

# ***Methodology for Formulating Diesel Surrogate Fuels with Accurate Compositional, Ignition-Quality, and Volatility Characteristics***

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## **Research Supported by**

***US DOE Office of Vehicle Technologies, Program Mgr. Kevin Stork, and  
Coordinating Research Council (CRC)***

*5th Annual MACCCR Fuels Research Review Meeting  
Sandia National Laboratories, Livermore, California  
September 19, 2012*

## ***Overall Objective***

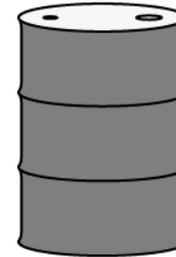
**Establish diesel surrogate fuels:**

- **As time-invariant, realistic reference fuels**
- **To better understand fuel-composition and property effects on engine processes**
- **Ultimately to enable computational engine optimization for evolving real fuels**

# Terminology

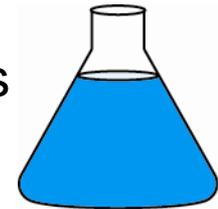
- **Target fuel**

- A “real” fuel with selected properties that are to be matched by a surrogate fuel



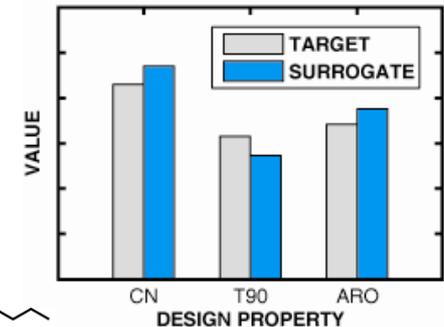
- **Surrogate fuel**

- Fuel composed of a small number of pure compounds that is formulated to match selected properties of a target fuel



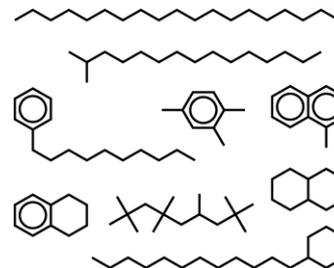
- **Design properties**

- Selected properties of the target fuel that are to be matched by the surrogate fuel

