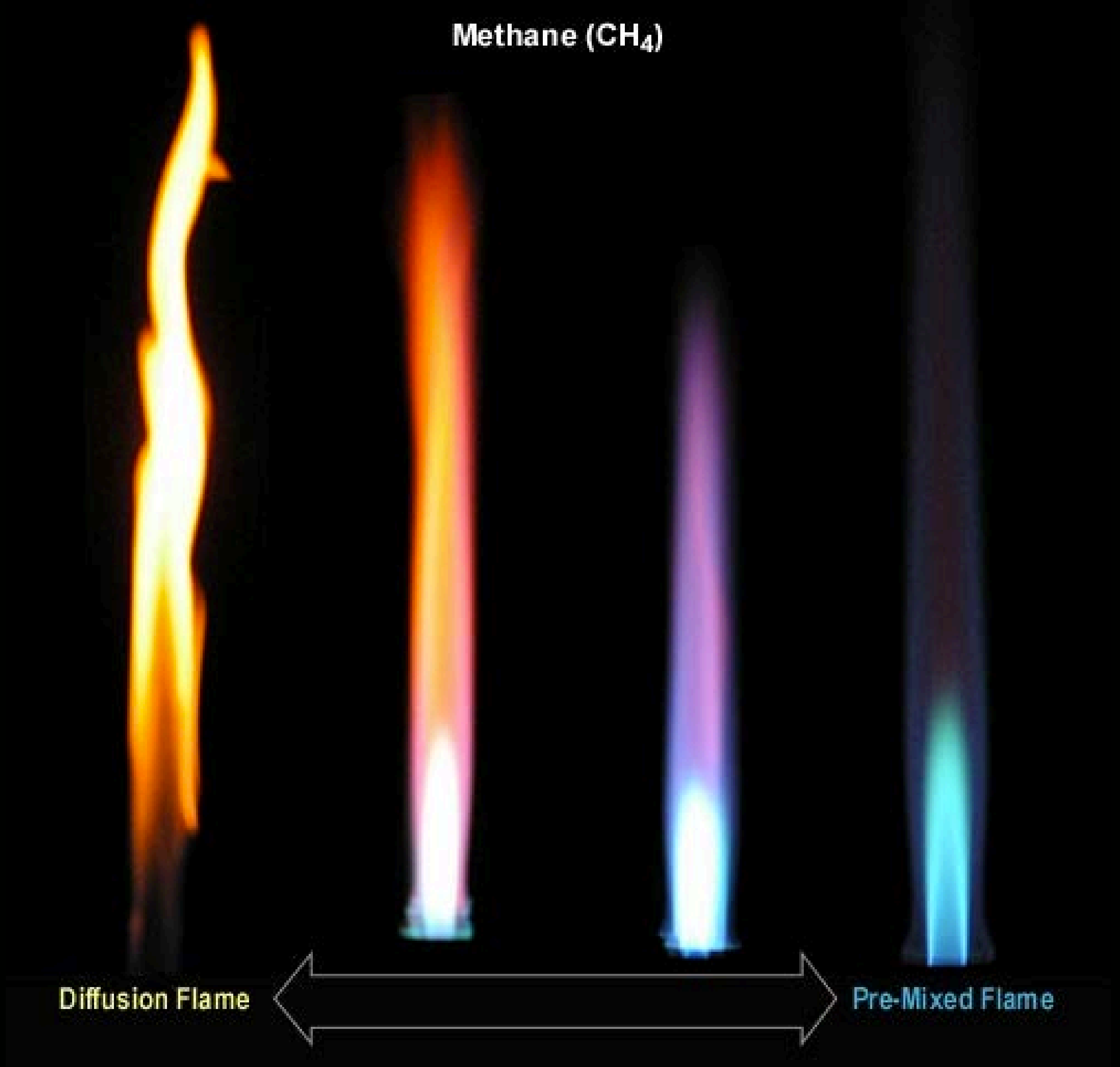
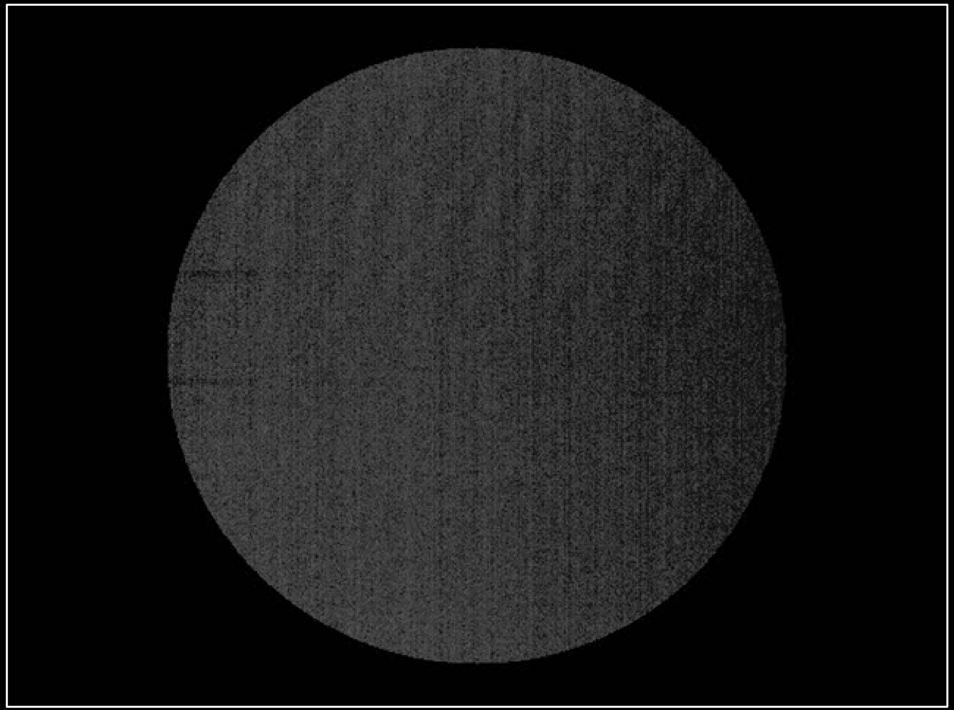


Photo: Wikipedia

It’s the local equivalence (fuel/air) ratio that matters

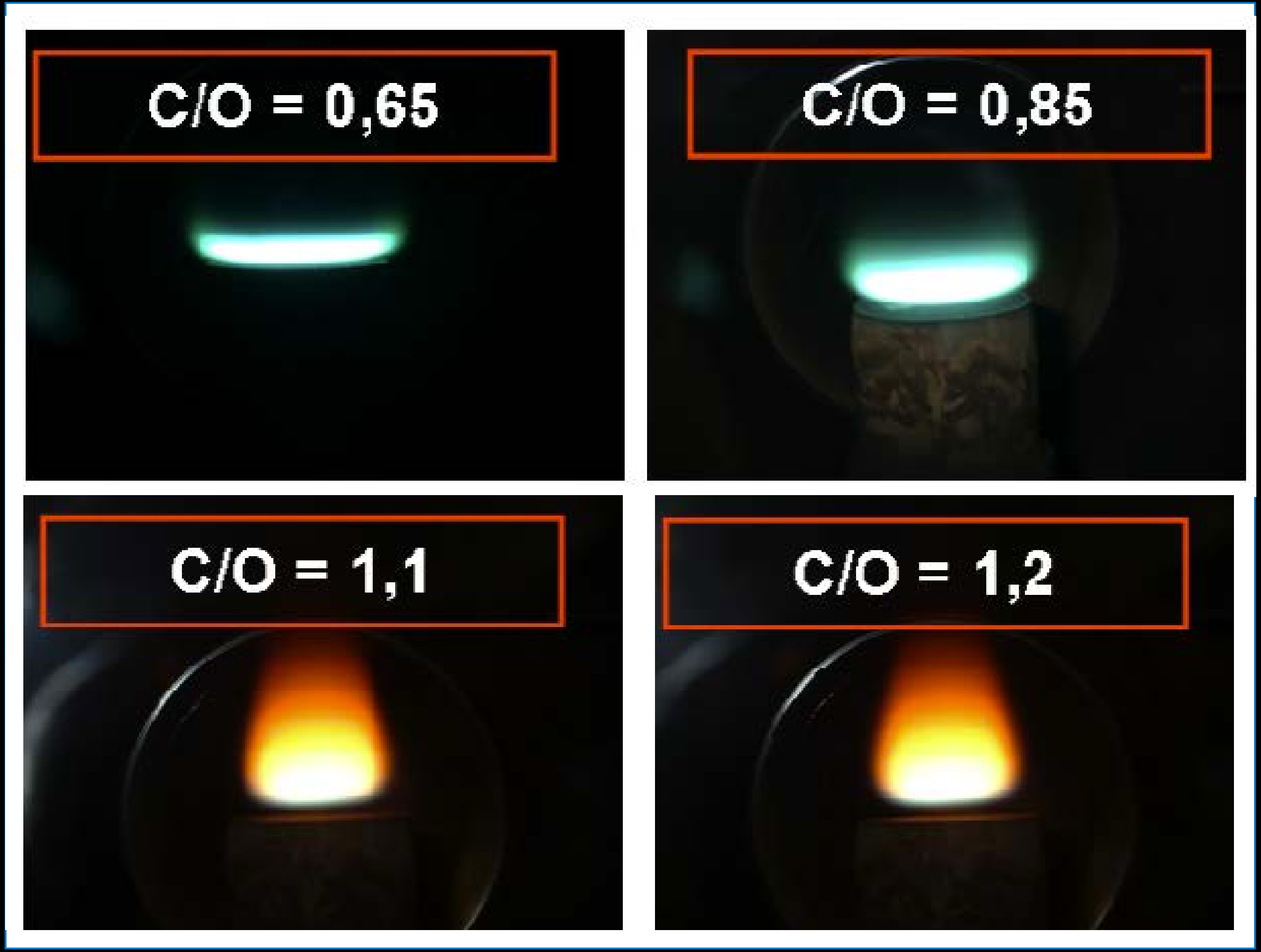
Diesel engines are overall fuel-lean but sooting is significant



