Mitigating Insoluble Engine Deposits by Revealing their Molecular Compositions and Origins with 3D OrbiSIMS

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• Internal combustion has the largest share of passenger vehicle.

• Trend will continue for foreseeable future – particularly in developing nations.

• Insoluble material can ‘stay behind’ in components – deposits.

• Deposits commonly affects fuel injectors and filters.
  • Greater impact on high efficiency vehicles

• Lead to increased emissions (5 x particulates), poor efficiency and air quality.
• Various mitigation strategies. All require compositional data.

• Fuel mixture is complex – fuel, additives and contaminants.

• Various techniques applied - elemental and visual analysis only.¹

• Need MS for more comprehensive work.

• But how can we overcome deposit insolubility?

¹ Edney. M.K et al., Fuel, 2020
ToF - Secondary ion mass spectrometry

- Solvent free analysis.
- Able to reveal layering of deposits through depth profiling.
- Distinguish different origins of species with imaging.
- ToF gives low resolution (< 20,000) and forms low mass ions (< \( m/z \) 400).
- Very little molecular information given.
The 3D OrbiSIMS technique

- New technique – ToF-SIMS with addition of Orbitrap mass analyser.
  - Resolution of 240,000.
  - Accuracy < 2 ppm.
  - Can generate molecular ions > \( m/z \) 1000.
  - Perform MS/MS.
  - Ideal technique for probing complex carbonaceous materials.

**In-situ** analysis on three engine components:

- High temperature gasoline injector (exposed to flame).
- Internal diesel injector.
- Diesel filter.

Speciation, comparison and MS/MS

• Identify molecular species and assign parent ions in-situ (> m/z 1000 & < 2 ppm error).
  • Lubricant oil derived sulfonates and linear carboxylic acids common.
  • Sodium salt only in diesel samples. Sulfonate parent highest in filter.
• Higher mass sulfonates above native additive only present in gasoline. Formed in the engine from reactions.
• MS/MS shows loss of alkyl chain and ‘extra proton’ – explains unsaturated C₈-sulfonate
• Positive data dominated by PAHs. Accurately identified up to high mass.

• Hypothesized to exist in deposits previously.
  • Formed by aromatization of hydrocarbons.

• Limited growth in diesel injector.

• High mass PAH formation in gasoline component.
X-ray photoelectron spectroscopy

- XPS gives quantified elemental data.

- C level correlates with PAH intensity.

- High Na deposition in diesel injector.

- Sulfates only in diesel injector ($\text{Na}_3\text{S}_2\text{O}_8^-$, 0.4695 ppm).

- Organic sulfonates trace contributors.

- Ca correlates with sulfonate SIMS intensity in the filter.
• Additive species surface localised.

• Delocalized PAHs occupy middle region in gasoline deposit.

• Localised carbonaceous ions in gasoline deposit.

• Sodium chloride dominates diesel deposit.

• Diesel injector surface may have a diamond-like surface coating.

In-situ analysis reveals mechanisms

- Focus on gasoline deposits.
- Range of samples analyzed from different components.
- We rationalize a mechanism of matrix formation after deposition \textit{via} aromatization and PAH build up from fuel.
In-situ analysis reveals mechanisms

• Translate for formation pathway to injector needle

• 3D OrbiSIMS analysis in three positions closer to combustion chamber – high T:
  • Growth of PAHs across needle surface.
  • Breakdown of lubricating oil species.

• Understand the composition, origin and formation mechanisms of engine deposits.

Polycyclic aromatic hydrocarbons

<table>
<thead>
<tr>
<th>Compound</th>
<th>Normalized intensity</th>
<th>m/z</th>
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<tbody>
<tr>
<td>Pyrene</td>
<td>2×10^{-4}</td>
<td>202.0825</td>
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<tr>
<td>Coronene</td>
<td>5×10^{-5}</td>
<td>300.0975</td>
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<tr>
<td>Ovalene</td>
<td>5×10^{-7}</td>
<td>398.11</td>
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</table>

Lubricating oil additives

<table>
<thead>
<tr>
<th>Additive</th>
<th>Normalized intensity</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salicylates</td>
<td>10^{-4}</td>
<td>137.026</td>
</tr>
<tr>
<td>Sulfonates</td>
<td>10^{-3}</td>
<td>325.185</td>
</tr>
</tbody>
</table>

Diagram of engine component and analysis methods.
Conclusions

- We can map the 3D distribution of molecules in deposits in-situ.
- Composition is affected by deposition of species (fuel, water and lubricant oil) and their reactivity.
- Data will inform next generation fuel additive design to solubilize deposits.
- Insight into formation may reveal new pathways to preventing formation.

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Thank you for your attention!