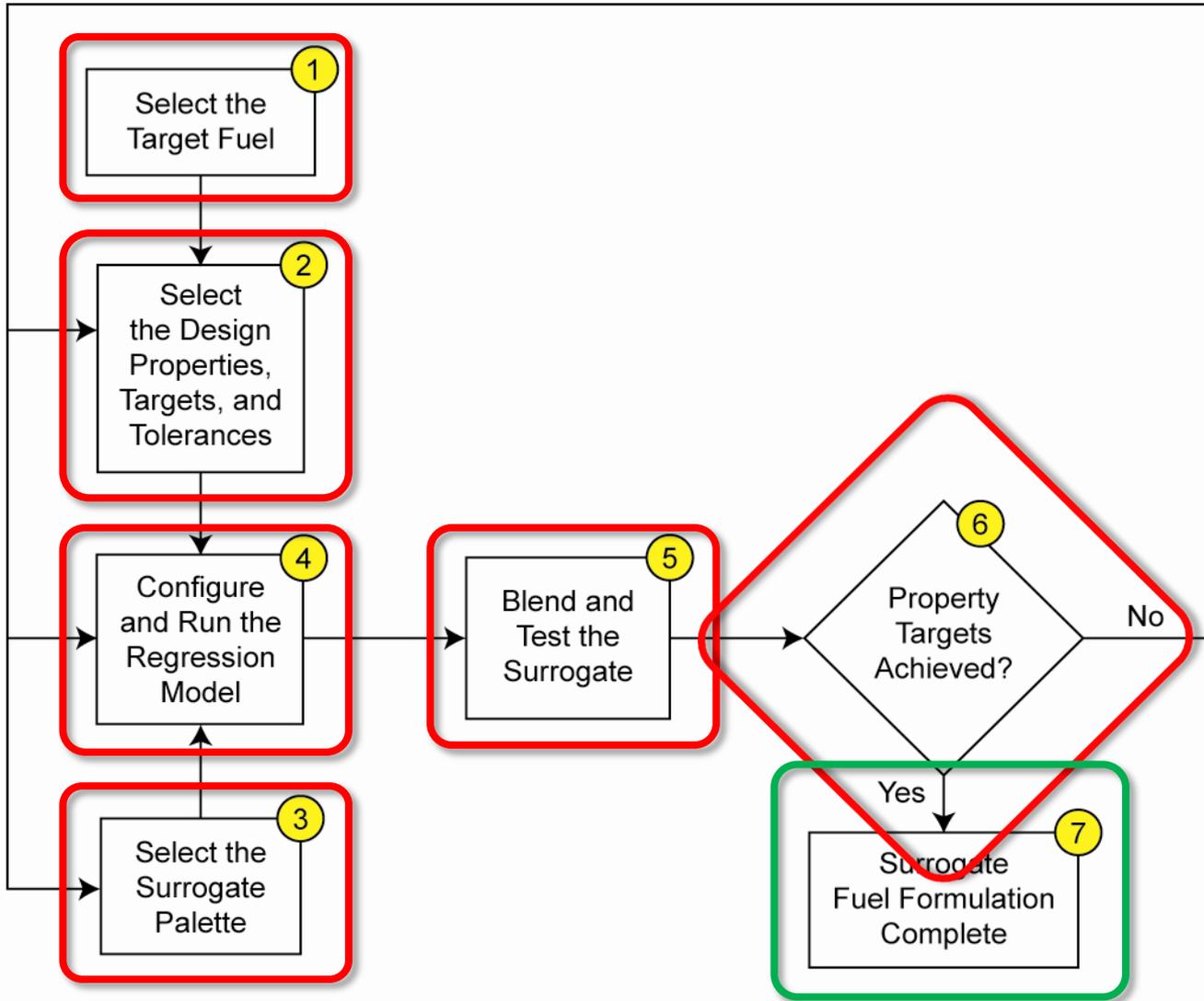


- **Surrogate palette**

- The set of pure compounds that are blended together to create a surrogate fuel

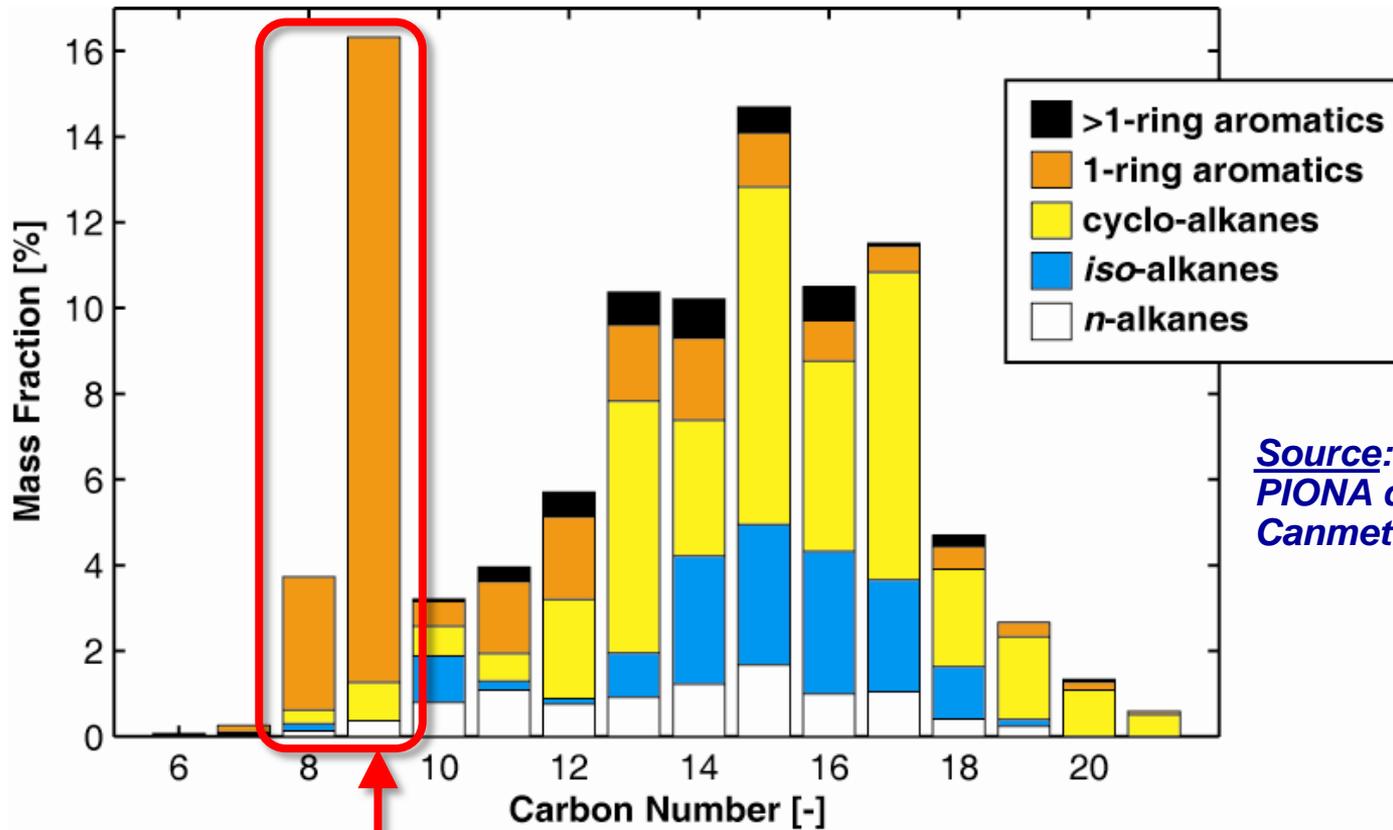


# Surrogate Formulation Process Overview



# Target Fuels: FD9A

- FD9A = CRC FACE Diesel #9, Batch A

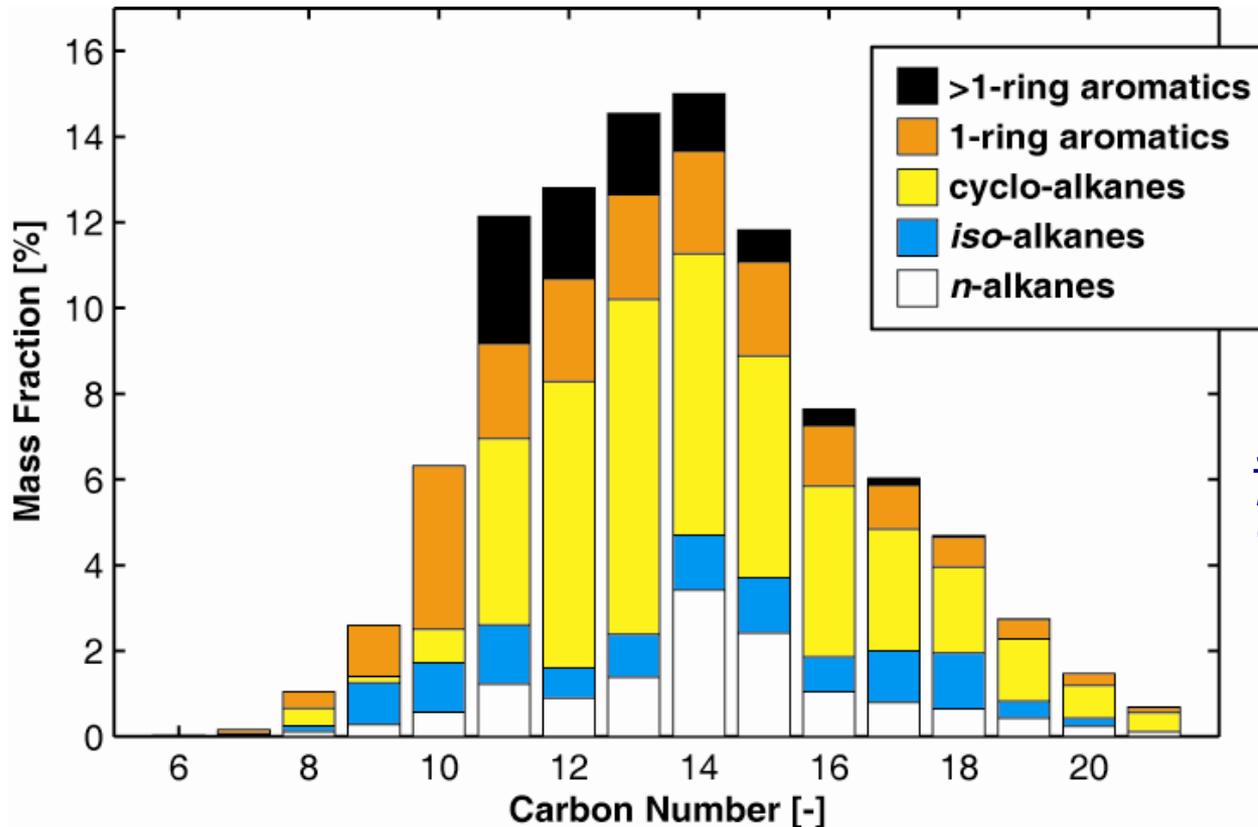


*Source: GC-FIMS and PIONA data from CanmetENERGY*

**Anomalously high levels of C8 and C9 mono-aromatics**

# Target Fuels: CFA

- CFA = 2007 #2 ULSD Emissions Certification Fuel, Batch A

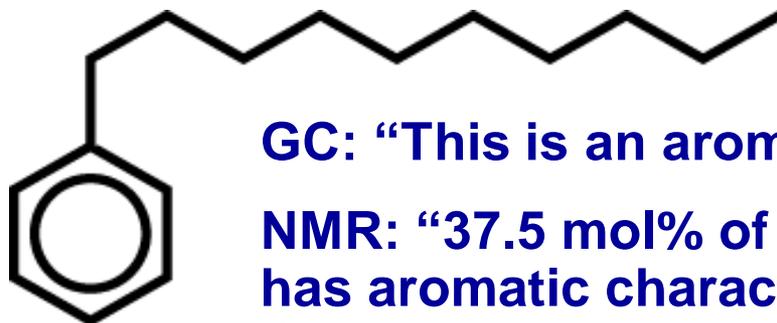


*Source: GC-FIMS and PIONA data from CanmetENERGY*

**CFA exhibits a more-typical distribution of HC type with carbon #**

## Surrogate Design Properties: Composition

- Quantified using  $^{13}\text{C}$  and  $^1\text{H}$  nuclear magnetic resonance (NMR) spectroscopy techniques
- NMR data give structural information on a *per-carbon-atom* basis, whereas GC techniques give info on a *per-molecule* basis

