Formulation and Some Applications of Jet Fuel Surrogates

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Outline

• Introduction
  – Jet Fuel Description
  – Reasons for Surrogates
• Formulation of Surrogates
  – Criteria
  – Approaches
  – Some Examples
  – Validation
• Case Study: Open Pool Fire
• Case Study: Droplet Combustion
• Summary
**JP-8 Description**

**Hydrocarbon Class Distribution in Jet-A (wt.%)**
- Cycloparaffins: 20%
- Naphthenes: 2%
- Alkylbenzenes: 18%
- i-Paraffins: 29%
- n-Paraffins: 28%
- Misc.: 2%
- ND: 1%

**Top Three Compounds**
- $n$-C$_{11}$, 4.43 wt.%
- $n$-C$_{10}$, 4.10 wt.%
- $n$-C$_{13}$, 3.85 wt.%
Reasons for Surrogate Development

• Chemical complexity in JP-8
  – More than 300 hydrocarbons exist
  – Few of these compounds are greater than 1% wt.
  – Detailed chemical kinetics are currently available for only a limited number of compounds

• Computational limitations
  – Tracking a large number of species in a CFD code is not yet feasible
  – the feed specification must be simplified to be tractable

• Experimental Uncertainties
  – Jet fuels manufactured to meet ASTM specification may have large compositional differences from each other, e.g., aromatic content, density, cetane index, and etc.
Formulation Methodology

• Key to surrogate formulation
  – Clear definition of properties to be matched
    – Understanding of physical and chemical processes that relate surrogate composition to desired properties

• Criteria for Surrogate Formulation

Application Driven

- Relevant Physical Properties
- Chemical Kinetics
- Cost

Species Driven

- Flame Properties
- Availability

Species Driven

- Flame Properties
- Availability
- Cost

Application Driven

- Relevant Physical Properties
- Chemical Kinetics
- Cost
Formulation Methodology

**Empirical Approach: Past**
- Select compounds from parent fuel composition profile, estimate mixture properties with available correlations.
- Has been used most widely.
- Trial and error based; the selection of compounds may not represent fuel well.

**Structural Group Contribution Approach: Future**
- Fuel structure determines its properties.
- Many properties could be estimated with structural group contribution theory.
- Currently, a lack of model integrating physical properties estimation and kinetics simulation.

**Hybrid Semi-empirical approach: Current**
- Combination/compromise of the above two approaches
- Set up a pool of candidates; filter the pool with constraints; study the effect of species change on mixture properties
- Has provided a preliminary working surrogate
### Selected Known Surrogates for Transportation Fuels ---

#### Based on Empirical Approach

<table>
<thead>
<tr>
<th>Author</th>
<th>Parent Fuel</th>
<th>Paraffins</th>
<th>Cyclo Paraffins</th>
<th>Aromatics</th>
<th>Objective</th>
</tr>
</thead>
<tbody>
<tr>
<td>Westbrook et al., '61-'99</td>
<td>Gasoline Diesel (+ additives)</td>
<td>$n \text{-} C_7$, $i \text{-} C_8$</td>
<td></td>
<td></td>
<td>Unburned HCs, Stratified Charge, autoignition, soot</td>
</tr>
<tr>
<td>Prabhu, '97</td>
<td>Gasoline</td>
<td>$n \text{-} C_7$</td>
<td>$i \text{-} C_8$</td>
<td>Toluene</td>
<td>Engine Ignition</td>
</tr>
<tr>
<td>Hallet, '92</td>
<td>Diesel</td>
<td>$n \text{-} C_{7-10,16,20}$</td>
<td></td>
<td>Toluene, Na., 1-me-Na.</td>
<td>Auto Ignation</td>
</tr>
<tr>
<td>Woods, '89</td>
<td>JP-4</td>
<td>$n \text{-} C_{6-10,12,14}$</td>
<td>Cyclo-$C_{6,8}$</td>
<td>Toluene, 1-me-Na.</td>
<td>Atomization, swirl stabilized lab. Combustor</td>
</tr>
<tr>
<td>Schulz, '91</td>
<td>JP-8</td>
<td>$n \text{-} C_{10,12,14,16}$</td>
<td>$i \text{-} C_8$</td>
<td>$M\text{CH}^d$, Cyclo-$C_8$</td>
<td>$M\text{-}Xylene$, Na., Butylbenzene, durene$^e$, Di-me-Na.</td>
</tr>
<tr>
<td>Maurice,'00</td>
<td>JP-8</td>
<td>$n \text{-} C_{10}$</td>
<td></td>
<td>Benzene, Toluene, ETB$^f$, Na.</td>
<td>Kinetics, NOx, CO, ...</td>
</tr>
<tr>
<td>Agosta,'02</td>
<td>JP-8</td>
<td>$n \text{-} C_{10}$</td>
<td>HMN$^g$</td>
<td>MCH, Decalin</td>
<td>1-me-Na.</td>
</tr>
</tbody>
</table>

