Non-Petroleum-Based Fuels: Effects on Emissions Control Technologies

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Project ID # ft_07_sluder

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Project Overview

Timeline

- Project is ongoing, but is re-focused each year to address current DOE and industry needs.
  - EGR fouling focus began FY'08
  - PM kinetics focus began FY'07

Barriers

- Inadequate data and predictive tools for fuel property effects on
  - combustion and engine optimization.
  - emission control system impacts.

Budget

- Funding received in
  - FY08: $720K
  - FY09: $700K allocated to date
- Anticipate similar funding level for FY'10.

Collaborations

Objectives and Milestones for FY 2009

Project Goal: To provide data in support of predictive tools that can be used to understand fuel-property impacts on combustion and emissions control systems.

- **Complete study of EGR cooler fouling with biodiesel blends at moderate HC level. ('09 Milestone)**
  - **Is fouling worse with biodiesel?**
  - **What role(s) do HCs play in deposits?**
- **Complete studies and model of PM oxidation kinetics for biodiesel blends. ('09 Milestone)**
  - **Why does biodiesel PM have different oxidation behavior?**
  - **How can this be beneficial rather than detrimental to DPFs?**
- **Complete successful analysis of several polar organic species from diesel soot. ('09 Milestone)**
  - **Are the compounds present in large enough amounts to be important?**

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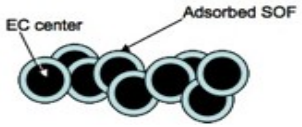
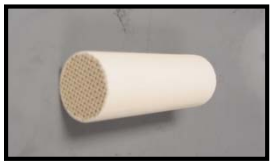
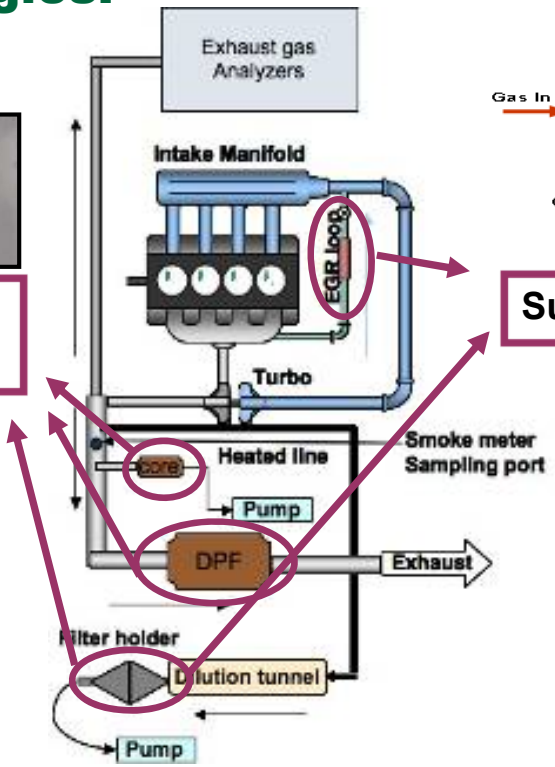
Approach

Bring together targeted, engine-based studies using NPBFs with in-depth characterization of PM and HCs to better understand behavior for specific technologies.





Monolith Cores, Powder PM Samples, and Sample Filters



Surrogate Tubes and Sample Filters

- Enable studies of PM from actual DPF conditions to support improved regeneration processes.
- Enable examination of EGR cooler deposits to support models and component development.

Chemical, physical, and thermodynamic characterizations underpin these activities.

Kinetic Studies, BET

Surface Analysis (XPS, TEM, Others)

Chemical Analysis

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Summary of Technical Accomplishments

- Completed experimental study on ULSD, B20 EGR cooler fouling at moderate HC levels.
  - Follow-up to last FY series.
  - Thermal and surface analyses ongoing, expect completion by summer.
  - Result so far are similar to last year and encouraging; B20 seems to continue to produce fouling very similar to ULSD.
  - Paper submitted for 2009 SAE Powertrain, Fuels, and Lubricants Meeting.
- Identified key relationships that explain differences in PM oxidation kinetics for biodiesel blends.
  - Completed microreactor experiments.
  - Oxidation model development nearing completion; anticipated this FY.
- Successfully demonstrated extraction and analysis of aromatic carboxylic acids and related anhydrides from PM.
  - Presence of these compounds provides insights into differences between thermal denuding and chemical extraction for SOF determinations.
  - Acids and anhydrides may be important in understanding physical properties of EGR cooler deposits.

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NPBF Effects on PM oxidation Kinetics:

Why does biodiesel PM oxidize differently than ULSD PM, and can this behavior be reduced to a kinetic model?

Benefit: Improved understanding of kinetic differences between PM produced by ULSD and biodiesels may enable more fuel-efficient and reliable regeneration of DPFs.

Accomplishment: Identified soot microstructure as the key influence on oxidation kinetics with adsorbed HCs also playing a significant role.

- Soot microstructural differences are characteristic of the PM produced when different fuels are burned in the engine. (In-cylinder combustion metrics similar.)
- Adsorbed organics on the PM act as accelerants to decrease lightoff temperature.
- The lightoff temperature advantage is more dependent on the amount of adsorbed organics than on their chemical identity.