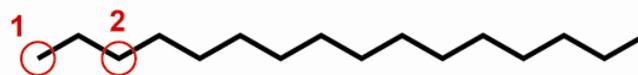


**GC:** “This is an aromatic molecule.”

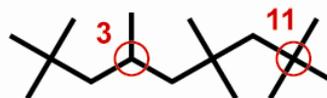
**NMR:** “37.5 mol% of the carbon in this molecule has aromatic characteristics. The rest has linear-alkane characteristics.”

- Surrogates based on more-accurate structural information from NMR characterization are expected to better match target-fuel combustion chemistry and emissions
- Measurements conducted at CanmetENERGY (H. Dettman) and PNNL (J. Franz)

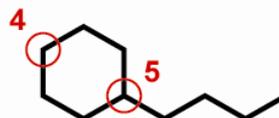
# Carbon Types from NMR Analysis



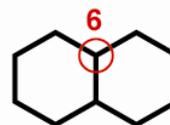
*n*-hexadecane  
(C<sub>16</sub>H<sub>34</sub>)



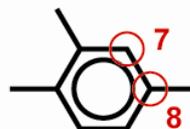
2,2,4,4,6,8,8-heptamethylnonane  
(C<sub>16</sub>H<sub>34</sub>)



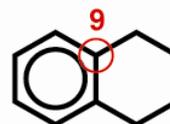
*n*-butylcyclohexane  
(C<sub>10</sub>H<sub>20</sub>)