**Note:**
- a, 1-pentene is not listed for gasoline surrogate;
- b, $i \text{-} C_8$, 2,2,4-trime-pentane;
- c, 1-me-Na., 1-methyl-
- d, MCH, me-cyclohexane;
- e, durene, 1,2,4,5 tetramethylbenzene;
- f, ETB, ethylbenzene;
- g, HMN, 2,2,4,4,6,8,8-heptane-nonane.
Example of Structural Group Analysis

DEPT Spectra of Hex-12
# Suggested JP-8 Surrogates

<table>
<thead>
<tr>
<th># of Species</th>
<th>Components</th>
<th>Objective</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(n-C_{12})</td>
<td>Thermal conductivity, heat capacity, density etc.</td>
</tr>
<tr>
<td>1*</td>
<td>decalin</td>
<td>Smoke Point, PAH and soot formation</td>
</tr>
<tr>
<td>2</td>
<td>(n-C_{12}, PMB)</td>
<td>Smoke point, average volatility, flame properties</td>
</tr>
<tr>
<td>3</td>
<td>(n-C_{12}, decalin, PMB)</td>
<td>Same</td>
</tr>
<tr>
<td>6</td>
<td>(n-C_{8,12,16}, xylene, tetralin, decalin)</td>
<td>Volatility, soot formation, pool fire, kinetics</td>
</tr>
<tr>
<td>7</td>
<td>(i-C_8, n-C_{10,12,15}, Decalin, PMB, Na_)</td>
<td>Same</td>
</tr>
</tbody>
</table>

**Hex-12, based on hybrid approach**
Boiling Range for Jet A and Selected Surrogates

* Distillation created in accordance with ASTM D86.

“Hex-12” Composition

- n-Octane, 3.0%
- Xylene, 15.0%
- Decalin, 27%
- Tetralin, 13%
- Dodecane, 30%
- Cetane, 12%
Validation of Gas-Phase Kinetics for Surrogate Mixture

Kerosene surrogate Composition: 73.5 mol% n-dodecane,
5.5 mol% i-octane,
10 mol% MCH
11 mol% aromatic

height above burner, cm
Case Study: Jet Fuel Pool Fires

Surrogate formulated to match

- **Physical properties**
  - Flash point
  - Boiling point distribution

- **Chemical properties**
  - Hydrocarbon classes distribution
  - Sooting index

- **Validation**
  - Pool burning rate, transient and steady state
  - Radiative heat flux

- **Application**
  - Coupled gas phase chemistry to HACA & CFD in simulation of pool fire
Experimental Setup

C-SAFE Pool Fire Facility
- 0.30 m diameter pool (up to 1 m)
- Fully closed 4.5 x 4.5 m chamber with floor-mounted dampers for flow control.
- Steady-state and transient pool fires
- Flame shape and height using still and high-speed digital photography

Compositional Analysis
- GC/GC-MS
- $^1$H and $^{13}$C NMR

Fuel Property Measurements
- Volatility/Boiling Curve
- Smoke point

Fire Measurements
- Burning rate
- Total and radiant heat flux
- Temperature profile
- Real-time and high-speed video
Experimental Results – Steady State

Comparison of Burning Rates

Note: Literature values and correlations for jet fuel/kerosene range from 1.9 – 2.1 mm/min
Experimental Results – Steady State