Mark Musculus, Sandia National Laboratories

Fuel-air ratio impacts soot formation

- Excess oxygen inhibits soot formation
- Insufficient oxygen promotes soot formation

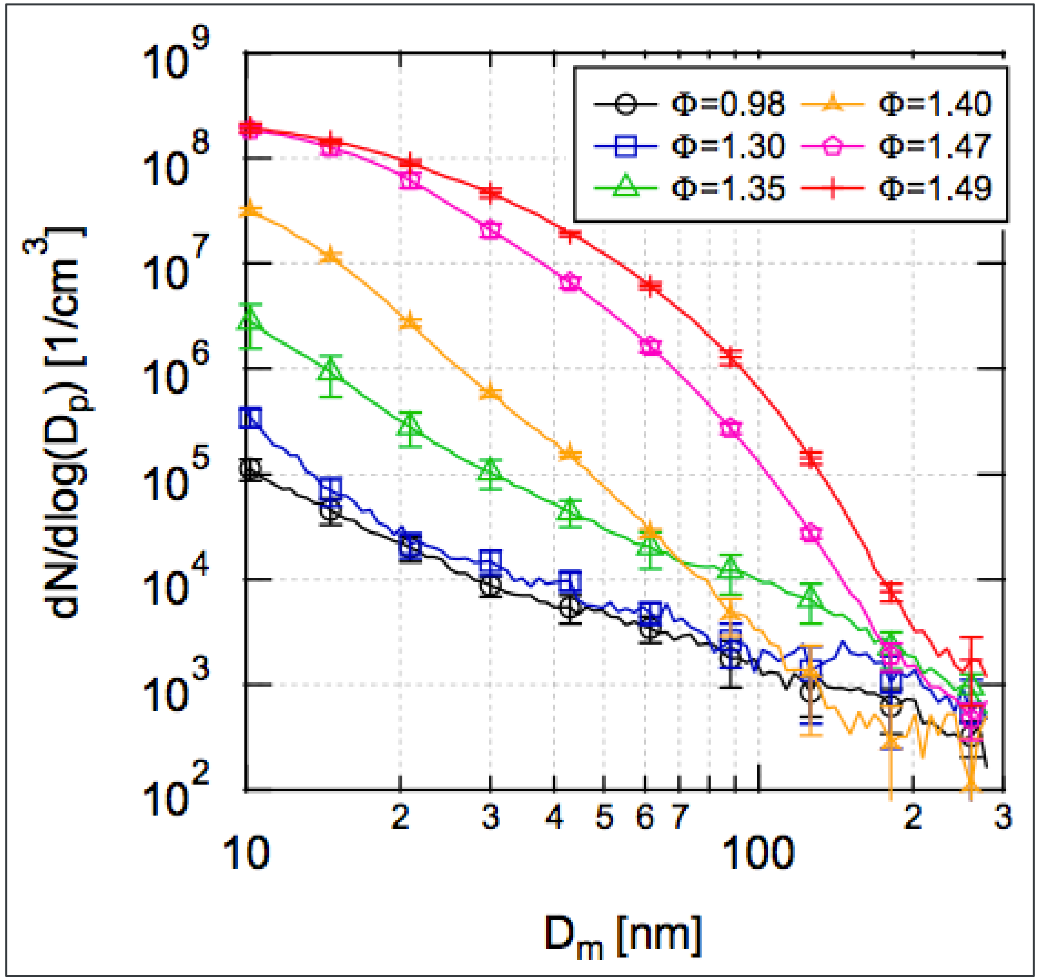


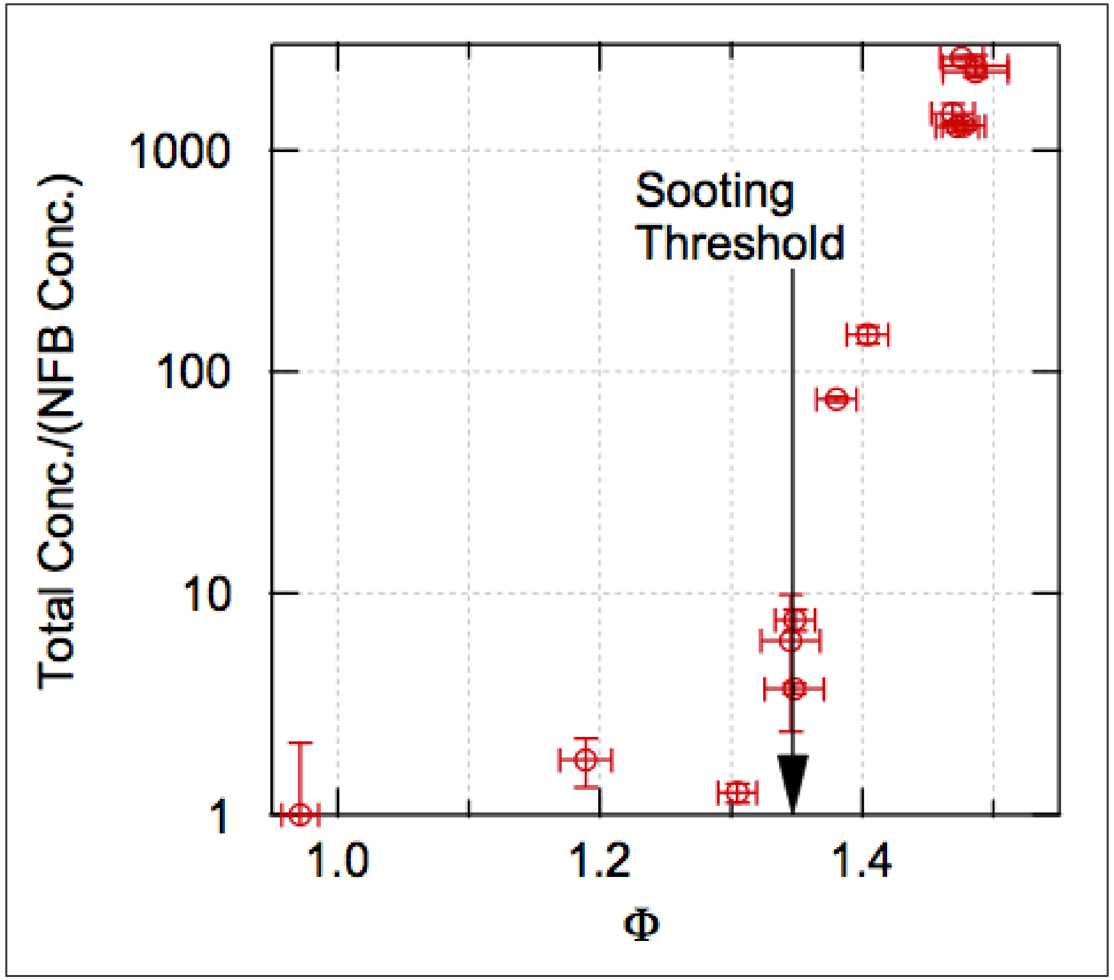
Acetylene/oxygen flame
C/O = ratio of carbon/oxygen;
C/O = 1 -> stoichiometric fuel/air mixture

