Property Measurement for Fuel Research: Physical Authenticity of Surrogates

Thomas J. Bruno
Physical and Chemical Properties Division
National Institute of Standards and Technology
Boulder, CO
Why Surrogates?
We all know the reasons-

• Aviation fuels are made of hundreds of components
  – Must meet general specifications,
    but an infinite number of combinations can do so
Why Surrogates?

We all know the reasons—

• Aviation fuels are made of hundreds of components
  – Must meet general specifications, but an infinite number of combinations can do so

For well controlled measurements and modeling, a more defined composition is required.
Why Surrogates?
We all know the reasons-

• Aviation fuels are made of hundreds of components
  – Must meet general specifications, but an infinite number of combinations can do so

For well controlled measurements and modeling, a more defined composition is required.
- repeatability
- tractability
“Surrogate” means different things to different people
“Surrogate” means different things to different people

Physical surrogate - property explicit

Chemical surrogate - moiety explicit
“Surrogate” means different things to different people

Operational Surrogates:
kinetics
flame characteristics
safety characteristics
“Surrogate” means different things to different people

Thermophysical property predictive surrogates
The (un)Holy Matrimony of Measurement and Theory
Data go in here

Model comes out here
Clearly, the most important role of the surrogate mixture is to fulfill the intended purpose:

- TSI,
- Kinetics,
- Pool fires,
- Thermophysical properties,
- what have you
• Beyond this primary role, we all desire our surrogate mixtures to be authentic: 

\textit{physicochemically}
• Beyond this primary role, we all desire our surrogate mixtures to be authentic:

\[ \text{physicochemically} \]

Physical Properties
\[ \rho, \eta, \lambda, \text{vle, ss, …} \]
Beyond this primary role, we all desire our surrogate mixtures to be authentic:

\textit{physicochemically}

\begin{itemize}
  \item Physical Properties
    \(\rho, \eta, \lambda, \text{vle}, \text{ss}, \ldots\)
  \item Chemical Properties:
    \text{group moieties-}
\end{itemize}
Beyond this primary role, we all desire our surrogate mixtures to be authentic: 

physicochemically

Physical Properties
\[ \rho, \eta, \lambda, \text{vle}, \text{ss}, \ldots \]

Chemical Properties:
- group moieties-

\[ \text{Chemical Properties:} \]

\[ \text{group moieties-} \]
For moiety family evaluation and analysis:

\(^1\)H, \(^{13}\)C NMR

Happily, I have one on order!

Multinuclear probe

Cryoprobe: \(^1\)H, \(^{13}\)C, \(^{19}\)F, \(^{31}\)P

Cross polarization MAS solids probe

Diffusion probe
Beyond this primary role, we all desire our surrogate mixtures to be authentic:

\[ \text{physicochemically} \]

**Physical Properties**
- \( \rho, \eta, \lambda, \text{vle}, \text{ss}, \ldots \)

**Chemical Properties:**
- group moieties-
Can we use any of the thermophysical properties for this?

• Density, $\rho$ (PVT surface), for a kerosene
  – write in 0.85 g/mL and you’ll be close

• Speed of sound, heat capacities, etc., change by a few %

• Viscosity and thermal conductivity change by 4 %

• In contrast, volatility changes appreciably with composition
The ADC:
–true thermodynamic state points
–consistent with historical data
–temperature, volume and pressure measurements of low uncertainty
–qualitative, quantitative and trace analysis of fractions
–energy content of each fraction
–corrosivity of each fraction
–greenhouse gas output of each fraction
–thermal and oxidative stability of the fluids

Apparatus for ADC.
So what will the ADC Provide *(that’s practical)*?