Comparison of Heat Flux Measurements

Real-Time Measurements

Minute-Averaged Measurements
Experimental Results – Transient

Surrogate matches burning rate in transient pool fire

Level vs. time – slope yields average rate

Derivative of level vs. time - yields instantaneous rate
Case Study: Droptube Combustion

Surrogate formulated to match

- **Physical properties**
  - Ignition Point
  - Similar list as before

- **Chemical properties**
  - Gross soot yield, sooting index
  - Tar (Soluble Organic Fraction) speciation

- **Validation**
  - Soot mass
  - Tar characterization

- **Application**
  - Soot/tar formation & evolution
  - Evaluate soot suppressing additives in turbines.
Experimental Set-up

A monodisperse droplet stream is injected into a hot, co-flow air stream, producing a laminar diffusion flame.

At the reactor exit, the flame is quenched and the soot is collected for further analysis.
NMR Spectrum of Soot Extracts from JP8 & Surrogate

Un-combusted Oil

Collected Soot Extracts
Comparison of GC Spectrum of Soot Extracts From Surrogate and JP8

JP-8 Neat Fuel

Hex-12 Neat Fuel

JP-8 700 C

Hex-12 700 C
## Properties of Soot Aerosols Collected in Droplet Combustion

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Ignition Point</th>
<th>Gross Soot Yield, Wt.%</th>
<th>Tar yield, wt.%</th>
<th>Tar Aromatic carbon ratio, mol.%</th>
<th>Graphite Factor, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>JP-8</td>
<td>10.5</td>
<td>8.2</td>
<td>30.0</td>
<td>73.9</td>
<td>44.10</td>
</tr>
<tr>
<td>Hex-12</td>
<td>11.5</td>
<td>8.9</td>
<td>19.5</td>
<td>55.4</td>
<td>34.10</td>
</tr>
<tr>
<td>Decalin</td>
<td>9.0</td>
<td>8.9</td>
<td>13.2</td>
<td>95.5</td>
<td>72.37</td>
</tr>
<tr>
<td>i-C8/Tol.</td>
<td>5.5</td>
<td>8.8</td>
<td>8.3</td>
<td>78.3</td>
<td>53.55</td>
</tr>
<tr>
<td>n-C12</td>
<td>13.0</td>
<td>4.5</td>
<td>42.0</td>
<td>98.0</td>
<td>72.51</td>
</tr>
</tbody>
</table>
Conclusion

- A series of JP-8 surrogates have been formulated under semi-empirical approach.
  - Results show that the surrogates can match properties such as boiling range, flash point, smoke point etc.
- Preliminary kinetics modeling on surrogate is encouraging.
- JP-8 surrogate and parent fuel were tested under pool fire tests.
  - Results show that surrogate capture most global flame characteristics, such as flame height, puffing frequency, etc.
  - Surrogate also showed to match burning rate and time average heat flux of parent fuel under both steady state and transient tests.
- Under droplet combustion, surrogate showed similar ignition point and gross soot yield.
  - Analysis of collected soot samples suggest a convergence of intermediate products from surrogate and parent fuel.
Future Work

• Future efforts on surrogate formulation will focus on formalizing the structural group contribution method.

• Current surrogates neglect the effect of branching and side chain substitution.
  – Suitable candidates to represent branched paraffin are needed.

• New correlations between physical properties of interest and models to incorporate kinetics are required.
Acknowledgements

• support of C-SAFE through the ASCI program under DOE
• guidance from Prof. Eddings, Prof. Pugmire and Prof. Sarofim
• help from Mr. Overacker, Dr. Marsh, Dr. Violi, Mr. Ciro, Mr. Preciado and the combustion research group
• help from Dr. Jiang, Dr. Solum, Dr. Ma from the NMR research group
The jet fuel and surrogate pool fires were found to have similar height: 1.0m for Jet-A and 1.1m for Hex-12.