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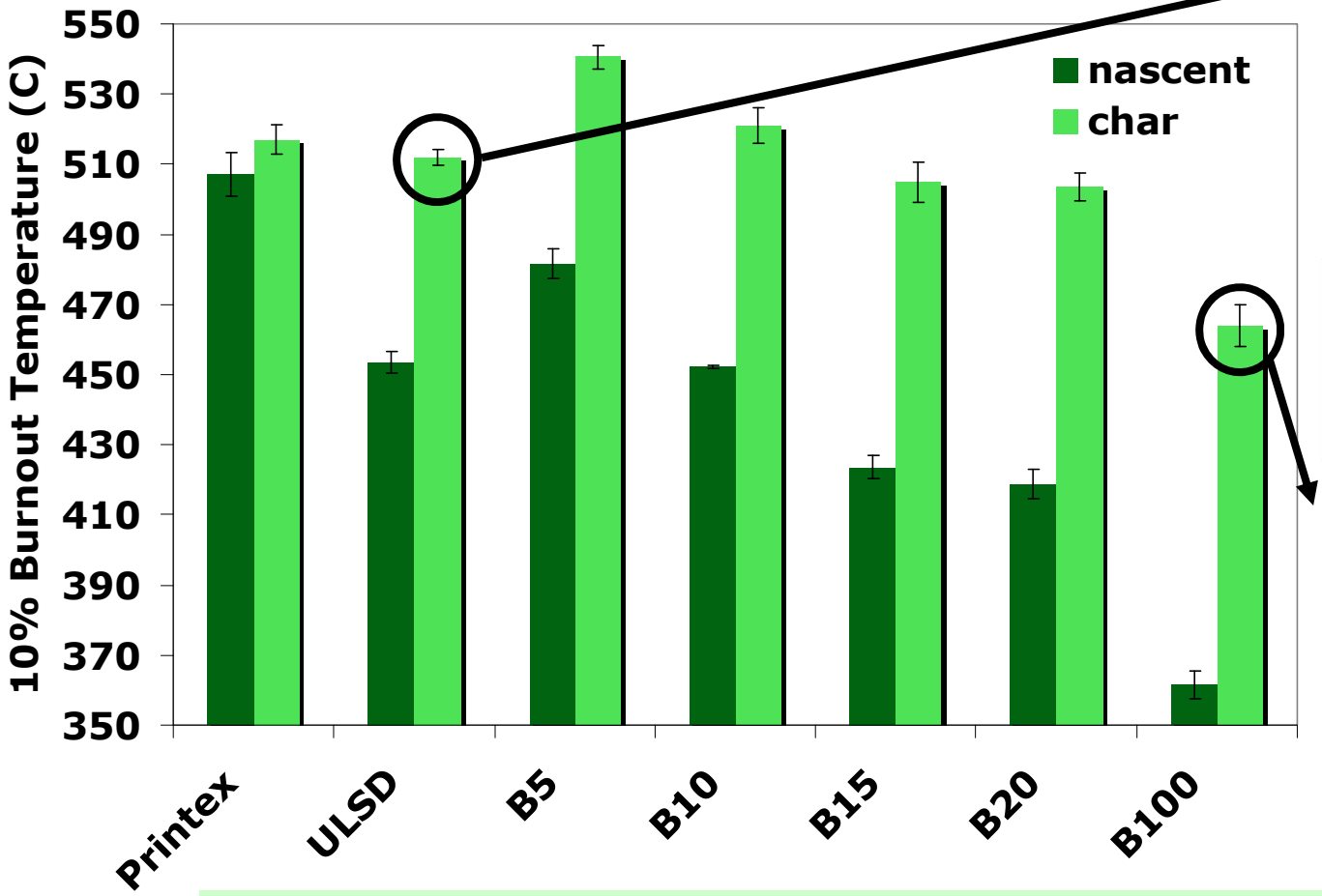
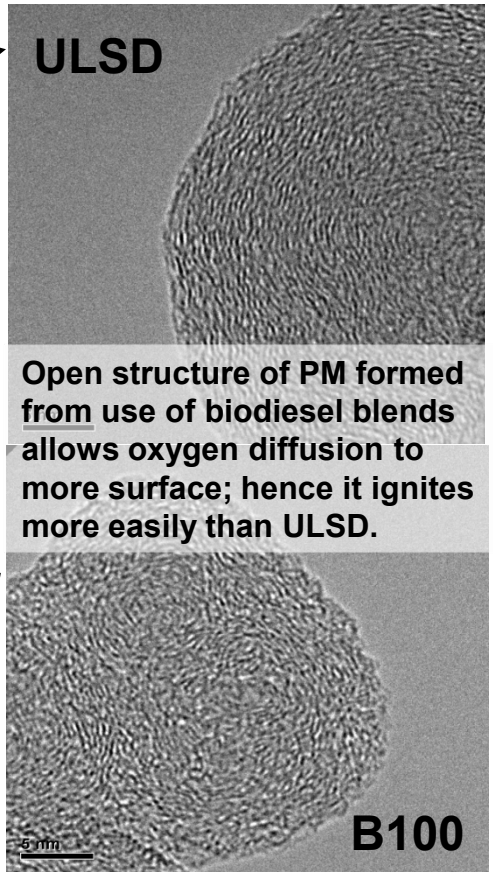
Ignition temperature depends on soot morphology and adsorbed organics.





Open structure of PM formed from use of biodiesel blends allows oxygen diffusion to more surface; hence it ignites more easily than ULSD.

B5 is anomalous; it produces PM with a less open structure.

Adsorbed HCs can act as accelerants, causing a decrease in ignition temperature. Amount of adsorbed HCs is not constant, leading to changes in the ignition temperature advantage.