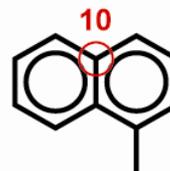
decalin  
(C<sub>10</sub>H<sub>18</sub>)



1,2,4-trimethylbenzene  
(C<sub>9</sub>H<sub>12</sub>)



tetralin  
(C<sub>10</sub>H<sub>12</sub>)



1-methylnaphthalene  
(C<sub>11</sub>H<sub>10</sub>)

1. CH<sub>3</sub> (primary C)
2. *n*-alkane CH<sub>2</sub> (secondary C)
3. *iso*-alkane CH (tertiary C)
4. cyclo-alkane CH<sub>2</sub> (secondary C)
5. cyclo-alkane to alkyl-chain CH (tertiary C)
6. cyclo-alkane to cyclo-alkane CH (tertiary C)
7. aromatic CH (tertiary C)
8. aromatic to alkyl-chain C (quaternary C)
9. aromatic to cyclo-alkane C (quaternary C)
10. aromatic to aromatic C (quaternary C)
11. aliphatic C (quaternary C)

Not found in market  
diesel fuels

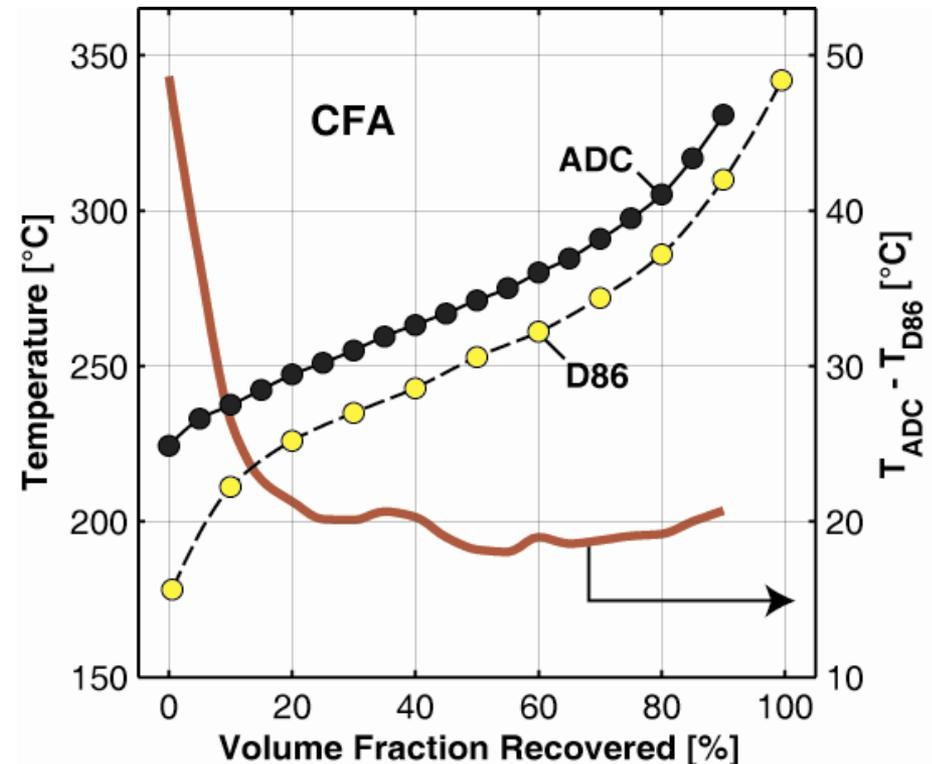
# Surrogate Design Properties: Ignition Quality and Volatility

## ● Ignition quality

- Quantified using derived cetane number (DCN) per ASTM D 6890
- Measurements conducted using IQT at NREL (M. Ratcliff)
  - Excellent repeatability 0.7 DCN vs. method repeatability 2.6 DCN

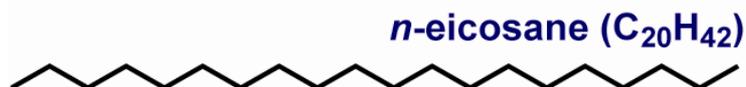
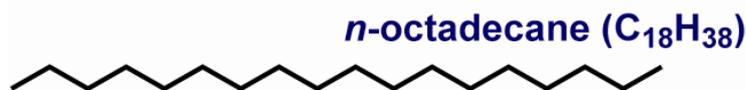
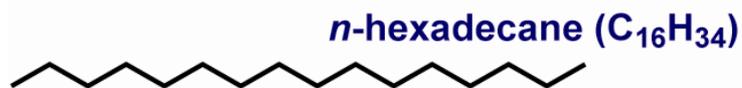
## ● Volatility

- Quantified using advanced distillation curve (ADC)
  - Developed by T. Bruno and co-workers at NIST
- Superior to ASTM D 86
  - ADC gives actual thermodynamic state points, analogous to normal boiling points
  - D 86 vapor temperatures underpredict liquid boiling temperatures

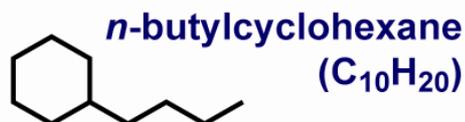


# Surrogate Palette, "Version 1"

## n-alkanes



## cyclo-alkanes



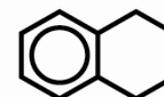
## iso-alkane

Not very representative  
of diesel *iso*-alkanes



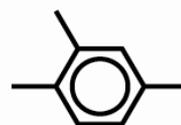
2,2,4,4,6,8,8-heptamethylnonane  
(C<sub>16</sub>H<sub>34</sub>)

