Gasoline: Formulation Issues and Constraints

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HEI Workshop: Effect of Fuel Composition on PM

Chicago, IL December 8, 2016

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.
Opportunities for today’s **AND** tomorrow’s fuel/engine systems
better fuels. better vehicles. sooner.

Co-Optimization of Fuels and Engines
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

**Brake Thermal Efficiency (%)**

- RON 100.9
- RON 90.7

**Brake Mean Effective Pressure (kPa)**

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?
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

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
Critical fuel/air ratio for onset of gasoline sooting $\sim 1.35$

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

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

Fuel oxidation  Precursor molecules  PAH formation  Particle inception  Surface reaction/coagulation  Agglomeration  Oxidation

OH

CH₃

C₂H₃

CO

Molecular Zone

Particle Zone

1 ms  10 ms  50 ms

Reaction Time
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
Oxygenation fuel strategy


PM number limit value in Euro 5 for compression ignition vehicles
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.

Fuel effects on PM emissions: PMI

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

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

- **Tendency to form soot**
- **Tendency to evaporate & mix**

<table>
<thead>
<tr>
<th>Fuel</th>
<th>DBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>2</td>
</tr>
<tr>
<td>Toluene</td>
<td>4</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>7</td>
</tr>
</tbody>
</table>

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

Wtᵢ = weight fraction of compound

VP(443K) = vapor pressure at 443K (170°C)
Fuel effects on PM emissions: PMI

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Aikawa et al. SAE 2010-01-2115.
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

Addition of ethanol to gasoline significantly impacts boiling point distribution.
Distillation properties impacted by blending

Higher ethanol levels suppress aromatic distillation until virtually all the ethanol has evaporated - effectively pushing aromatic evaporation to higher temperatures.
Higher PM observed for oxygenated aromatics

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

Does PMI breakdown for other oxygenates?

![Graph showing PMI breakdown for different oxygenates](image-url)

*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

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

• 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