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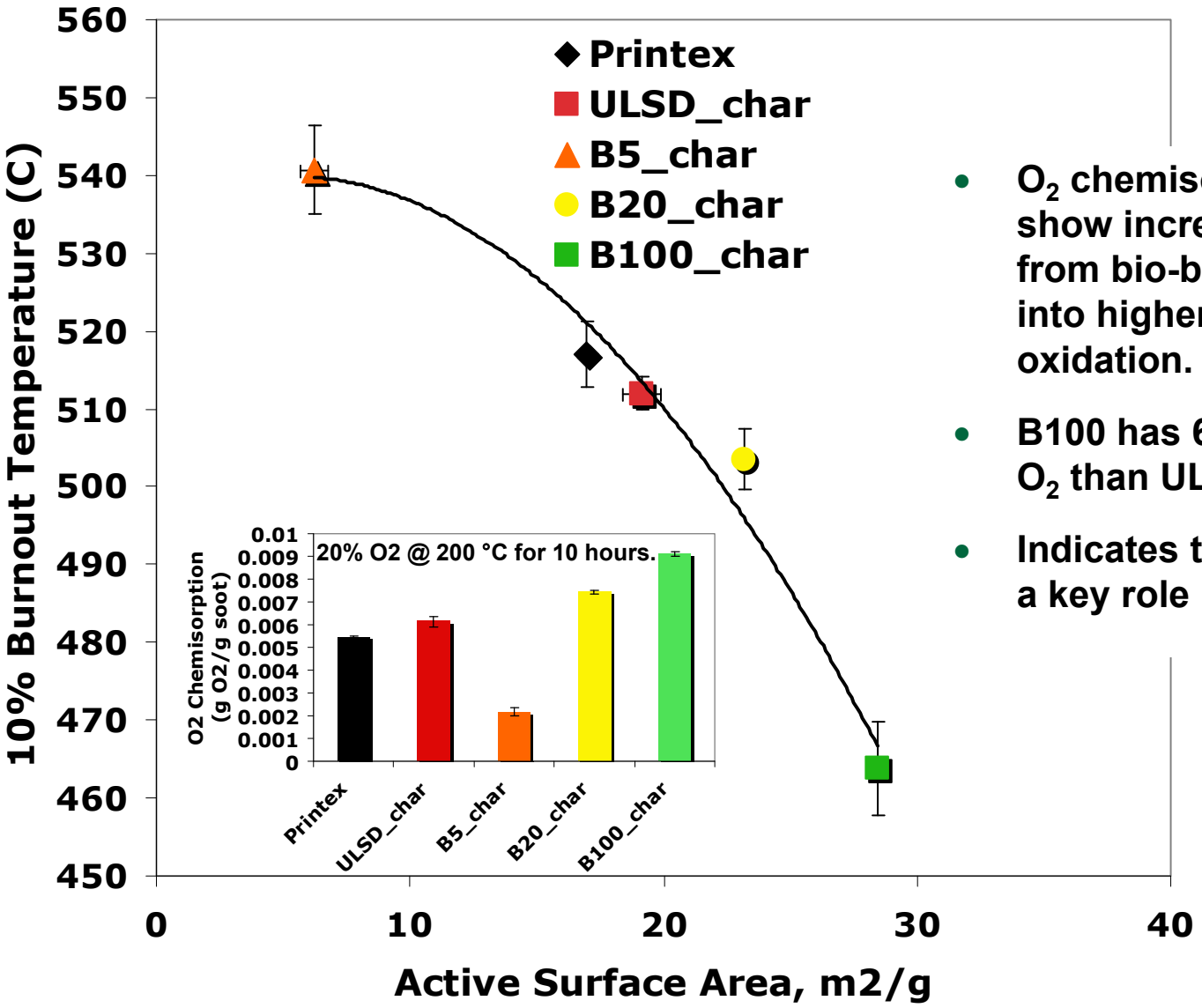
Soot structures formed during use of biodiesel blends are more accessible to O_2 diffusion, leading to higher active surface area.



- O_2 chemisorption experiments show increased O_2 affinity of soot from bio-blends; this translates into higher active surface area for oxidation.
- B100 has 60% greater affinity for O_2 than ULSD; B5 is anomalous.
- Indicates that soot structure plays a key role in PM oxidation kinetics.

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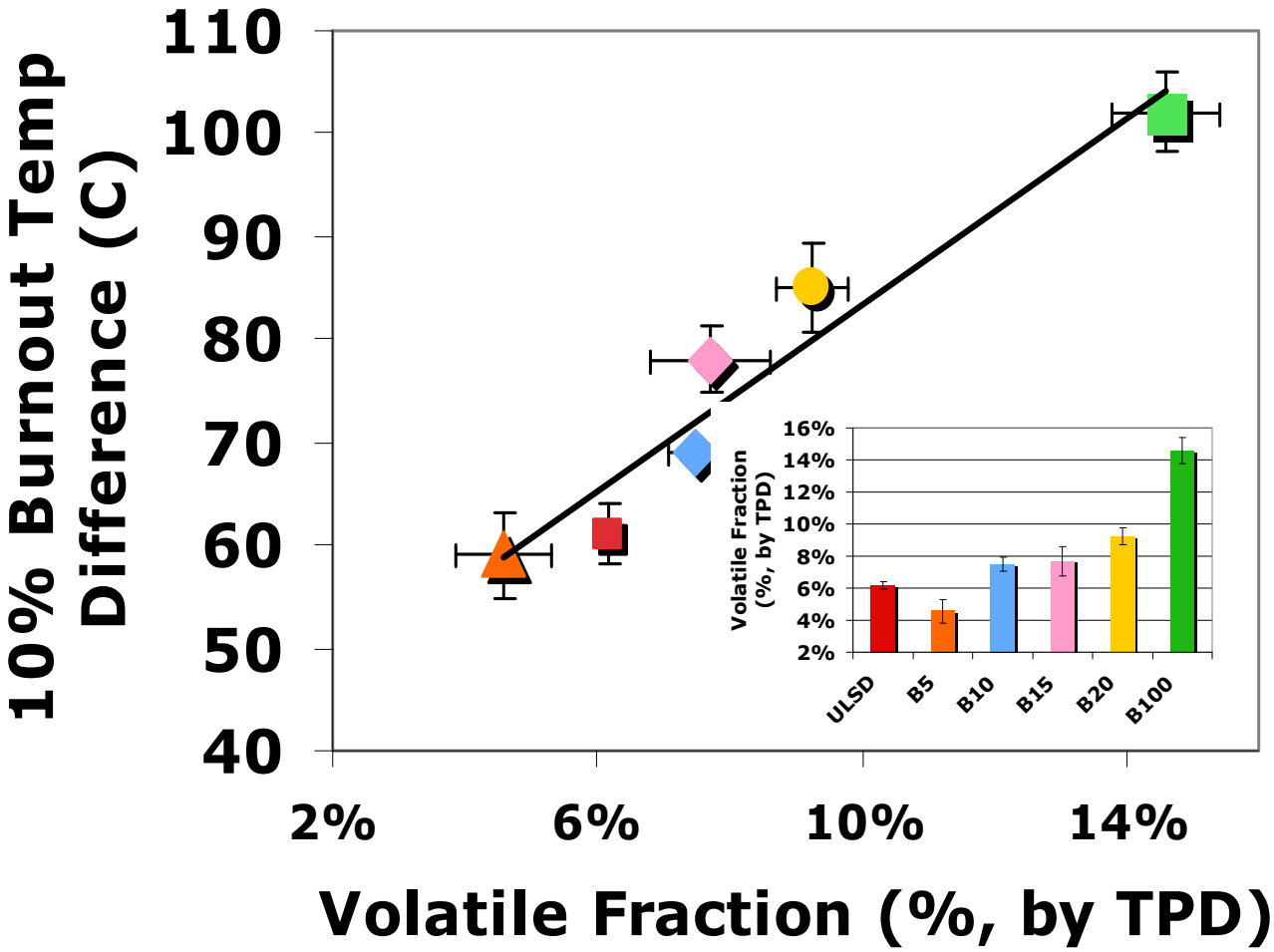
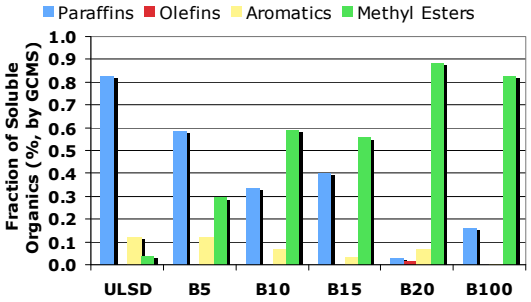
The advantage offered by volatiles is more a function of the amount, rather than the type of compounds present.