Paur et al., Nanotechnology 16 (2005) S354–S361

Critical fuel/air ratio for onset of gasoline sooting ~ 1.35

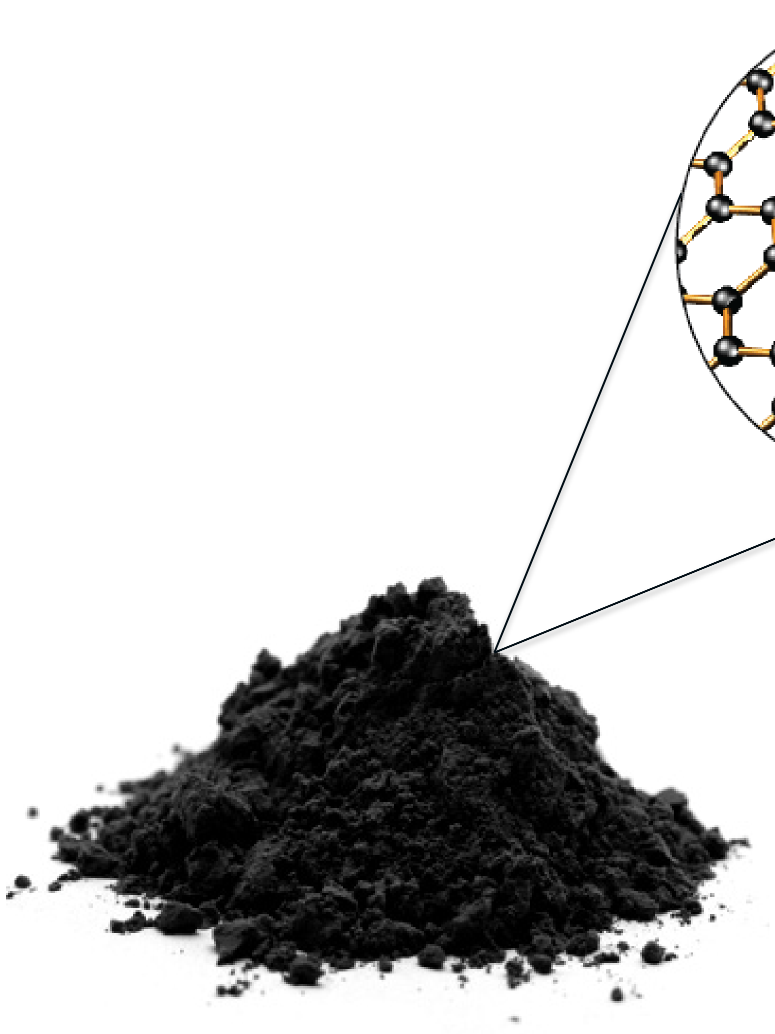
The critical equivalence ratio for onset of sooting = 1.35 (C/O = 0.461–0.462) for gasoline certification fuel





Hagerman et al., Proc. Combust. Inst. (2015) V35 (3), 2949

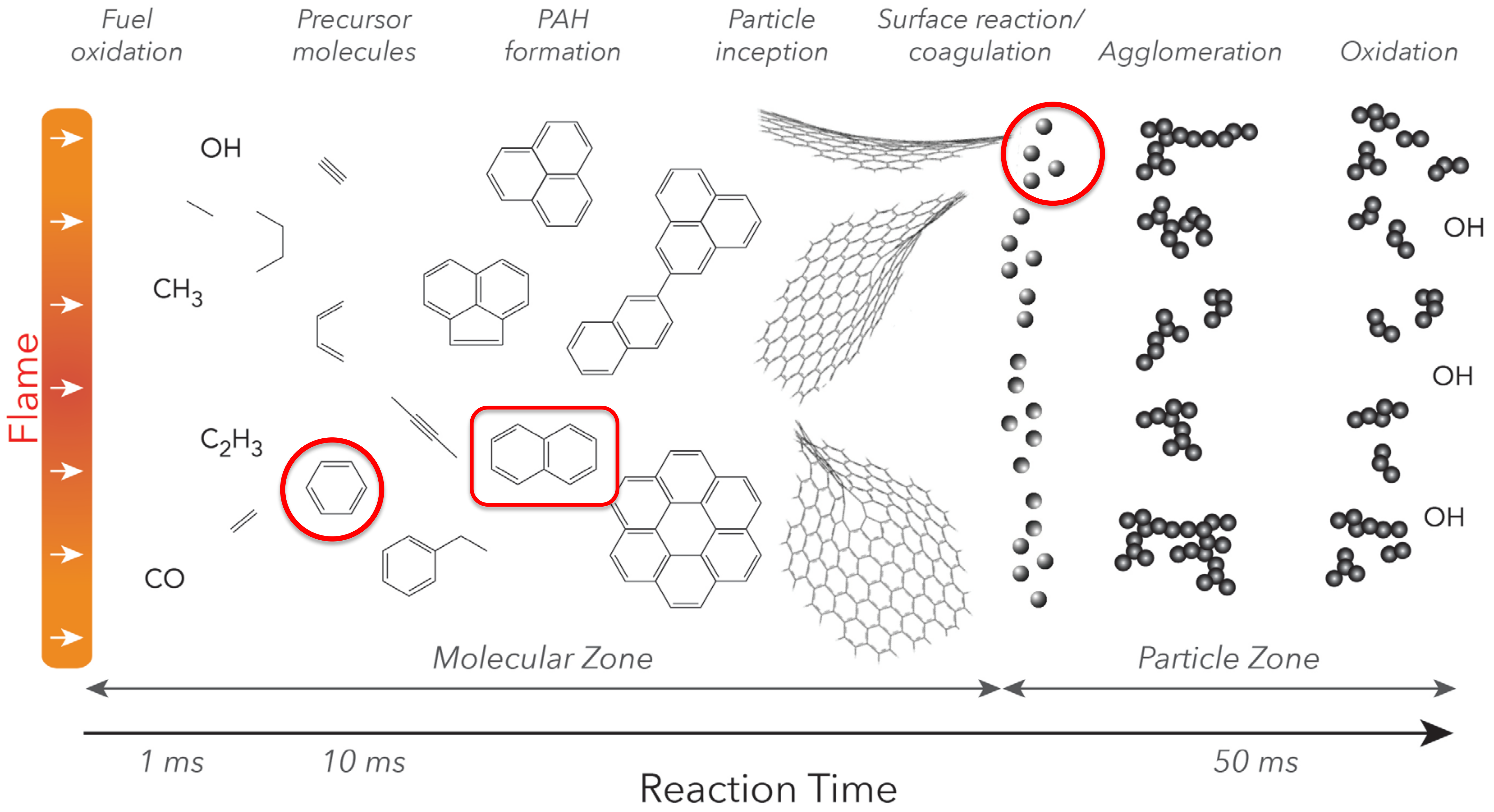
Fuel structure impacts soot formation



Sooting implies formation of carbon framework comprised of graphitic networks

Fuels with structures that facilitate formation of graphitic rings will have higher sooting tendency