## naphtho-aromatic

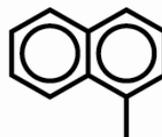


tetralin  
(C<sub>10</sub>H<sub>12</sub>)

## aromatics



1,2,4-trimethylbenzene  
(C<sub>9</sub>H<sub>12</sub>)



1-methylnaphthalene  
(C<sub>11</sub>H<sub>10</sub>)

Version 1 palette contains all of the major hydrocarbon classes that are present in the target fuels

## ***Regression Model***

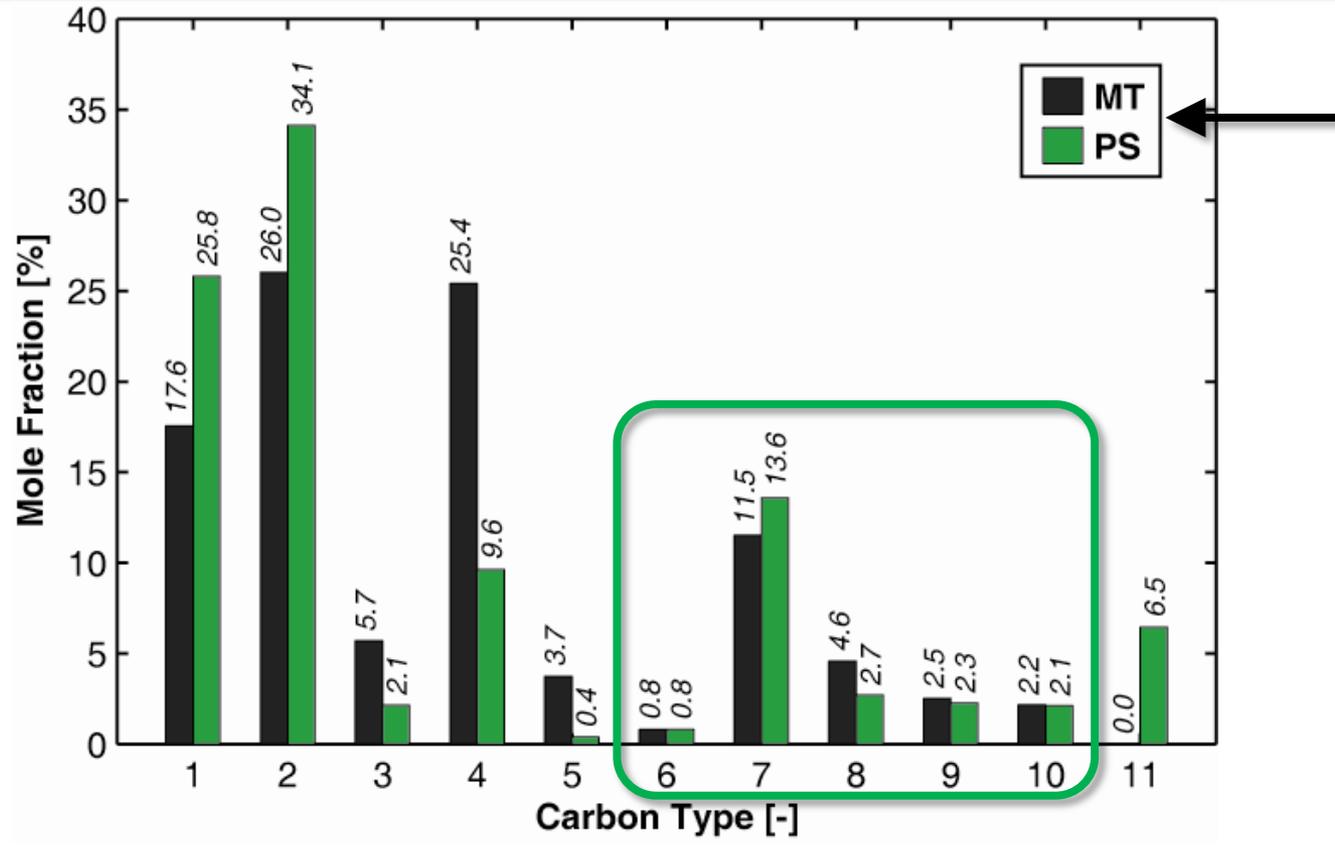
- Approach developed at NIST (M. Huber)
- Minimizes objective function  $S$ ,

$$S = \sum_{i=1}^{N_{CT}} W_{i,CT} F_{i,CT}^2 + W_{DCN} F_{DCN}^2 + \sum_{i=1}^{N_{ADC}} W_{i,ADC} F_{i,ADC}^2 + W_{\rho} F_{\rho}^2$$

where  $N_{CT}$  is the number of carbon types,  $N_{ADC}$  is the number of ADC points, each  $W$  is a weighting factor, and each  $F$  is a normalized difference between predicted and target values