GC/MS analysis affirms differering chemistry of volatiles from soot formed by burning biodiesel blends.

The advantageous effect of adsorbed volatiles appears to be a linear function of the volatile fraction. Bio-blends tend to have more adsorbed volatiles than ULSD, and hence experience a larger "accelerant" effect on lightoff.

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NPBF PM Chemistry:

Why do thermal denuding and chemical extraction produce different SOF information, and are these unreported compounds important?

Benefit: **Improved characterization of soot-bound organics supports other technical activities related to fuel-efficient emissions control technologies for use with NPBFs.**

Accomplishment: **Successfully demonstrated extraction and analysis of aromatic carboxylic acids and related anhydrides from PM.**

- Presence of these compounds provides insights into differences between thermal denuding and chemical extraction for SOF determinations.
- Acids and anhydrides may be important in understanding aging effects on the physical properties of EGR cooler deposits, DPF soot cakes, and catalyst substrates.

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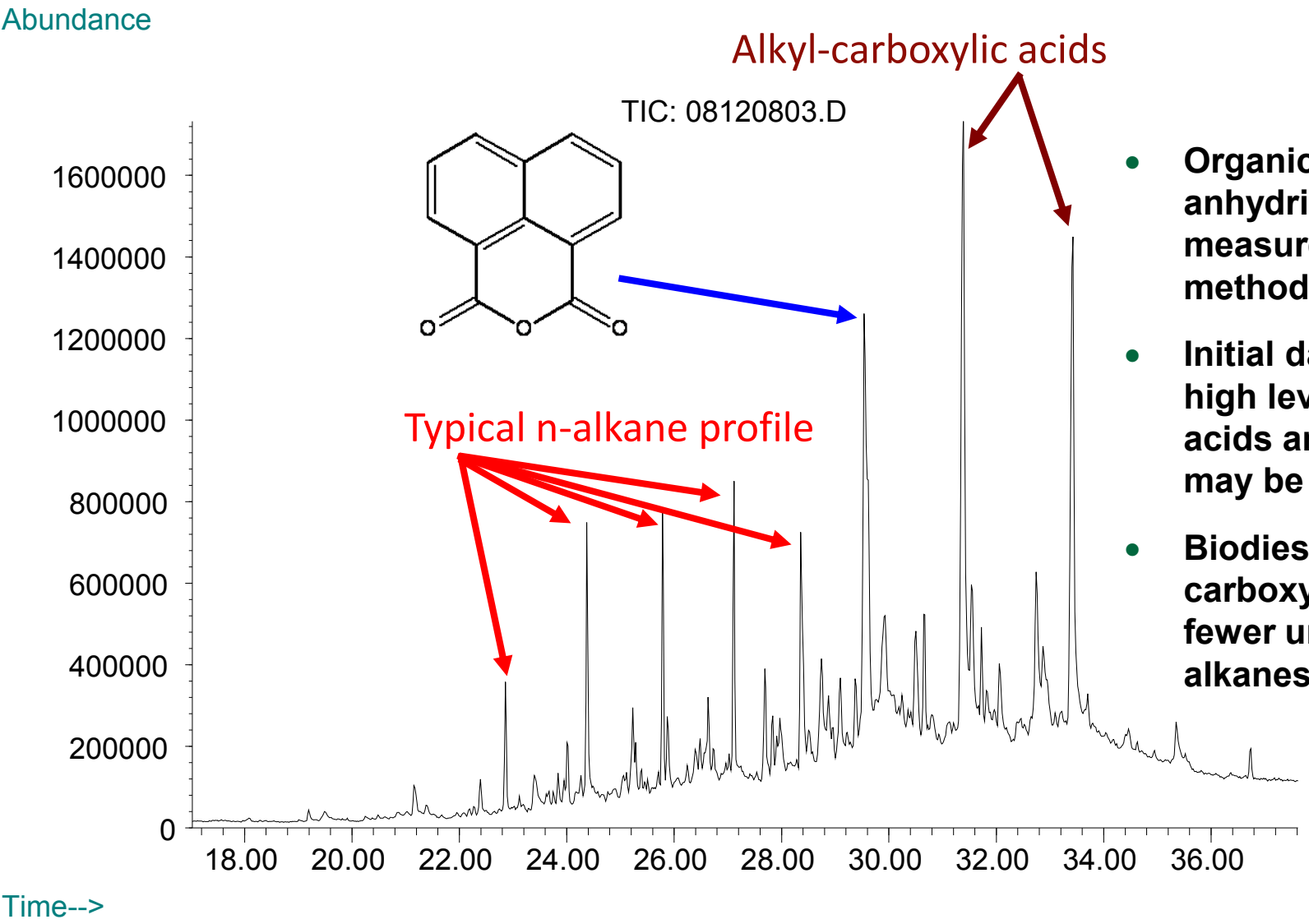
Thermal desorption of soot samples into a GC/MS revealed the presence of aromatic- and alkyl-carboxylic acids and anhydrides.