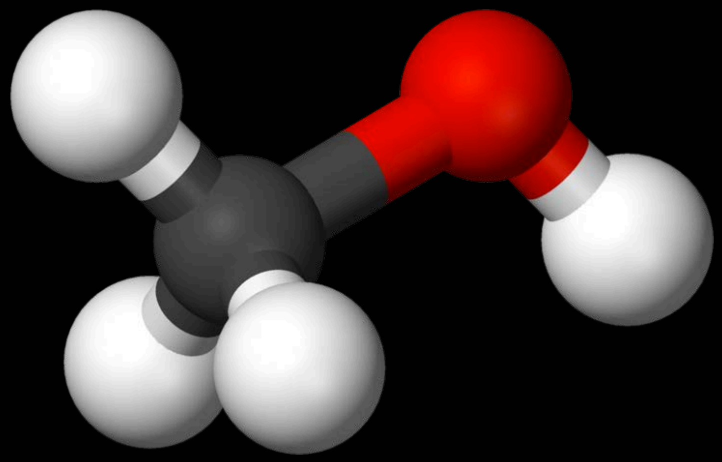
Soot formation processes



Some fuels do not soot readily

Sooting threshold for methanol flames occurs around equivalence ratio of ~ 7

C-O bond is strong; C not available for soot formation reactions

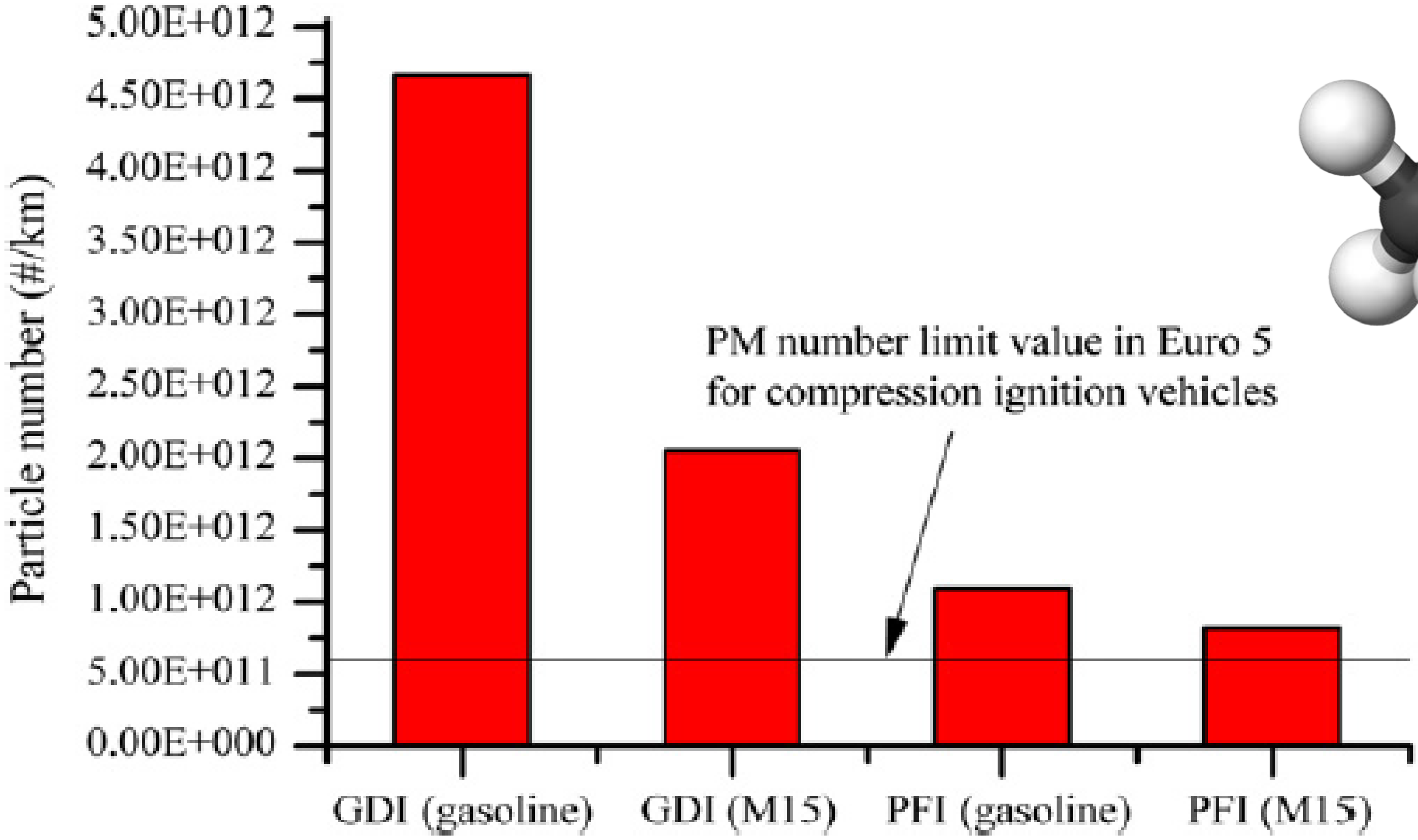


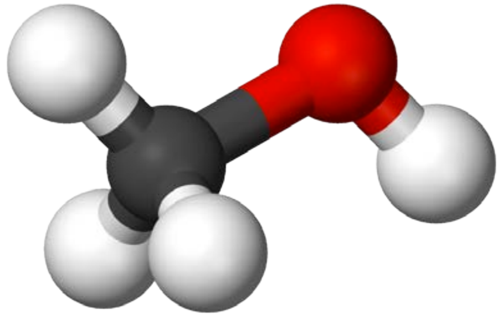
https://commons.wikimedia.org/w/index.php?curid=1999966

Methanol flame

Oxygenation fuel strategy

B. Liang et al. / Journal of Aerosol Science 57 (2013) 22–31

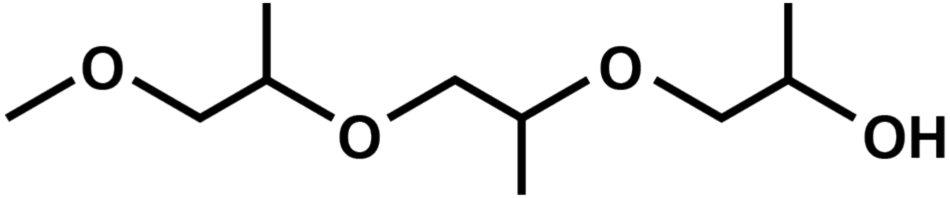




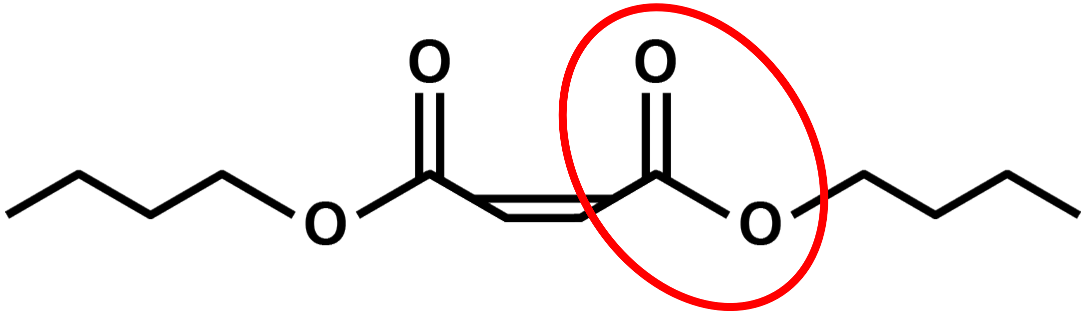
Not all oxygenates are alike – structure matters

Esters are not as effective as ethers for lowering soot because they can lead to prompt CO_2 production, wasting ½ of their oxygen

Fueling with a neat poly-ether can prevent in-cylinder soot production



tri-propylene glycol mono-methyl ether (TPGME), $C_{10}H_{22}O_4$



di-butyl maleate (DBM), $C_{12}H_{20}O_4$

See Mueller et al., SAE 2001-01-3631, 2001-01-3632, 2002-01-1631, 2003-01-1791, 2005-01-2088

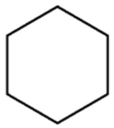
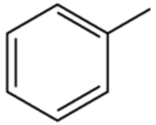
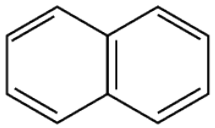
Fuel effects on PM emissions: PMI

Particulate Matter Index (PMI) works (surprisingly) well for conventional fuels

Tendency to form soot

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

Tendency to evaporate & mix

Fuel		DBE	
CH_4	=	0	
Cyclohexane	=	2	
Toluene	=	4	
Naphthalene	=	7	

DBE = double bond equivalents = (2C + 2 – H)/2

Wt_i = weight fraction of compound

VP(443K) = vapor pressure at 443K (170° C)

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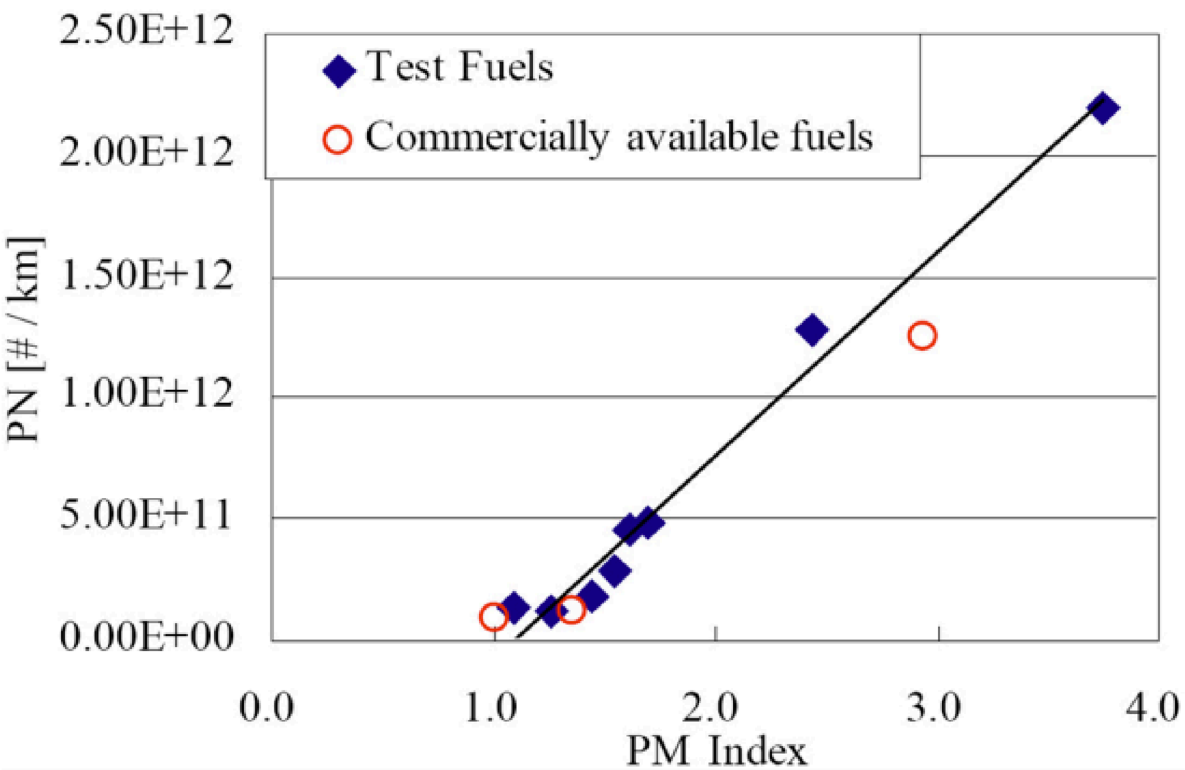