Both fires have a puffing frequency \( \sim 3 \text{Hz} \).
JP-8 Composition

Hydrocarbon Class Distribution in Jet-A (wt.%) 

- Cycloparaffins: 20%
- Naphthenes: 2%
- Alkylbenzenes: 18%
- n-Paraffins: 28%
- i-Paraffins: 29%
- Misc.: 1%
- ND: 2%

Top Three Compounds
- \( n-C_{11} \), 4.43 wt.%
- \( n-C_{10} \), 4.10 wt.%
- \( n-C_{13} \), 3.85 wt.%

GC Chromatography of JP-8

- \( n-C_9 \)
- \( n-C_{11} \)
- \( n-C_{13} \)
- \( n-C_{15} \)
- \( n-C_{17} \)
## Properties of Jet Fuels

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Formula</td>
<td>C_{9}H_{20}</td>
<td>C_{12}H_{22}</td>
<td>C_{12}H_{25}</td>
<td>C_{12}H_{24}</td>
</tr>
<tr>
<td>Density, Kg/L</td>
<td>0.76</td>
<td>0.81</td>
<td>0.79</td>
<td>0.81</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>-20</td>
<td>60</td>
<td>60</td>
<td>38</td>
</tr>
<tr>
<td>Freezing Point, °C</td>
<td>-60</td>
<td>-50</td>
<td>-38</td>
<td>-47</td>
</tr>
<tr>
<td>Net Comb. Heat, MJ/Kg</td>
<td>42.9</td>
<td>42.7</td>
<td>43.9</td>
<td>42.8</td>
</tr>
<tr>
<td>Boiling Range, °C</td>
<td>60-230</td>
<td>180-260</td>
<td>180-250</td>
<td>140-260</td>
</tr>
</tbody>
</table>
The Raman spectra of soot residues are in agreement with results from Solid State NMR, ESR and Graphite Factor tests:

1. All spectra of soot residues feature both “D-band” and “G-band” as in graphite and other graphene materials.
2. The amount of disorder-induced D-band ($\omega_D = 1200 \sim 1400 \text{ cm}^{-1}$) is ~ the same as the G-band ($\omega_G = 1580 \text{ cm}^{-1}$) derived from in plane displacement in graphite.
3. The spectra indicate that these residues are highly disordered pre-graphitic materials.
4. Under current test conditions, no significant structure differences are noted.
Ignition Delay Predictions for Jet Fuels

Equivalence ratio = 0.5, $P = 1.0$ atm.

Note: The Violi et al. mechanism has not been tuned to match this data.

Source: Montgomery, ’03
Experimental Results – Transient

Heat Transfer versus Compositional Effects

![Graph showing regression rate versus volume loss for Jet-A and Norpar-15.]
Tailored Surrogates for Transient Tests

Smoke Point (SP) Variation in Batch Distillation Tests

New surrogates are designed to address the composition change during a typical batch pool fire test.

- The rapid decrease of aromatic carbon ratio with fuel consumption in Hex-12 explain the dramatic increase of smoke point during the batch test.
- SP of Hex-14b could be contained in the range of 23.5 ~ 30 mm during most of the process.
Experimental Results - Transient

Effect of Data Sampling Rate

Regression Rate, mm/min

Burning Time, minute

○ 5 min.
● 10 min.
▲ 15 min.
▼ 20 min.
△ 30 min.
Experimental Results - Transient

Narrow versus Wide Boiling Range Mixtures for Transient and Steady State Pool Fires
### Multiple Solutions for the Surrogates

#### Fuel Properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>Jet-A</th>
<th>Hex-12</th>
<th>Hex-12a</th>
<th>Hex-12b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smoke Point, mm</td>
<td>24.5</td>
<td>25.1</td>
<td>25.8</td>
<td>26.4</td>
</tr>
<tr>
<td>MW, g/mol</td>
<td>167.0</td>
<td>152.2</td>
<td>154.3</td>
<td>153.9</td>
</tr>
<tr>
<td>Density, g/mL</td>
<td>0.805</td>
<td>0.818</td>
<td>0.814</td>
<td>0.814</td>
</tr>
<tr>
<td>VABP, °C</td>
<td>210.7</td>
<td>215.7</td>
<td>214.6</td>
<td>213.7</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>37.8</td>
<td>41.3</td>
<td>40.7</td>
<td>40.6</td>
</tr>
<tr>
<td>Latent Heat, kJ/kg</td>
<td>254.6</td>
<td>281.8</td>
<td>277.4</td>
<td>279.5</td>
</tr>
<tr>
<td>Combustion Heat, MJ/kg</td>
<td>44.9</td>
<td>44.6</td>
<td>44.6</td>
<td>44.6</td>
</tr>
</tbody>
</table>