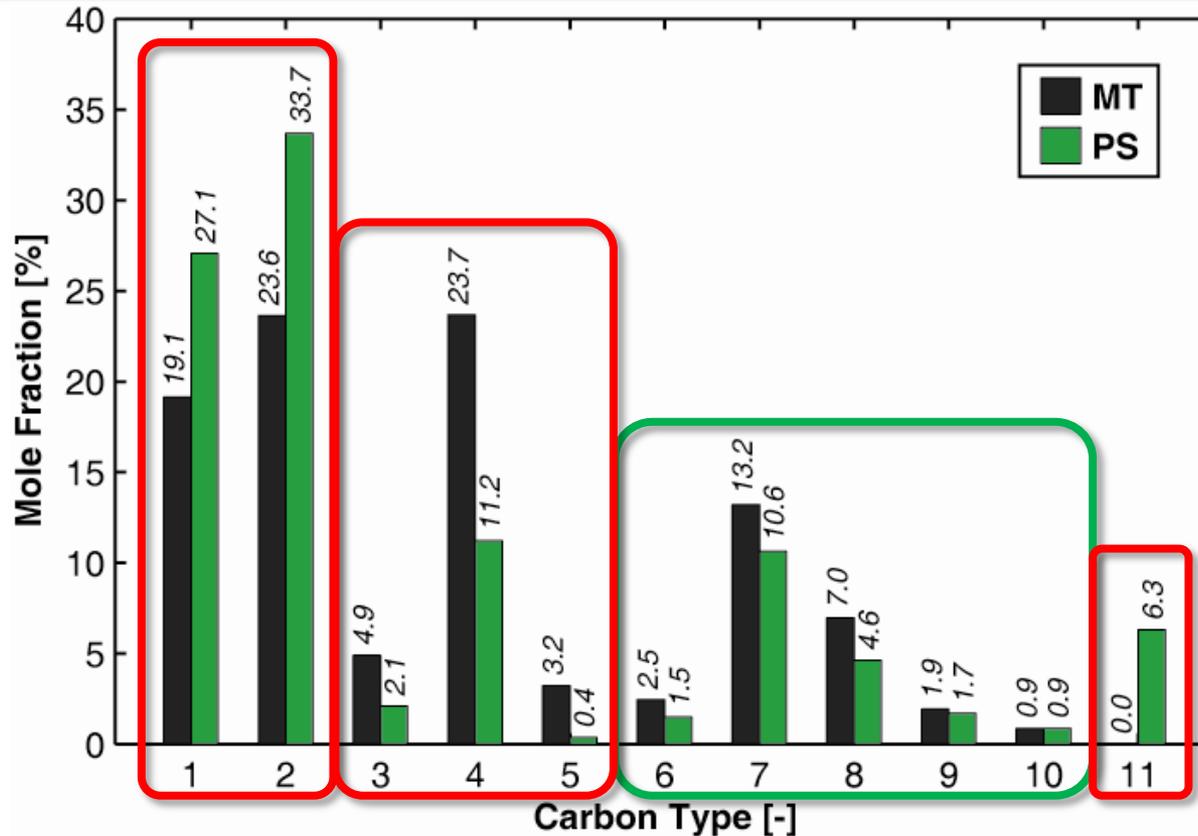
- Assumes DCN of mixture = volume-fraction-weighted sum of DCNs of palette compounds
  - This is a reasonably accurate assumption (see Slide 15)
- ADC calculated using an equation-of-state based mixture model

# Composition Matching: CFA



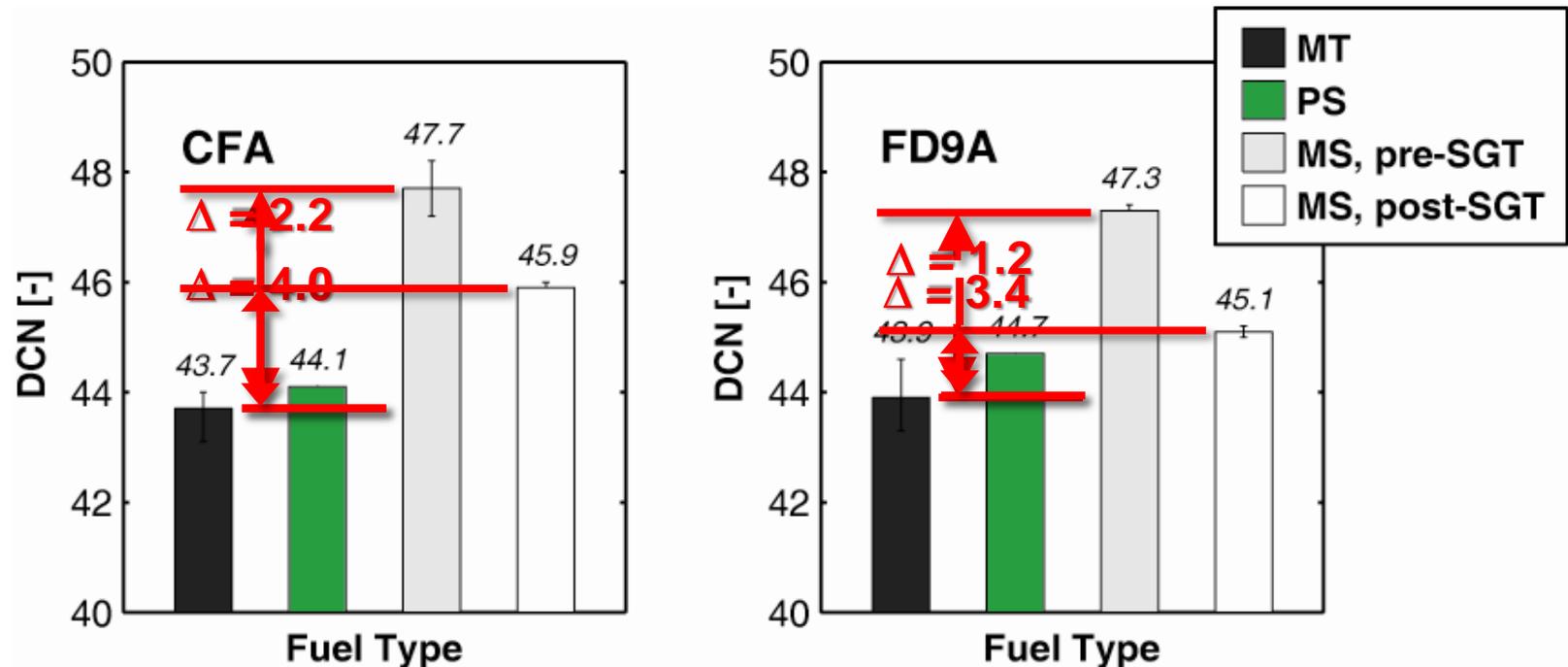
- **MT = Measured for Target fuel, PS = Predicted for Surrogate fuel**
- **Carbon Types 6-10 are well matched**
  - Agreement of other carbon types could be improved