Aikawa et al. SAE 2010-01-2115.

DBE = double bond equivalents = (2C + 2 – H)/2
Wt_i = weight fraction of compound
VP(443K) = vapor pressure at 443K (170° C)

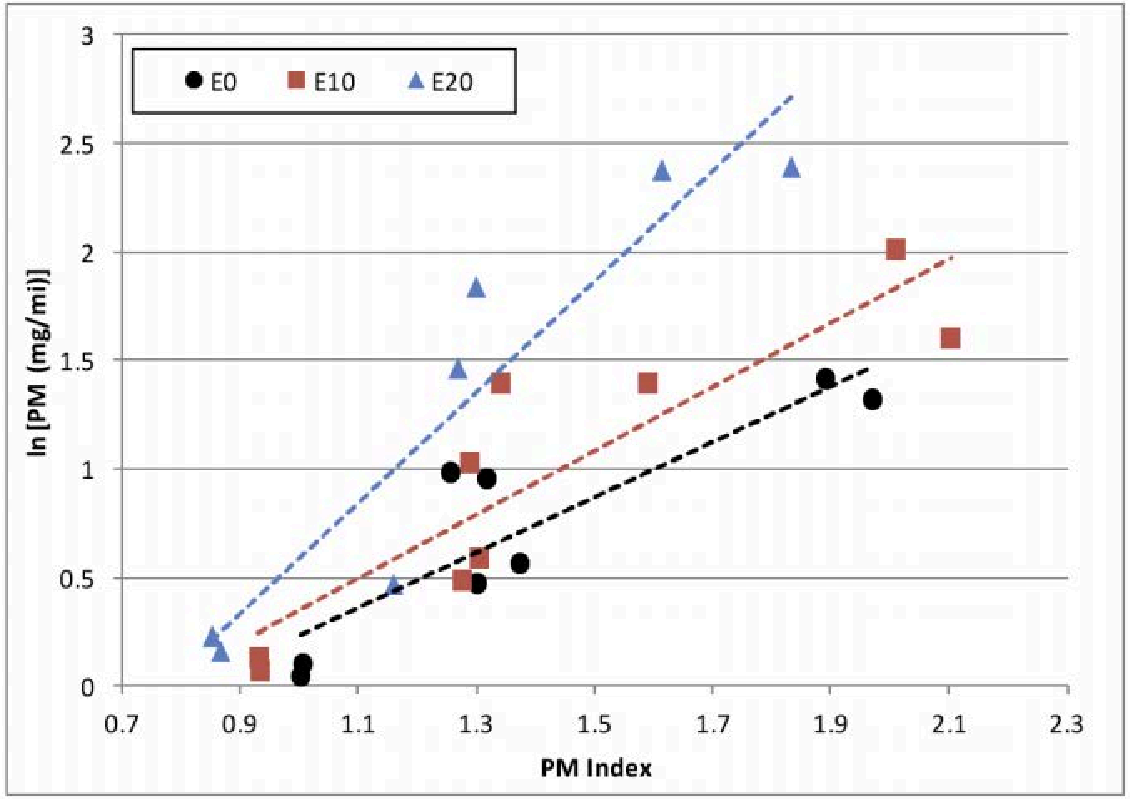
Does PMI breakdown for ethanol?

- Some studies show PM reductions with mid-level ethanol blends, while other show increases

- Results reflect competition between chemical/physical effects

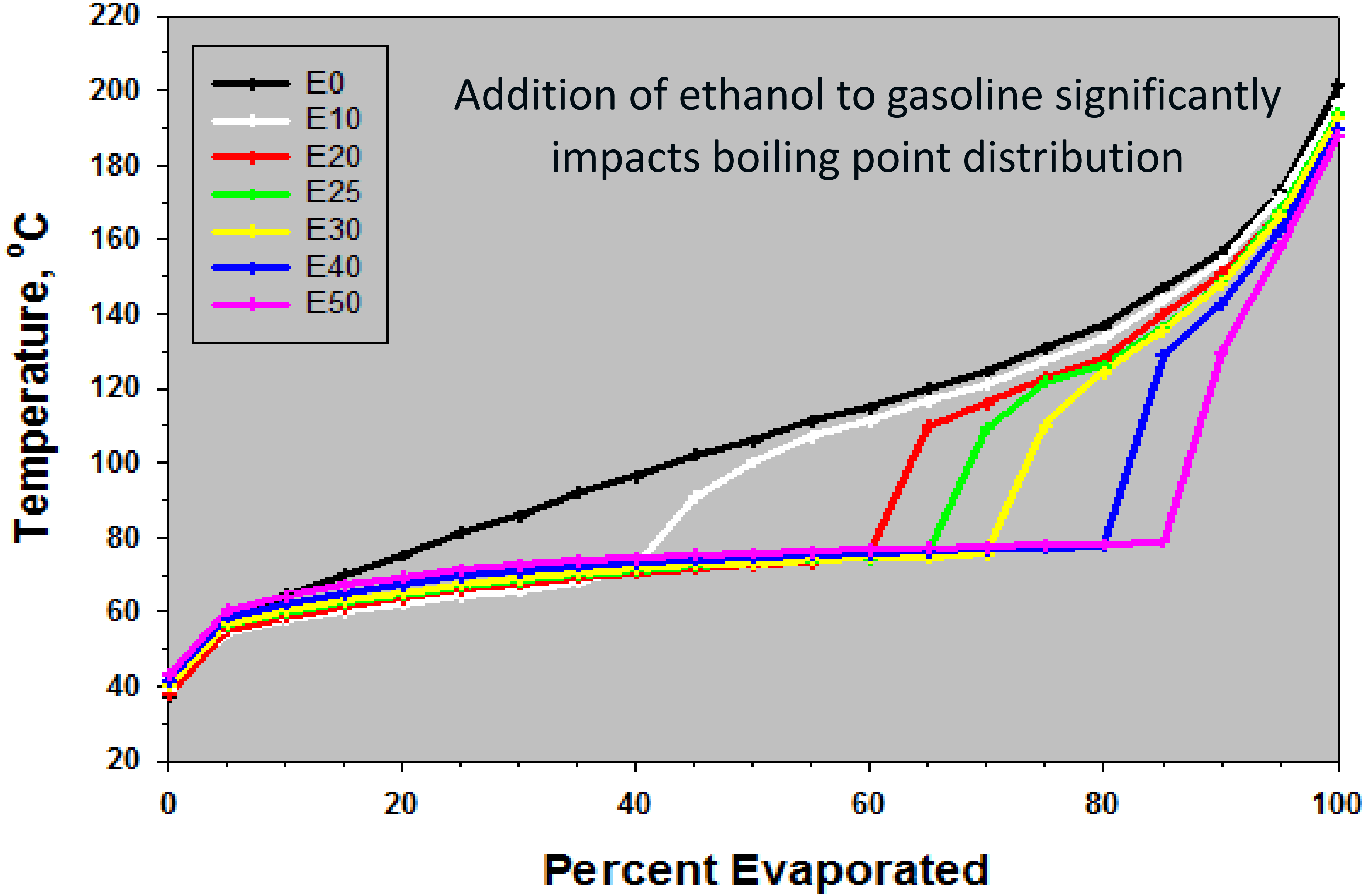
  - Chemical – reduced soot formation tendency