#### Surrogate Compositions (mol%)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Hex-12</th>
<th>Hex-12a</th>
<th>Hex-12b</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Octane</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>m-xylene</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Tetralin</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Decalin</td>
<td>27</td>
<td>27</td>
<td>31</td>
</tr>
<tr>
<td>PMB</td>
<td></td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>2-Me-Na</td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>30</td>
<td>30</td>
<td>32</td>
</tr>
<tr>
<td>n-cetane</td>
<td>12</td>
<td>12</td>
<td>12</td>
</tr>
</tbody>
</table>

---

*a: Mass-weighted average value.
*b: Vapor Antoine point.
*c: Latent heat of vaporization.
Fuel Burning Rate Study

**JET-A: Batch vs. Steady-State**

- The steady-state burning rate of Jet-A, 2.07mm/min is close to the prediction value, the literature value and the peak burning rate in transient tests.
- Both steady-state & transient tests with Norpar-15 show relative constant rate of burning.

**Batch Pool Fires**

- With JET-A, burning rate changes rapidly in batch tests, peak rate is twice as high as average rate.
- With Norpar-15, burning rate is constant as expected.
Fuel Burning Rate Study

Postulation of burning rate variation in transient JET-A pool fire

- Thermal equilibrium and possible composition change in the induction period are often used to explain the higher burning rate in this period and constant rate in the rest
- Norpar-15 tests don’t support thermal equilibrium idea
- ‘Quasi steady-state’ may not exist in transient pool fire
- Measurement resolution is important

Change of Fuel Composition in Transient Pool Fire

GC/MS Analyses of Liquid Fuel in a Batch Experiment

- Light components are preferentially destroyed
  - compounds with boiling points below \( n\text{-C12} \) are depleted as the burn progresses
  - naphthalenes might be enriched though light aromatics are destroyed

<table>
<thead>
<tr>
<th>Sample</th>
<th>Toluene /Na.\textsuperscript{i}</th>
<th>Na./Me-Na.\textsuperscript{iii}</th>
<th>( n\text{-C12}/n\text{-C17} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jet-A_B-0</td>
<td>1.5</td>
<td>0.4</td>
<td>7.7</td>
</tr>
<tr>
<td>Jet-A_B_95</td>
<td>0.0\textsuperscript{ii}</td>
<td>0.2</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Note: \textsuperscript{i} Na. is Naphthalene; \textsuperscript{ii} Toluene peak is non-detectable in this sample; \textsuperscript{iii} Me-Na. is mixture of 1-Me-naphtahlene, 2-Me-naphthalene and isomers of dimethyl naphthalene
Change in Paraffins?

13C NMR Spectrum of Liquid Fuel in Batch Experiment

\[ \cdots C_\varepsilon - C_\varepsilon - C_\delta - C_\gamma - C_\beta - C_\alpha \]

(Assignment scheme for \( n \)-C12)

\( \alpha_C / \varepsilon_C \) decreases with burning implying that the aliphatic chain length increases as observed in GC-MS data.

Less cyclic aliphatics are found in burned oil samples, same trend is found in 1H NMR spectra.
Change in Aromatics?

No major difference is found

- Aromatics content increases slightly with burning
- Indan like compounds increase as much as 60%

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aro. C, %</th>
<th>Aro. H, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jet-A_B-0</td>
<td>10.6</td>
<td>3.3</td>
</tr>
<tr>
<td>Jet-A_B-39</td>
<td>11.4</td>
<td>3.3</td>
</tr>
<tr>
<td>Jet-A_B-95</td>
<td>12.2</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Note: i- Aro. C % is the ratio of aromatic carbon atoms to total carbon atoms; ii- Aro. H % is the ratio of aromatic hydrogen atoms to total hydrogen atoms.
Change in Selected Fuel Properties

- D86 distillation tests agree with GC-MS analysis
- Volatility of burned-off oil is lower than initial JET-A

<table>
<thead>
<tr>
<th>Sample</th>
<th>API, °C</th>
<th>MW, g/mol</th>
<th>Flash Point, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jet-A_B-0</td>
<td>43.3</td>
<td>164.2</td>
<td>38.2</td>
</tr>
<tr>
<td>Jet-A_B-39</td>
<td>42.2</td>
<td>171.8</td>
<td>52.0</td>
</tr>
<tr>
<td>Jet-A_B-95</td>
<td>41.3</td>
<td>177.9</td>
<td>54.9</td>
</tr>
</tbody>
</table>

Note: i- Molecular weight (MW) is estimated; ii- Flash point is estimated.
Prediction of Composition Change as Distillation?