• **Initial boiling temperature, IBT**
  – thermodynamically consistent
  – theoretically meaningful

• **Distillation Curves**
  – thermodynamically consistent
  – theoretically meaningful
Let’s look at some surrogate mixtures, ignoring for the moment, the underlying motivation:

• Simple
  – 2 or 3 components

• Complex
  – More than 3 components
Let’s look at some surrogate mixtures, ignoring for the moment, the underlying motivation:

• Simple
  – 2 or 3 components

• Complex
  – More than 3 components

• With the nomenclature used in the literature and at past Fuel Summits
Let’s look at some surrogate mixtures, ignoring for the moment, the underlying motivation:

- **Simple**
  - 2 or 3 components

- **Complex**
  - More than 3 components

- With the nomenclature used in the literature and at past Fuel Summits
  - Older mixtures, to develop the methodology
Simple:

- **Surrogate A:**
  - 60% n-decane + 20% methylcyclohexane + 20% toluene
- **Surrogate B:**
  - 60% n-decane + 20% methylcyclohexane + 20% o-xylene
- **Surrogate C:**
  - 60% n-dodecane + 20% methylcyclohexane + 20% o-xylene
- **Surrogate F:**
  - 60% n-decane + 20% butylcyclohexane + 20% butylbenzene
- **Surrogate G:**
  - 60% n-decane + 40% iso-octane
- **Aachen Surrogate:**
  - 80% n-decane + 20% 1,2,4-trimethylbenzene
- **Modified Aachen Surrogate:**
  - 80% n-dodecane + 20% 1,2,4-trimethylbenzene
Complex:

- **Utah Surrogate:**
  - 30% n-dodecane + 20% n-tetradecane + 20% methylcyclohexane + 15% o-xylene + 10% iso-octane + 5% tetralin

- **Drexel Surrogate 1:**
  - 36% isocetane + 26% n-dodecane + 14% methylcyclohexane + 18% 1-methylnaphthalene + 6% decalin

- **Drexel Surrogate 2:**
  - 43% n-dodecane + 27% isocetane + 15% methylcyclohexane + 15% 1-methylnaphthalene

- **Schulz Surrogate:**
  - 21% n-dodecane + 16.2% n-decane + 15.6% n-tetradecane + 10.2% n-hexadecane + 5.7% iso-octane + 5.1% methylcyclohexane + 4.7% cyclo-octane + 4.6% butylbenzene + 4.5% m-xylene + 4.4% 1,2,4,5-tetramethylbenzene + 4.1% tetralin + 3.9 % 1-methylnaphthalene

- **Surrogate 1:**
  - 30% n-dodecane + 20% n-tetradecane + 20% methylcyclohexane + 15% m-xylene + 10% iso-octane + 5% tetralin

- **Surrogate 3:**
  - 73.5% n-dodecane + 10% methylcyclohexane + 10% toluene + 5.5% iso-octane + 1% benzene

- **Violi Surrogate:**
  - 20% n-tetradecane + 25% n-dodecane + 25% n-decane + 20% toluene + 5% methylcyclohexane + 5% iso-octane
Compare these with “real” fuel behavior

• IBT departure
  – But still, it’s only one point
  – The rest of the curve can do funny things

• Total curve departure
  – On the basis of objective, point by point metrics

• Total curve shape
  – Subjective and objective descriptors
Jet A, S-8

Temperature (°C) vs. Volume Fraction, %
Jet A, S-8

Made from 5 “typical” Jet-A samples by Tim “Mr. Average”
Jet A, S-8

Within spec, but unusual
The Simple Surrogates:

“average”

“unusual”
The Complex Surrogates:
Point by point evaluations:
A Surrogate Mixture
A Surrogate Mixture

Jet-A-4658, “Mr. Average”

Temperature, $T_k$ (°C)

A Surrogate Mixture

Distillate Volume Fraction
Metric $l = \frac{1}{n} \sum_{i=1}^{n} \left| T_{\text{Jet-A-4658}}^i - T_{\text{surrogate}}^i \right|$
Metric 2 = \( \frac{1}{n} \sum_{i=1}^{n} \left| \frac{T^i_{\text{Jet-A-4658}} - T^i_{\text{surrogate}}}{T^i_{\text{Jet-A-3638}}} \right| \)
Metric 3 = \frac{1}{n} \sum_{i=1}^{n} \text{Min} \left( |T_{\text{Jet-A-4658}}^{i} - T_{\text{Surrogate}}^{i}|, |T_{\text{Jet-A-3638}}^{i} - T_{\text{Surrogate}}^{i}| \right)
### Point by Point Evaluation Results:

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Surrogate A</th>
<th>Surrogate B</th>
<th>Surrogate C</th>
<th>Surrogate D</th>
<th>Surrogate E</th>
<th>Surrogate F</th>
<th>Aachen</th>
<th>Modified Aachen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metric 1</td>
<td>69.20</td>
<td>64.00</td>
<td>32.40</td>
<td>44.90</td>
<td>66.50</td>
<td>49.30</td>
<td>13.50</td>
<td></td>
</tr>
<tr>
<td>Metric 2</td>
<td>4.25</td>
<td>3.77</td>
<td>2.20</td>
<td>2.36</td>
<td>4.06</td>
<td>2.63</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>Metric 3</td>
<td>50.26</td>
<td>45.11</td>
<td>14.85</td>
<td>26.01</td>
<td>47.58</td>
<td>30.34</td>
<td>4.51</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Utah</th>
<th>Drexel 1</th>
<th>Drexel 2</th>
<th>Schulz</th>
<th>Surrogate 1</th>
<th>Surrogate 3</th>
<th>Violi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metric 1</td>
<td>31.50</td>
<td>10.50</td>
<td>10.70</td>
<td>10.10</td>
<td>31.20</td>
<td>21.00</td>
<td>28.90</td>
</tr>
<tr>
<td>Metric 2</td>
<td>2.39</td>
<td>0.70</td>
<td>0.70</td>
<td>0.80</td>
<td>2.39</td>
<td>1.46</td>
<td>2.21</td>
</tr>
<tr>
<td>Metric 3</td>
<td>23.33</td>
<td>9.82</td>
<td>9.02</td>
<td>5.90</td>
<td>23.51</td>
<td>10.51</td>
<td>20.06</td>
</tr>
</tbody>
</table>
The winners are:

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Surrogate A</th>
<th>Surrogate B</th>
<th>Surrogate C</th>
<th>Surrogate F</th>
<th>Surrogate G</th>
<th>Aachen</th>
<th>Modified Aachen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metric 1</td>
<td>69.20</td>
<td>64.00</td>
<td>32.40</td>
<td>44.90</td>
<td>66.50</td>
<td>49.30</td>
<td>13.50</td>
</tr>
<tr>
<td>Metric 2</td>
<td>4.25</td>
<td>3.77</td>
<td>2.20</td>
<td>2.36</td>
<td>4.06</td>
<td>2.63</td>
<td>0.60</td>
</tr>
<tr>
<td>Metric 3</td>
<td>50.26</td>
<td>45.11</td>
<td>14.85</td>
<td>26.01</td>
<td>47.58</td>
<td>30.34</td>
<td>4.51</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Utah</th>
<th>Drexel 1</th>
<th>Drexel 2</th>
<th>Schulz</th>
<th>Surrogate 1</th>
<th>Surrogate 3</th>
<th>Violi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metric 1</td>
<td>31.50</td>
<td>10.50</td>
<td>10.70</td>
<td>10.10</td>
<td>31.20</td>
<td>21.00</td>
<td>28.90</td>
</tr>
<tr>
<td>Metric 2</td>
<td>2.39</td>
<td>0.70</td>
<td>0.70</td>
<td>0.80</td>
<td>2.39</td>
<td>1.46</td>
<td>2.21</td>
</tr>
<tr>
<td>Metric 3</td>
<td>23.33</td>
<td>9.82</td>
<td>9.02</td>
<td>5.90</td>
<td>23.51</td>
<td>10.51</td>
<td>20.06</td>
</tr>
</tbody>
</table>
Shape and Slope Evaluations:

• Go – No-Go test
  – Eliminate flat and bimodal curves
Curve is dead flat
Curve is bimodal
Shape and Slope Evaluations:

• Go – No-Go test
  – Eliminate flat and bimodal curves

• Shape Rating (on simple linear model: $y = mx + b$)
  – Linear normal probability plot
  – Residual plot with 2 nodes
  – Residual magnitude less than 2 °C
Shape and Slope Evaluations:

- **Go – No-Go test**
  - Eliminate flat and bimodal curves

- **Shape Rating (on simple linear model: \( y = mx + b \))**
  - Linear normal probability plot
  - Residual plot with 2 nodes
  - Residual magnitude less than 2 °C