  - Physical – cooling effect of ethanol due to high heat of vaporization

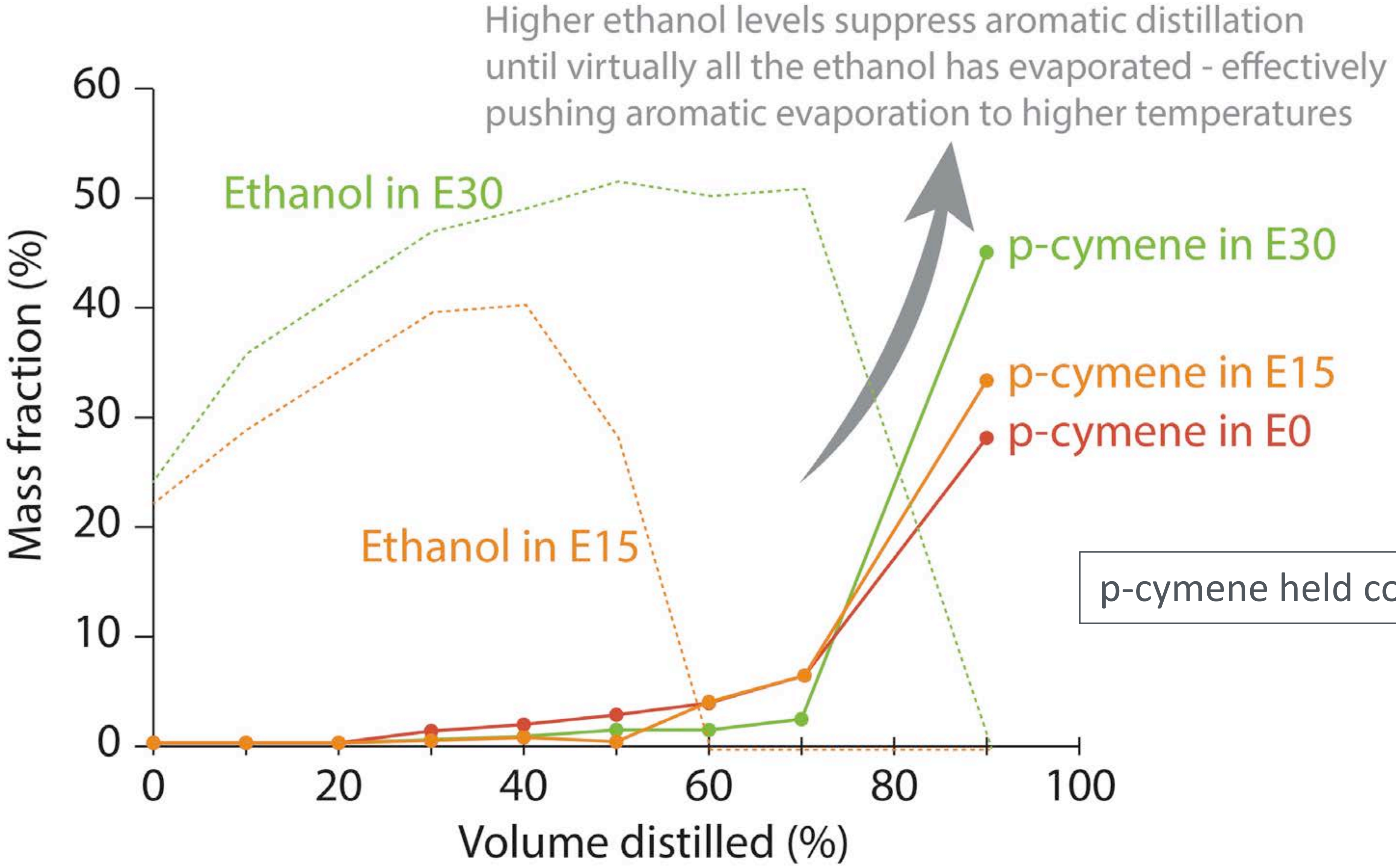


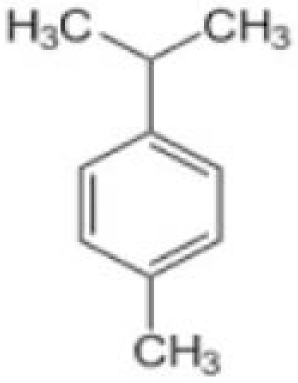
Butler et al., SAE Technical Paper 2015-01-1072, 2015, doi:10.4271/2015-01-1072.

Ethanol-gasoline blend distillation curves



Distillation properties impacted by blending





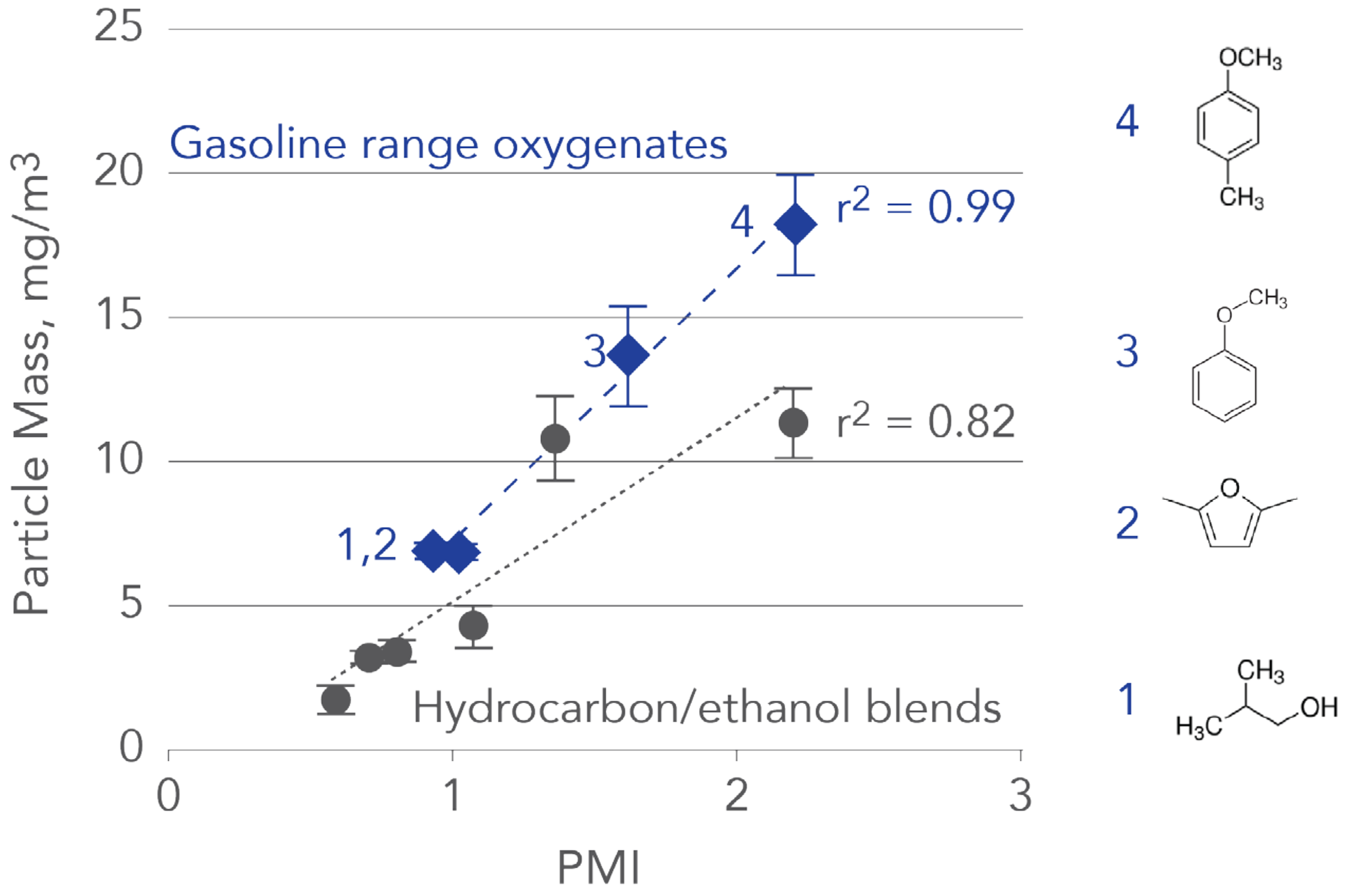
p-cymene

p-cymene held constant at 10%

Does PMI breakdown for other oxygenates?