- **Organic acids and anhydrides not measured in typical methods.**
- **Initial data suggests high levels of organic acids and anhydrides may be present.**
- **Biodiesel: more alkyl-carboxylic acids, fewer unburned fuel alkanes present.**

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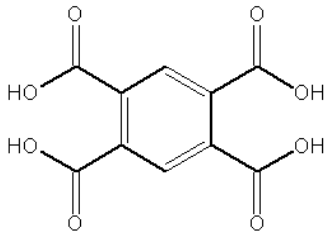
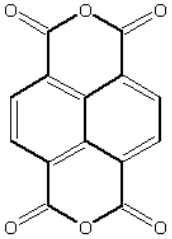
Solvent method identified to remove organic acids and anhydrides from soot.

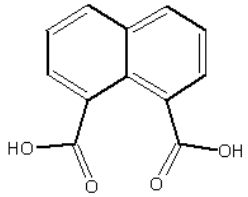
5 aromatic acids and anhydrides studied:



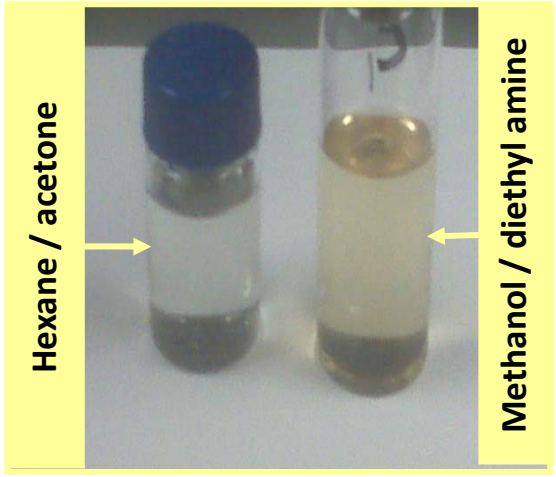
1,2,4,5-Benzenetetracarboxylic acid (and related dianhydride)

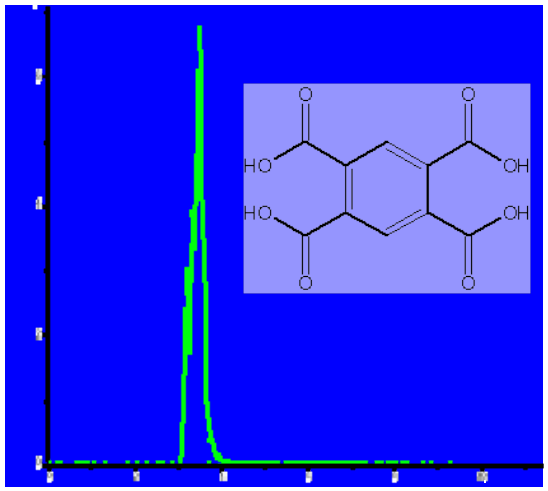


1,4,5,8-Napthalenetetracarboxylic dianhydride



1,8-Napthalene-dicarboxylic acid (and related annhydride)





- **Aromatic acids and anhydrides had poor solubility in typical hexane/acetane solvent.**
- **Analysis of standards showed very low response by GC/MS; requires extraction of large soot quantities.**
- **Benzenetetracarboxylic acid not measureable by GC/MS even with high quantities on-column.**
- **LC/MS analysis showed 100x higher sensitivity, but separation of acids from anhydrides a challenge.**

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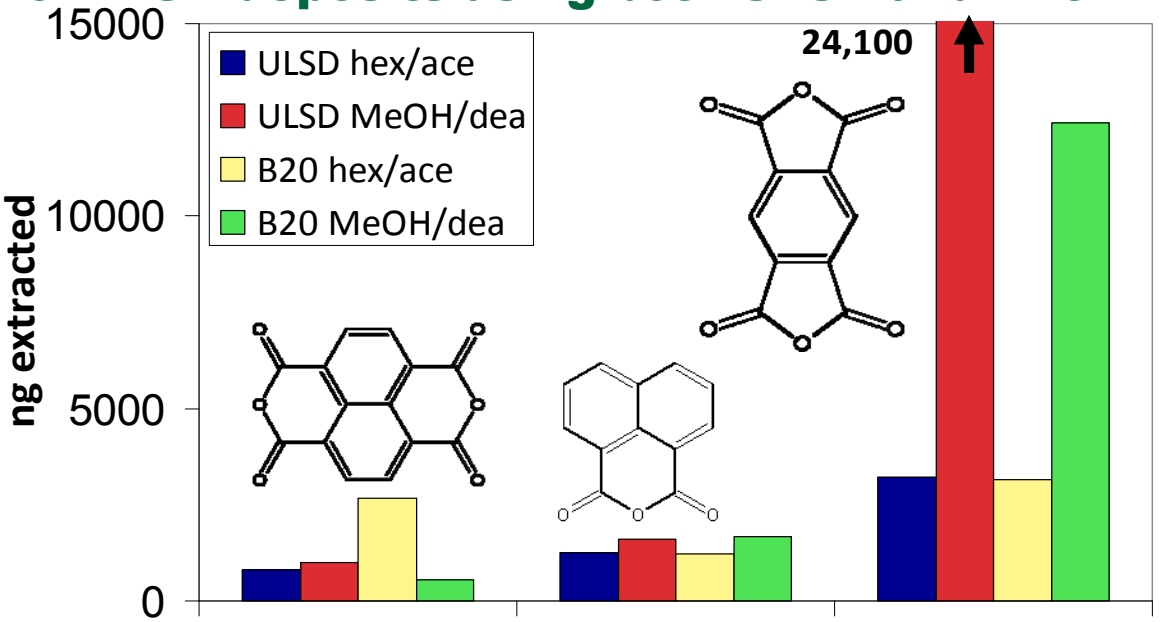
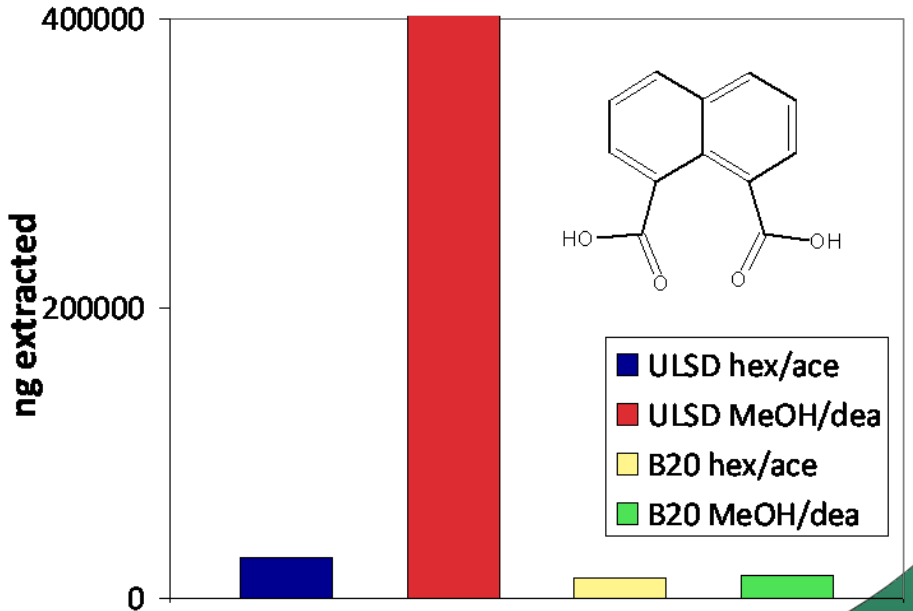
GC/MS analyses show large amounts of aromatic carboxylic acids are present in samples taken from EGR deposits using both ULSD and B20.