## Composition Matching: FD9A



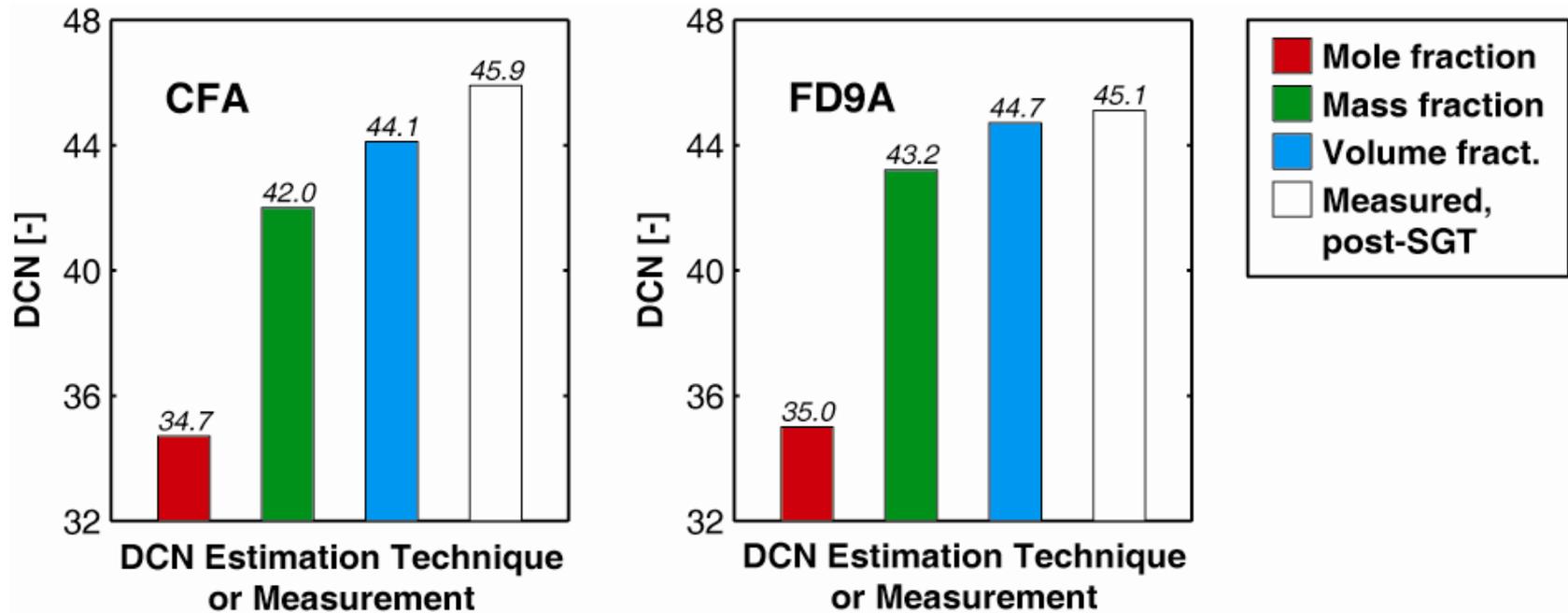
- **Same trends evident with FD9A as were seen with CFA**
  - Too much *n*-alkane C (CTs 1&2) and quaternary aliphatic C (CT11)
  - Not enough *iso*- and cyclo-alkane C (CTs 3-5)