Higher PM observed for oxygenated aromatics

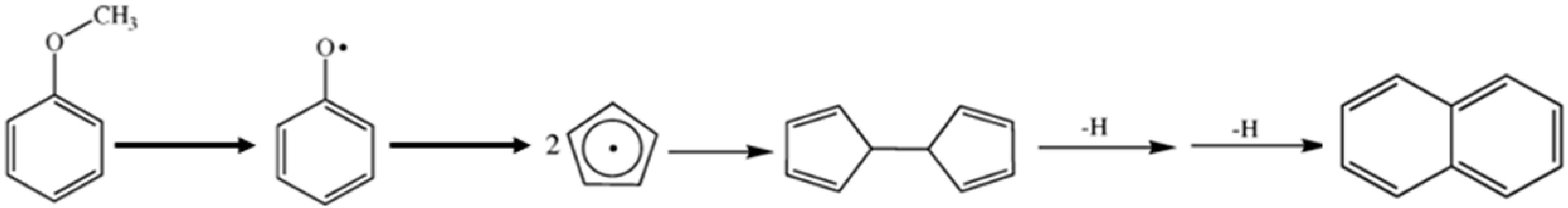
Heat of vaporization of blends similar, so results must reflect chemical effect



Ratcliff et al / SAE Int. J. Fuels Lubr. / Volume 9, Issue 1 (April 2016)

Phenolics readily form soot precursors

Formation of cyclopentadienyl radical is relatively facile, which couples to form the soot precursor naphthalene



Scheer, A., et al., J. Phys. Chem. A 2010, 114, 9043–9056

Conclusions

- Fuel structure and physical properties significantly impact PM emissions from GDI engines
- Many of the hardware and fuel changes that increase gasoline engine efficiency exacerbate PM formation
- Biomass-derived oxygenates have beneficial properties but <u>some</u> have chemical and physical properties that could impact PM emissions

Acknowledgements

The authors thank Kevin Stork with the U.S. DOE's Vehicle Technologies Office for supporting this work through Funding Opportunity Announcement DE-FOA-0000239.

Questions?

Backup slides

Cycloalkanes are “clandestine” aromatics

- Cycloalkanes have DBE = 2 and thus are more prone to sooting than paraffins

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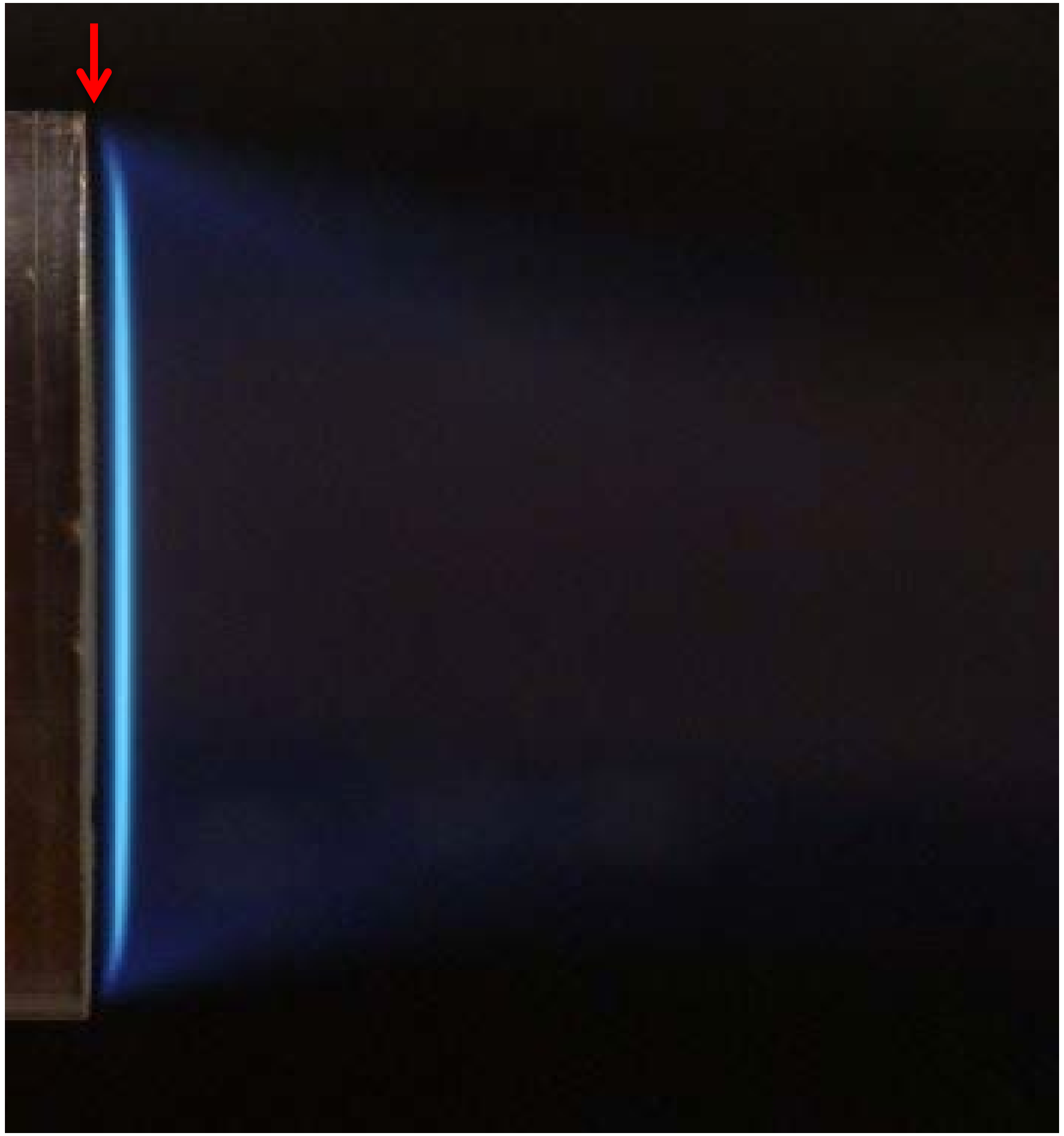
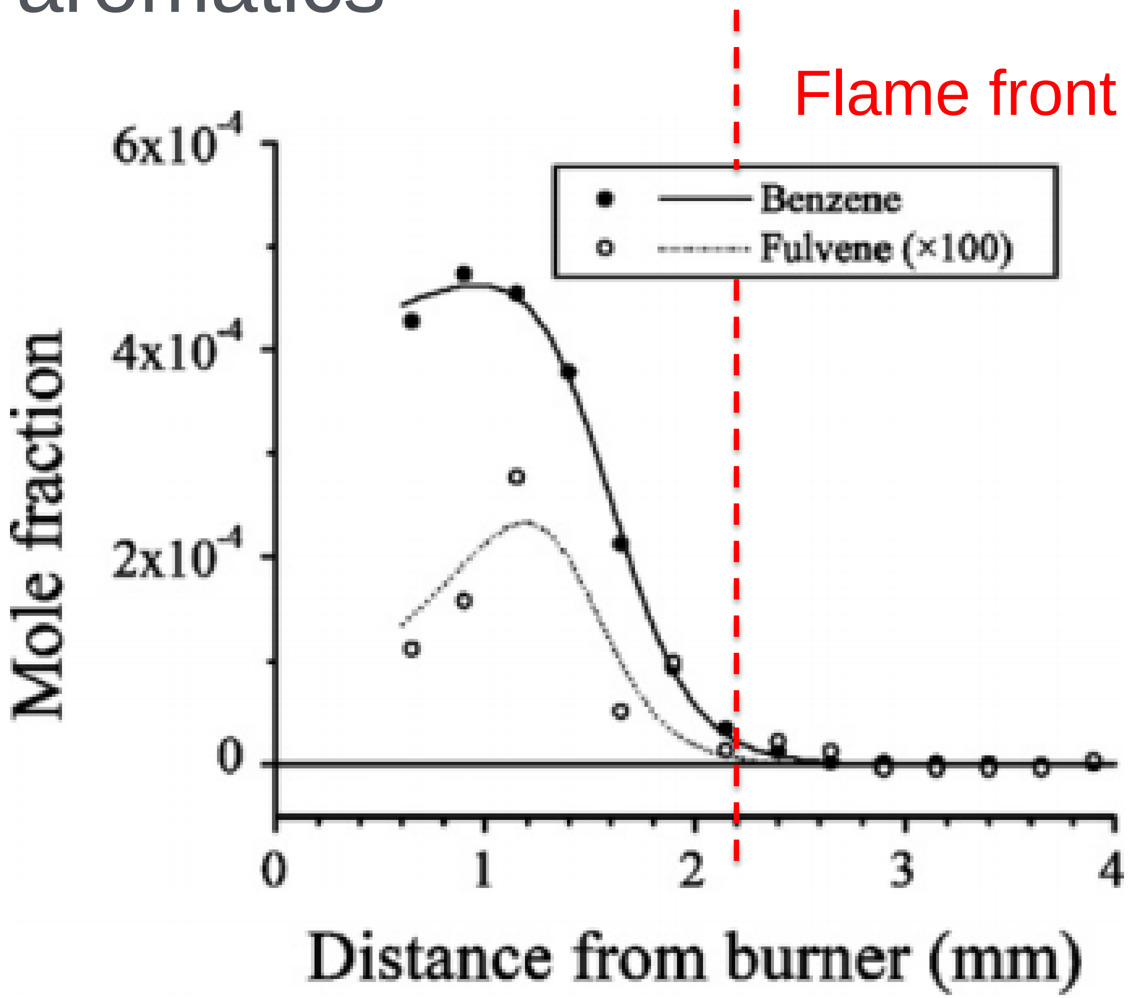