39% v. off
Top – Pool Fire Pan

80% v. off
Top – Pool Fire Pan

Batch Pool Fire vs. Boil-off Experiments

- Composition changes in both tests show similar trends
- Large conc. & temp. gradients exist in fire tests: well-mixed condition exists in distillation
- Fuel at bottom of pan changes more slowly than at the top: molecular diffusion & convection are important factors in fire tests

Batch pool fire tests appear more complicated than distillation process
Cost of chemicals for bench scale experiments

Only **three** *n*-paraffins under $50/L;

Only **one** branched paraffins under $100/L

<table>
<thead>
<tr>
<th>Normal Paraffins</th>
<th>Cost/Liter</th>
<th>Branched Paraffins</th>
<th>Cost/Liter</th>
<th>Cyclo Paraffins</th>
<th>Cost/Liter</th>
<th>Aromatics</th>
<th>Cost/Liter</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>n</em>-C&lt;sub&gt;7&lt;/sub&gt;</td>
<td>$24</td>
<td><em>i</em>-C&lt;sub&gt;7&lt;/sub&gt;</td>
<td>$11k</td>
<td><em>MCH</em></td>
<td>$69</td>
<td><em>Benzene</em></td>
<td>$18</td>
</tr>
<tr>
<td><em>n</em>-C&lt;sub&gt;10&lt;/sub&gt;</td>
<td>$118</td>
<td><em>i</em>-C&lt;sub&gt;8&lt;/sub&gt;</td>
<td>$12</td>
<td><em>Cyclo-C&lt;sub&gt;8&lt;/sub&gt;</em></td>
<td>$135</td>
<td><em>m-cymene</em></td>
<td>&gt;$100k</td>
</tr>
<tr>
<td><em>n</em>-C&lt;sub&gt;11&lt;/sub&gt;</td>
<td>$300</td>
<td><em>i</em>-C&lt;sub&gt;9&lt;/sub&gt;</td>
<td>$25k</td>
<td><em>Decalin</em></td>
<td>$52</td>
<td><em>1-phenyldecane</em></td>
<td>$2k</td>
</tr>
<tr>
<td><em>n</em>-C&lt;sub&gt;12&lt;/sub&gt;</td>
<td>$143</td>
<td><em>i</em>-C&lt;sub&gt;12&lt;/sub&gt;</td>
<td>$12k</td>
<td><em>Cyclo-C&lt;sub&gt;10&lt;/sub&gt;</em></td>
<td>$25k</td>
<td><em>Naphthalene</em></td>
<td>$21</td>
</tr>
<tr>
<td><em>n</em>-C&lt;sub&gt;16&lt;/sub&gt;</td>
<td>$143</td>
<td>HMN</td>
<td>$411</td>
<td><em>Cyclo-C&lt;sub&gt;12&lt;/sub&gt;</em></td>
<td>$100</td>
<td><em>Anthracene</em></td>
<td>$240</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><em>Phenanthrene</em></td>
<td>$340</td>
</tr>
</tbody>
</table>
## Fuel components available for reproducible pilot-scale testing

<table>
<thead>
<tr>
<th>Parent Fuel</th>
<th>Characteristics/Description</th>
<th>Applications</th>
<th>Cost</th>
</tr>
</thead>
</table>
| **Gasoline** | *Known octane # gasoline blends w/o additive or oxygenates*  
PRF’s or toluene standardized fuel | Engine Test  
Octane # | Very low high |
| **Diesel** | U-15, cetane # 18.7, ~75% paraffin and ~25% aromatics, from 154~271 °C  
T-22, cetane # 74.8, ~50% paraffin, ~40% kerosene and ~10% aromatics, from 172 ~ 278°C | Engine Test | high low |
| **Jet Fuel** | Norpar series, for normal paraffins from C11 to C16  
Isopar series, for branched paraffins from 98 ~ 329°C (C_{11}~C_{18} ?)  
Aromatic series for alkylbenzenes within 154 ~ 293°C | Pool Fire,  
Ignition delay,  
Engine test,  
Flame properties,  
Stability | ~$300 (55 gal.) |