# Ignition-Quality Matching



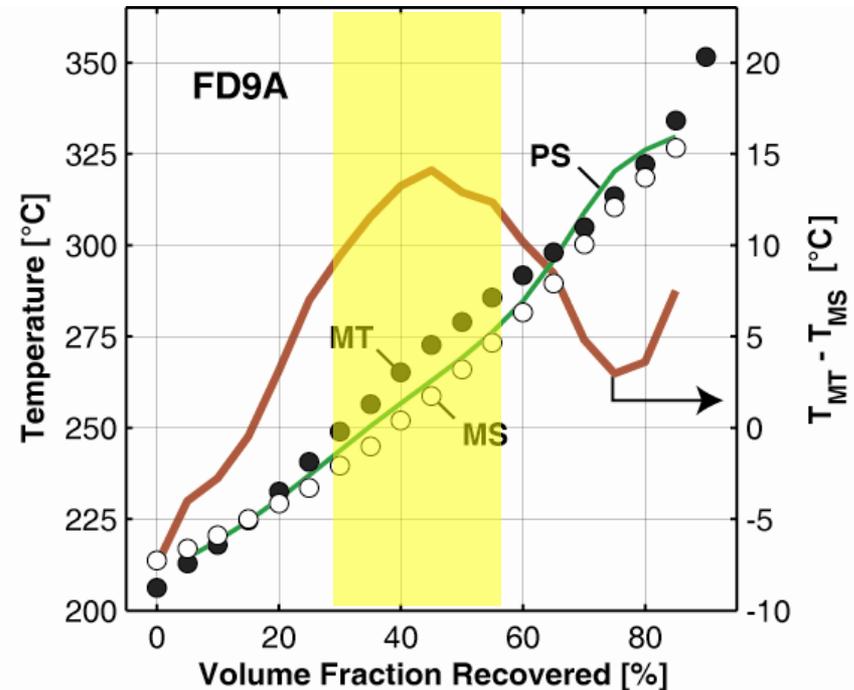
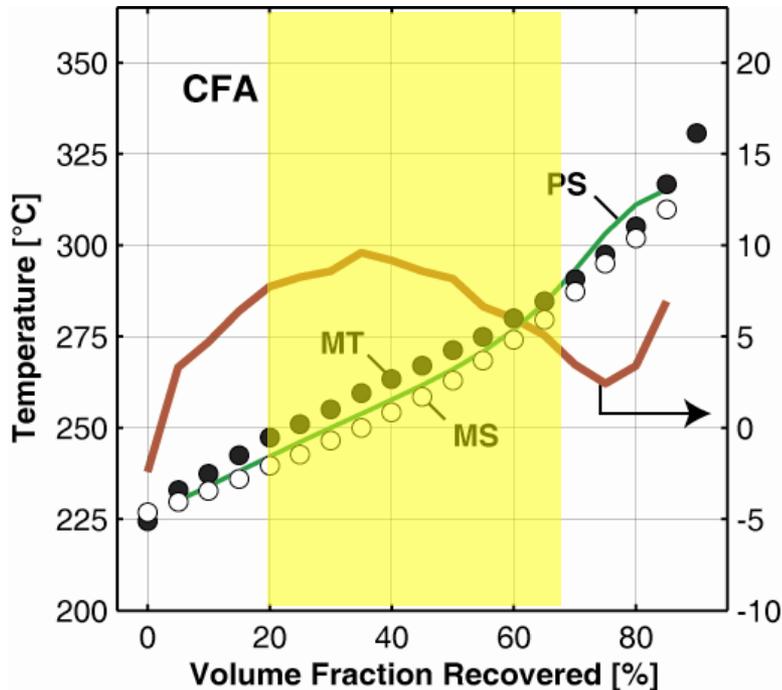
- Initially, Measured Surrogate (MS) DCNs were 3.4 to 4.0 numbers higher than MT values
- Passing surrogates through baked silica gel (*i.e.*, “silica-gel treatment,” SGT) mitigated this issue somewhat
  - Presumably, ignition-accelerating contaminants were removed

# Evaluation of Volumetric Linear Blending Assumption for DCN Prediction



- Volume-fraction-weighted estimate is closest to measured value
- Other potential causes of DCN disagreement
  - Non-linear blending effects
  - Uncertainties in palette-compound DCNs

# Volatility Matching



- Surrogates have higher *initial* boiling temperatures, but lower temperatures across rest of distillation curve
- $T_{MT} - T_{MS}$  peaks in temperature range that does not contain palette-compound boiling points (247 – 286 °C)

# Summary

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- **Two 8-component diesel surrogate fuels were created**
- **Each surrogate contains all of the major hydrocarbon classes found in its corresponding target fuel**
  - *n*-alkanes; *iso*-alkanes; mono- and di-cyclo-alkanes; mono- and di-aromatics; and naphtho-aromatics
- **Good matching of property targets was achieved**
  - 5 of 11 carbon types were matched within 3 mol%, error in others averaged 7.3 mol%
  - Surrogate DCNs averaged 3.9% higher (post silica-gel treatment)
  - Surrogate ADC points averaged 2.1% lower
  - Surrogate densities averaged 4.1% lower
- **Good matching of other properties also was achieved**
  - Molar C/H ratio within 3.4%, net heat of combustion within 0.6%, smoke point within 2-mm repeatability of the test method

## ***Summary (cont'd)***

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- **Awareness of ignition-accelerating contaminants is important**
  - Silica-gel treatment (or similar) is recommended for groups measuring ignition delays in other venues (shock tubes, RCMs,...)
- **Final paper is available (free) from**
  - <http://www.crcao.org/publications/advancedVehiclesFuelsLubricants/index.html>; click on “CRC Project No. AVFL-18” link
  - Or go to <http://pubs.acs.org/doi/abs/10.1021/ef300303e>

# *Current/Future Work*

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- **Diesel surrogates**
  - Refine surrogate-formulation methodology
    - Improved palette
    - Improved property modeling
  - Single-cylinder engine testing
  - CFD modeling for mechanism validation and/or refinement

# ***Acknowledgments***

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- **John Luecke (NREL) – IQT measurements, silica-gel treatment, net heat of combustion measurements**
- **Rafal Gieleciak, Darcy Hager (CanmetENERGY) – GC purity analyses of palette compounds**
- **Sara Salmon (CanmetENERGY) – NMR analyses**
- **Craig Fairbridge (CanmetENERGY) – GC-FIMS analyses of target fuels**
- **Chris Tennant, Brent Bailey, Jane Beck (CRC) – administrative support, guidance**
- **Scott Jorgensen (GM)**
- **Krystal Wrigley (ExxonMobil)**
- **Bill Leppard (consultant)**
- **Tim Bays (PNNL)**