Cycloalkanes are “clandestine” aromatics

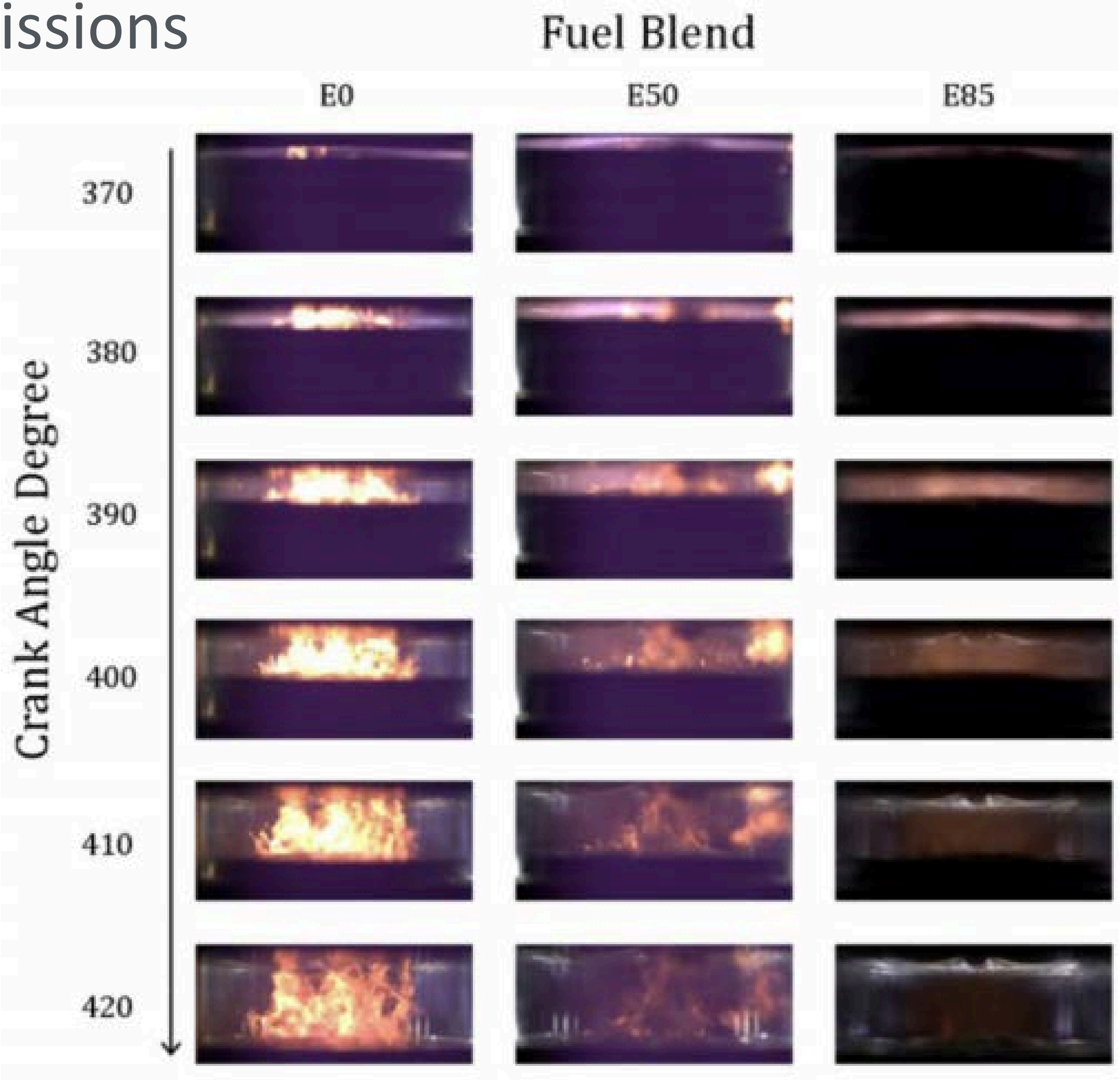
- Cycloalkanes have DBE = 2 and thus are more prone to sooting than paraffins
- Cycloalkane ring can dehydrogenate to benzene <u>before</u> flame zone
- Diesel engine experiments show that soot formation tendency can be ~ half that of aromatics



Law et al., Proc. Comb. Inst. 31 (2007) 565–573

Direct Injection SI Engine PM Emissions

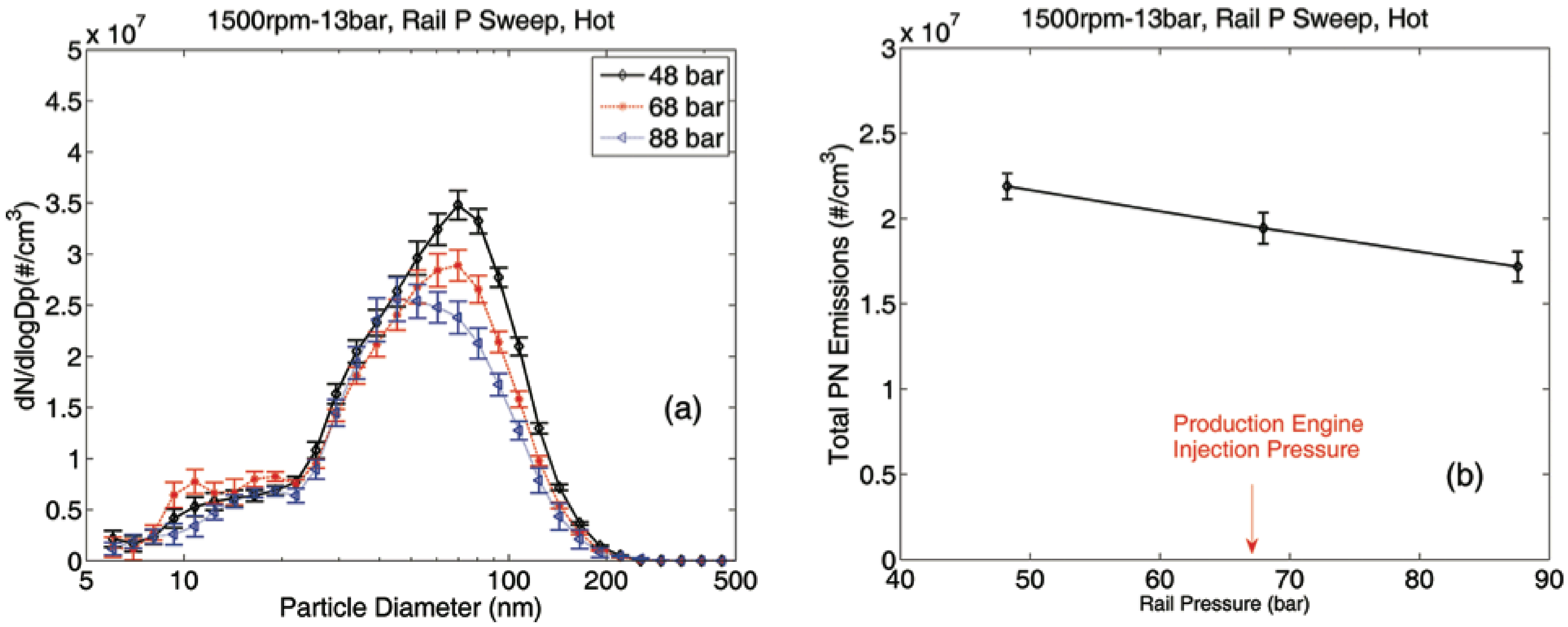
- Yet many studies show increased emissions of particles for DI
- Fuel spray may impinge on cylinder wall or piston top
  - o Low vapor pressure/high boiling components burn as diffusion flame



Fatouraie et al., *SAE Int. J. Fuels Lubr.* 6(1):2013

Higher injection pressure reduces PM

But this comes at a cost and has limitations



He et al., Energy Fuels 2012, 26, 2014−2027