Norpar-15 = 34.4% n-C_{14} + 49% n-C_{15} + 13.5% n-C_{17} + 3.1% n-C_{17+}
Group Analysis of JP-8

DEPT Spectra of JP-8
## Smoke Point Projection w/ SOL Approach

<table>
<thead>
<tr>
<th>Compound</th>
<th>A6</th>
<th>A4</th>
<th>A2</th>
<th>N6</th>
<th>N5</th>
<th>N4</th>
<th>N3</th>
<th>N2</th>
<th>N1</th>
<th>R</th>
<th>Br</th>
<th>Me</th>
<th>IH</th>
<th>AA</th>
<th>SP</th>
<th>SP*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-dimethylpentane</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>7</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>109</td>
<td>117</td>
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<tr>
<td>isooctane</td>
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<td>0</td>
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<td>3</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>90</td>
<td>86</td>
<td>8</td>
<td>7.8</td>
<td>8</td>
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<tr>
<td>n-propylbenzene</td>
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<td>0</td>
<td>0</td>
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<td>0</td>
<td>0</td>
<td>42</td>
<td>38</td>
<td>8</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>
Formulation Methodology

Empirical Approach

- The basis is species concentration profile of parent fuel. The Selection of candidate compounds is often arbitrary.
- Mixture properties are estimated with empirical correlations.
- Example of estimation equation: Closed cup flash point, API

\[ T_{FP} = 0.68 \times T_{10\%} - 109.6, \]

where \( T_{10\%} \) is the temp. at 10 v.\% recovery in ASTM D86 test

Pros & Cons

- Easy to apply
- Available empirical correlations
- Has most available references
- Trial and error based
- Often inaccurate representation of HC’s in parent fuel
- Not suitable for use in multiple applications
Structural Group Contribution Approach

- Fuel properties are determined by its structure.
  - Surrogates could be proposed by analyzing the existing functional groups in parent fuel and their correlations with fuel properties.

- The $i$th properties ($P_i$) of surrogate may be predicted as
  $$P_i = |A_{ij}| \times |f(Y_j)|$$
  Where, $A_{ij}$ is the contribution on $P_i$ from the $j$th group in the surrogate, and $Y_j$ is the mole fraction of group $j$ in the surrogate.

- Example of group classifications: Quann et al, 1992 proposed Structural Orientation Lumping method to describe compounds found in crude oil with 22 structural increments.

- Example of estimation equation: boiling point, Joback, 1987
  $$T_b = 198 + \sum N_k \times T_{bk}$$

Pros & Cons

- Accurate representation of real fuel structure
- Systematically study the effect of each group on various properties
- Easily adapt to change in parent fuel composition
- Lack of model to integrate physical property estimation and chemical kinetics simulation
Hybrid: Semi-empirical Approach

- The basis is still the species concentration profile of the parent fuel.
  - Set up a surrogate candidates pool from the basis;
  - filter candidates with quantitative constraints from prior formulation criteria;
  - propose surrogate formula and estimate properties from both empirical correlation and group contribution theory;
  - tailor the surrogate fuel composition towards specific application.

- Candidate compounds
  - n-paraffins
    - decane, dodecane, cetane, ...
  - i-paraffins
    - iso-octane, iso-cetane (2,2,4,4,6,8,8 heptamethyl nonane), ...
  - Napthenes (cycloaliphatic, alicyclic)
    - Methyl cyclohexane, decalin, tetralin, ...
  - Aromatics
    - Benzene, alkylated benzenes, napthalenes, ...

- Constraints
  - boiling range, flash point, $T_{10\%}$, $T_{FBP}$, smoke point, density, latent heat, etc.

- Example of surrogate: Hex-12