Because this is how Jet-A, JP-8 behaves
Shape and Slope Evaluations:

• Go – No-Go test
  – Eliminate flat and bimodal curves

• Shape Rating (on simple linear model: \( y = mx + b \))
  – Linear normal probability plot
  – Residual plot with 2 nodes
  – Residual magnitude less than 2 °C

• Slope Departure
  – Based on a simple linear model: \( y = mx + b \)
Simple Linear Model: \( y = mx + b \)

\[ m = 0.70 \]

\[ m = 0.43 \]
Simple Linear Model: $y = mx + b$

$m = 0.70$

$m = 0.43$

A minor criteria; high variability
Now, add shape and slope evaluation:

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Surrogate A</th>
<th>Surrogate B</th>
<th>Surrogate C</th>
<th>Surrogate F</th>
<th>Surrogate G</th>
<th>Aachen</th>
<th>Modified Aachen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metric 1</td>
<td>69.20</td>
<td>64.00</td>
<td>32.40</td>
<td>44.90</td>
<td>66.50</td>
<td>49.30</td>
<td>13.50</td>
</tr>
<tr>
<td>Metric 2</td>
<td>4.25</td>
<td>3.77</td>
<td>2.20</td>
<td>2.36</td>
<td>4.06</td>
<td>2.63</td>
<td>0.60</td>
</tr>
<tr>
<td>Metric 3</td>
<td>50.26</td>
<td>45.11</td>
<td>14.85</td>
<td>26.01</td>
<td>47.58</td>
<td>30.34</td>
<td>4.51</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Slope Validity</th>
<th>Poor</th>
<th>Good</th>
<th>Poor</th>
<th>Invalid</th>
<th>Poor</th>
<th>Invalid</th>
<th>Good</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>0.70</td>
<td>0.42</td>
<td>0.99</td>
<td>NA</td>
<td>0.66</td>
<td>NA</td>
<td>0.25</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Utah</th>
<th>Drexel 1</th>
<th>Drexel 2</th>
<th>Schulz</th>
<th>Surrogate 1</th>
<th>Surrogate 3</th>
<th>Violi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metric 1</td>
<td>31.50</td>
<td>10.50</td>
<td>10.70</td>
<td>10.10</td>
<td>31.20</td>
<td>21.00</td>
<td>28.90</td>
</tr>
<tr>
<td>Metric 2</td>
<td>2.39</td>
<td>0.70</td>
<td>0.70</td>
<td>0.80</td>
<td>2.39</td>
<td>1.46</td>
<td>2.21</td>
</tr>
<tr>
<td>Metric 3</td>
<td>23.33</td>
<td>9.82</td>
<td>9.02</td>
<td>5.90</td>
<td>23.51</td>
<td>10.51</td>
<td>20.06</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Slope Validity</th>
<th>Poor</th>
<th>Invalid</th>
<th>Invalid</th>
<th>Fair</th>
<th>Good</th>
<th>Invalid</th>
<th>Fair</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>0.97</td>
<td>NA</td>
<td>NA</td>
<td>0.97</td>
<td>0.99</td>
<td>NA</td>
<td>0.99</td>
</tr>
</tbody>
</table>
Overall Ratings:

• Modified Aachen Surrogate:
  – 80% n-dodecane + 20% 1,2,4-trimethylbenzene

• Schulz Surrogate:
  – 21% n-dodecane + 16.2% n-decane + 15.6% n-tetradecane + 10.2% n-hexadecane + 5.7%
  isoctane + 5.1% methylcyclohexane + 4.7% cyclooctane + 4.6% butylbenzene + 4.5% m-xylene + 4.4% 1,2,4,5-tetramethylbenzene +
  4.1% tetralin + 3.9 % 1-methylnaphthalene
Can we use our modeling approach in reverse, to design a surrogate?
Helmholtz Free Energy EOS:

\[ a = a^{\text{idsol}} + a^{\text{excess}}, \]

\[ a^{\text{idsol}} = \sum_{j=1}^{m} x_i \left[ a_i^0 (\rho, T') + a_i^r (\delta, \tau) + RT \ln x_i \right], \]

\[ a^{\text{excess}} = RT \sum_{i=1}^{m-1} \sum_{j=i+1}^{m} x_i x_j F_{ij} \sum_k N_k \delta^{dk} \tau^{t_k} \exp(-\delta^{l_k}), \]

Complex mixtures are represented by surrogates

Surrogate components each have an EOS

We can predict the composition of the vapor and liquid phases as a function of T and P: VLE
Can we use our modeling approach in reverse, to design a surrogate?