- Potentially 5-10% of "OC" accounted for by these 5 compounds.
- Other related compounds likely account for additional fraction of "OC".
- Acids and anhydrides are present in relative abundance and may have significant impact to some technologies.
  - EGR valve sticking
  - EGR cooler fouling
  - DPF issues?





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NPBF Effects on EGR Cooler Fouling:

Does use of biodiesel blends cause worse cooler fouling than with ULSD?

Benefit: Improved understanding of EGR cooler fouling processes will enable better models to guide component development in an effort to reduce the impacts of fouling; this can directly result in improved engine efficiency.

Accomplishment: Completed experiments with ULSD, B20 at elevated HC condition and began analysis.

- Early results show increased HC levels in the deposit, but affirm little difference in observed short-term fouling behavior with B20 compared with ULSD at study conditions.
- Other experiments including a designed experiment series to investigate the interactions between fuel distillation and coolant temperature on deposit processes are ongoing at the time of submission of this presentation.
- Long-term impacts of HCs in the deposit remain an open issue.

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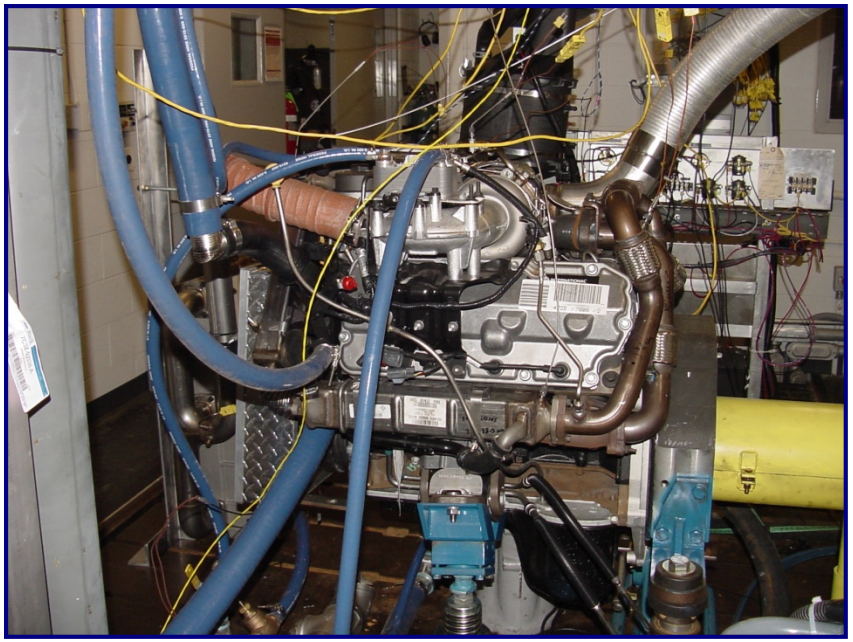
NPBF effects on EGR cooler fouling is based on studying surrogate EGR cooler tubes to enable multiple analyses of deposits.

- Ford 6.4-L V-8 used as exhaust generator.
- Surrogate tubes provide more accessible samples for study than full-size coolers.
- Exhaust passed through surrogate EGR cooler tubes at constant flow rate and coolant temperature.
  - Tubes were ¼ inch square cross-section stainless tubes.
  - Thermal effectiveness of tubes is assessed during exposure.
- Subsequent analyses of tube deposits:
  - Total mass of deposits
  - Volatile / non-volatile deposit mass
  - GC/MS characterization of the deposit HCs
  - Deposit layer thermal properties