- Limit ourselves to a simple surrogate mixture (2 - 3 components only)

- Limit ourselves to components on hand or easily obtained

- Properties to consider:
  - ADC, ρ, ss
Result: the Huber-Bruno Surrogate:

After 30 iterations:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-dodecane</td>
<td>0.31</td>
</tr>
<tr>
<td>n-tetradecane</td>
<td>0.38</td>
</tr>
<tr>
<td>1,2,4-trimethylbenzene</td>
<td>0.31</td>
</tr>
</tbody>
</table>
Result: the Huber-Bruno Surrogate:

After 30 iterations:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-dodecane</td>
<td>0.31</td>
</tr>
<tr>
<td>n-tetradecane</td>
<td>0.38</td>
</tr>
<tr>
<td>1,2,4-trimethylbenzene</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Easy to mix and measure!
Predicted ADC:

![Graph showing predicted ADC vs distillate volume fraction]

- Red line: Huber-Bruno Surrogate, model prediction

Axes:
- Y-axis: Temperature $T_k$ °C
- X-axis: Distillate Volume Fraction

Values:
- Temperature range: 190 to 260 °C
- Distillate Volume Fraction range: 0.0 to 1.0
Now, mix it up and measure it:
Now compare with Jet-A-4658:
Now compare with Jet-A-4658:

All are within combined experimental uncertainty.
Evaluations, with H-B:

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Surrogate A</th>
<th>Surrogate B</th>
<th>Surrogate C</th>
<th>Surrogate F</th>
<th>Surrogate G</th>
<th>Aachen</th>
<th>Modified Aachen</th>
<th>Huber-Bruno</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metric 1</td>
<td>69.20</td>
<td>64.00</td>
<td>32.40</td>
<td>44.90</td>
<td>66.50</td>
<td>49.30</td>
<td>13.50</td>
<td>2.70</td>
</tr>
<tr>
<td>Metric 2</td>
<td>4.25</td>
<td>3.77</td>
<td>2.20</td>
<td>2.36</td>
<td>4.06</td>
<td>2.63</td>
<td>0.60</td>
<td>0.16</td>
</tr>
<tr>
<td>Metric 3</td>
<td>50.26</td>
<td>45.11</td>
<td>14.85</td>
<td>26.01</td>
<td>47.58</td>
<td>30.34</td>
<td>4.51</td>
<td>2.69</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Slope Validity</th>
<th>poor</th>
<th>good</th>
<th>poor</th>
<th>invalid</th>
<th>poor</th>
<th>invalid</th>
<th>good</th>
<th>excellent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>0.70</td>
<td>0.42</td>
<td>0.99</td>
<td>NA</td>
<td>0.66</td>
<td>NA</td>
<td>0.25</td>
<td>0.68</td>
</tr>
</tbody>
</table>
Going along for the ride:

<table>
<thead>
<tr>
<th>Property</th>
<th>Jet-A-4658</th>
<th>H-B Surrogate</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW</td>
<td>156.9</td>
<td>158.4</td>
</tr>
<tr>
<td>H/C</td>
<td>1.87</td>
<td>1.89</td>
</tr>
</tbody>
</table>
Summary:

- **Evaluation strategy for surrogate mixture authenticity**
  - The technique is more important than the specific results

- **Used in reverse, the strategy can be used to design surrogate mixtures**
  - Can extend objective function to include operational properties
    - CN, TSI, etc., in addition to ADC, ρ, ss.
  - Again, the technique is more important than the specific result: the H-B surrogate mixture
Future Work

• Make the existing Jet-AJP-8 model “tunable”

• Add additional properties

• Add the chemical in physicochemical
  • With the new toy
Acknowledgements:

• AFOSR financial support
  – Julian Tishkoff
• Beverly Smith
  • University of Oregon
• Marcia Huber
• Tim Edwards