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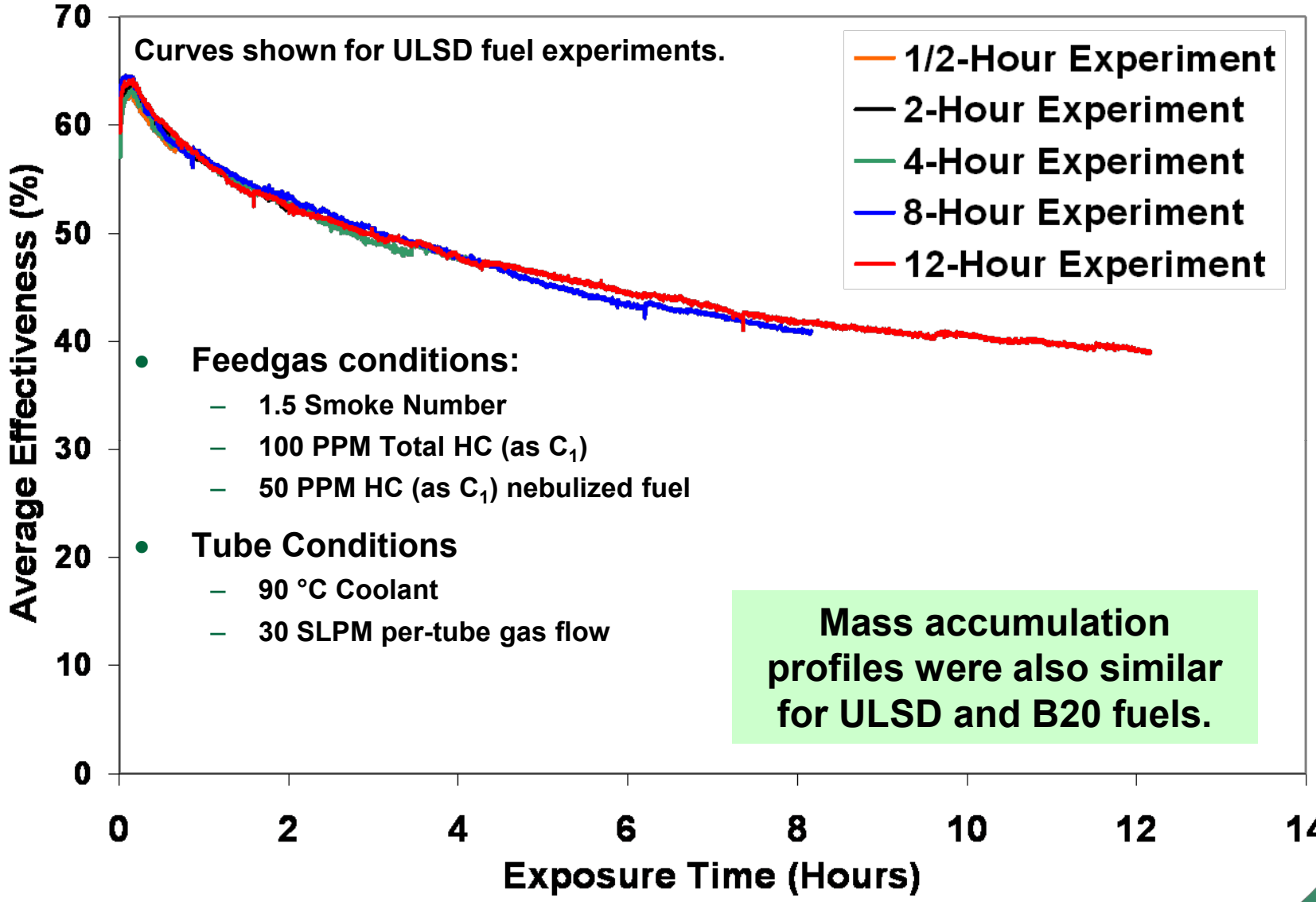
Results show that significant thermal effectiveness loss due to deposit formation occurs within a few hours.



- **Feedgas conditions:**
  - 1.5 Smoke Number
  - 100 PPM Total HC (as C_1)
  - 50 PPM HC (as C_1) nebulized fuel
- **Tube Conditions**
  - 90 °C Coolant
  - 30 SLPM per-tube gas flow

Mass accumulation profiles were also similar for ULSD and B20 fuels.

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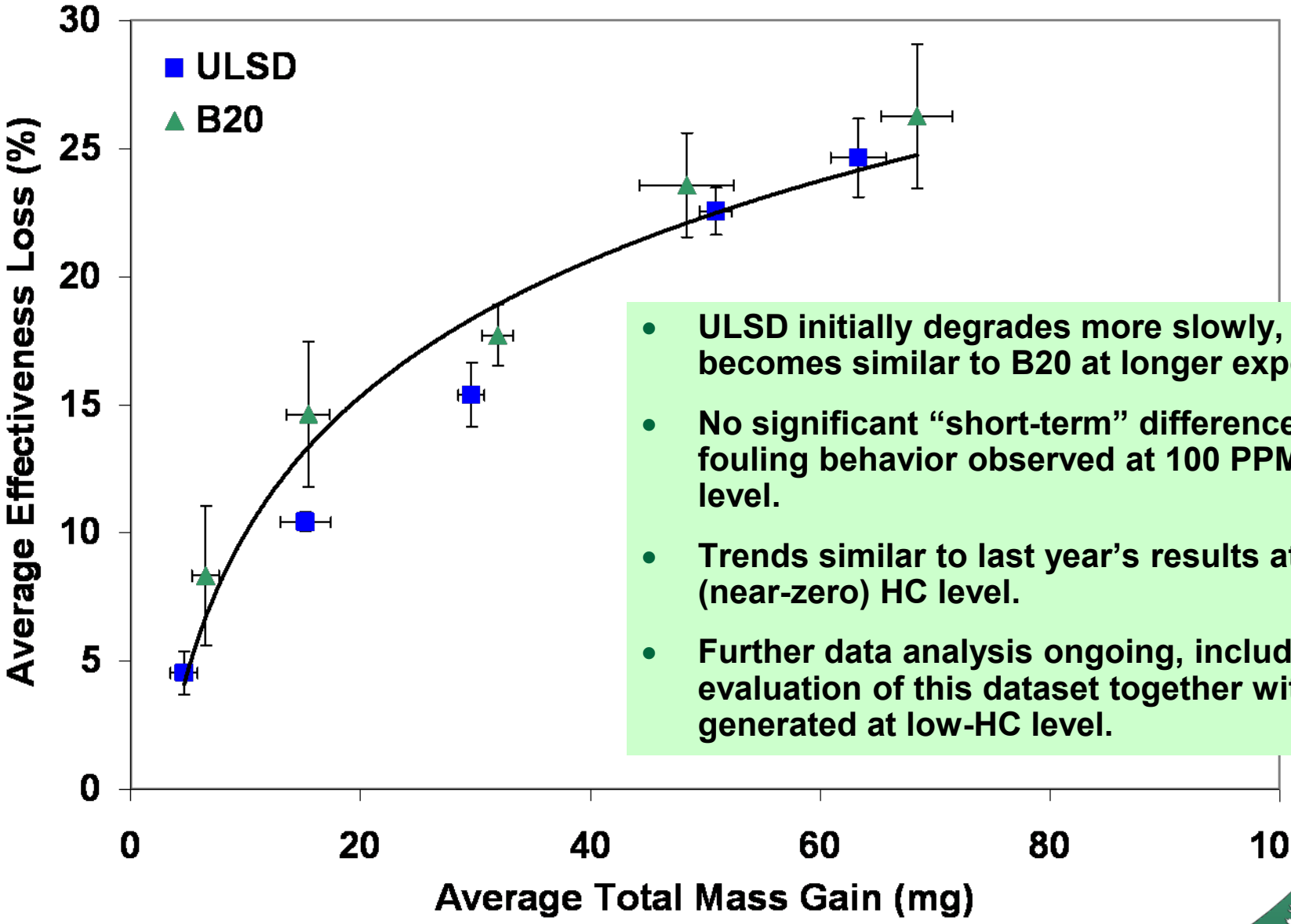
Fuel-specific differences in fouling behavior seem limited to shortest exposures; long exposures show little difference.



- ULSD initially degrades more slowly, but becomes similar to B20 at longer exposures.
- No significant "short-term" differences in fouling behavior observed at 100 PPM HC level.
- Trends similar to last year's results at lower (near-zero) HC level.
- Further data analysis ongoing, including evaluation of this dataset together with data generated at low-HC level.

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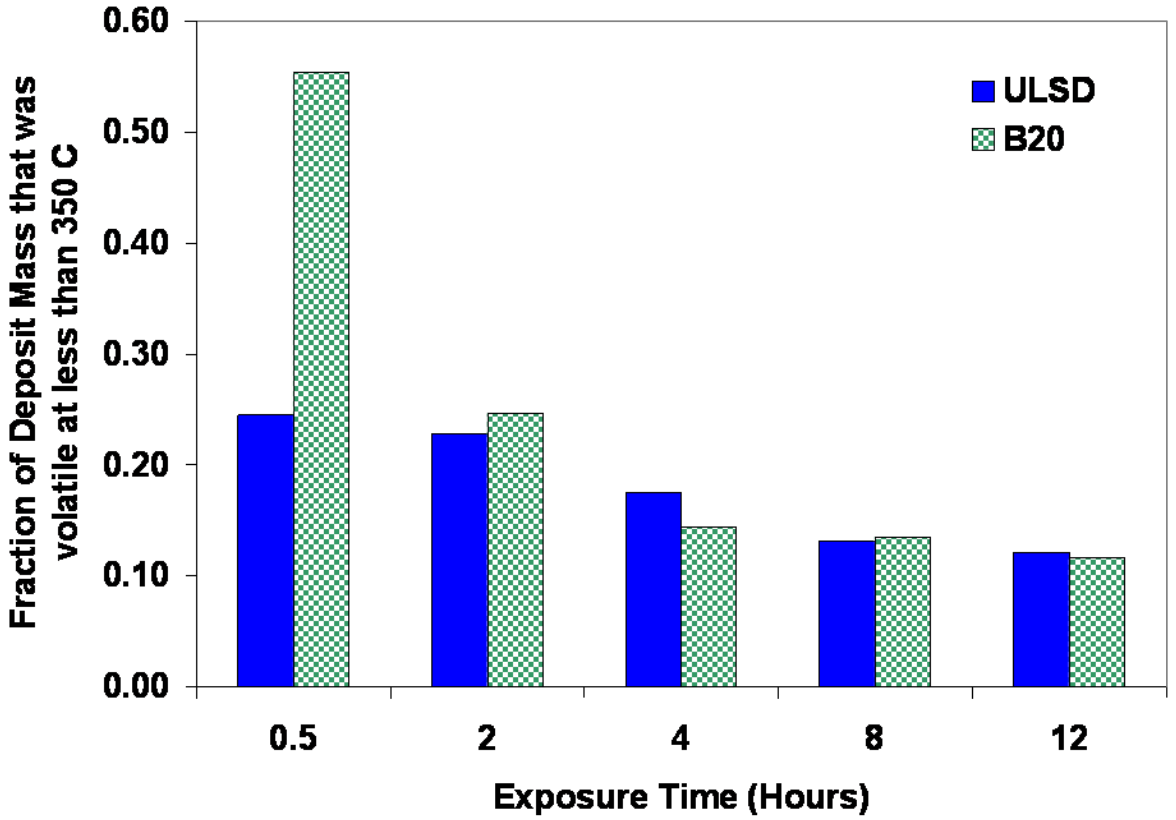
Fractionation of deposit showed that the deposits had increased volatile fractions.

- B20 initially had very high volatile fraction, ULSD was similar to previous data.
- Steady-values at longer exposures are 3x higher than previous data showed.
- Higher-boiling HC fraction appears marginally higher in current dataset.



How does the presence of HCs impact the cooler performance in the longer term as the deposits age? DOE Materials program-funded effort to study deposit properties.

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Future Directions (Beyond FY09)

- PM kinetics study uncovered a degradation of a DPF monolith associated with biodiesel use. A new effort will investigate why this failure occurred, whether this condition may be widespread, and measures to resolve the issue.
- Soot oxidation kinetics work will be expanded to include oxidation kinetics with NO2 and will open a collaboration with NREL to examine additional effects.
- Analytical development will continue to improve methods for analysis of aromatic acids and anhydrides and will expand to further investigate alkyl carboxylic acids that are more prevalent in soot from biofuels.
- EGR studies will focus on investigating differences in deposit adhesion in transient-flow conditions that may arise from differences in morphology and volatile content.
  - Close collaboration with activity funded by DOE Materials Program that is investigating the thermophysical properties of deposits.
- As always, we welcome specific concerns from industry, whether in these areas or other topics, for future studies.

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Summary

- This project is targeted towards providing data and predictive tools to address gaps in information needed to enable broad use of NPBFs. (DOE Technical Barrier)
- Collaborations with several industry stakeholders and universities are being used to maximize the impact of this work.
- The approach being pursued is to bring together targeted, engine-based studies using NPBFs with in-depth characterization of PM and HCs to better understand behavior for specific technologies. (Currently DPFs and EGR Systems)
- Several technical accomplishment this FY:
  - Resolution of soot structure and adsorbed HC effects on soot oxidation kinetics; kinetic model expected later this FY.
  - Successful analysis and quantification of aromatic acids and anhydrides in diesel soot at percent levels.
  - Completion of experiments in support of EGR fouling studies with B20 at moderate HC levels; short-term results so far suggest the problem is not worse with B20.
- Future work plans are in place; industry input towards those plans or other NPBF-emissions control effect concerns is needed and welcomed.

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