Flow Reactors for Validation Data Base Development

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Generation of Comprehensive Surrogate Kinetic Models and Validation Databases for Simulating Large Molecular Weight Hydrocarbon Fuels

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In This Presentation

• Describe Variable Pressure Flow Reactor (VPFR) Experiment, Demonstrate principal of operation, type of data, analysis methods, and utility of Variable Pressure Flow Reactor (VPFR) Results in building surrogate models

• Show exemplar methodologies of concepts for building surrogate validation databases
  – Use surrogate database for gasoline model development as an example

• Emphasize additional complexities of building data base and modeling concepts for gas turbine fuels
Ideal Plug Flow Reactor Assumptions

\[- D \rho \frac{d^2(Y)}{dx^2} + \rho u \frac{d(Y)}{dx} + \dot{w} = 0 \]
\[- \lambda \frac{d^2T}{dx^2} + \rho u c_p \frac{dT}{dx} + \dot{w} Q = 0 \]

- Theoretically, the solution of the governing equations is an initial-value problem
  - Any single matching point of experiment and theory should be equivalent
- Where is “time = 0” for the problem? Many use the “instantaneous” mixing location” as a location of t=0 for comparison with predictions – this assumption is discussed in depth later
Princeton Variable Pressure Flow Reactor

Typical experimental approaches:
- Species time history as a function of initial conditions.
- Species distributions as a function of initial conditions at a constant residence time.
- Either of previous experiments, with perturbations by other components.
- Near-adiabatic or isothermal (high dilution) operation.

Reactor Duct Material: Fused Silica
Pressure: 0.2 - 20 atm
Temperature: 300 - 1200 K

Reactor Section Dia.: 10 cm
Mass Flow rate: 10 - 30 grams/sec
Residence Time: 0.015 - 5 sec
Liquid Fuel Metering and Vaporization System

- Need to improve liquid fuel delivery vaporization and sampling system heating to conduct experiments with carbon number compounds greater than C_{12}-C_{14}.
Measured Axial Flow Velocity

Velocity is normalized by the calculated plug flow velocity in the constant area section of the reactor tube.

Relate distance to time by effective area function vs distance and reactor volumetric flow rate.

Effective area versus distance from injection to sampling point.
CO and O$_2$ Profiles, “Reacting” Case

- The reaction rate of “dry” CO/O$_2$ at these conditions is extremely slow.

- These data demonstrate the ability to achieve constant composition and reaction temperature over a wide range of relative reaction time scales.
VPFR Sample System Schematic
(Double lines represent heated Teflon tubing)

- Sample probe
- Teflon diaphragm pump
- Multiport sampling valves
- Back pressure regulator
- Exhaust
- Needle valve
- Calibration gases
- Flow controller
- Flow meter
- FTIR cell
- Cold trap
- H₂
- O₂
- CO₂
- CO
- Exhaust
Example, Toluene Oxidation Data (and Modeling)

- Reactivity behavior in the VPFR captures the lack of NTC chemistry experimentally observed (slightly higher reactivity as temperature increases)
- Species time histories for major species profiles are well reproduced. Agreement for intermediates (benzene, formaldehyde, not shown) is less satisfactory
- Further work needs to be done to determine alternative channels for these species
- Refinements important to other aromatic oxidation model developments
Comparing Experimental Data and Predictions

As important as conducting well defined experiments is the method in which computational results are compared with the observations

- **Time Shifting**
  - Experimental data is “time-shifted” to match a well defined observation in experiment and prediction (e.g. maximum gradient, maximum concentration, etc.)
  - Applies in cases where little reaction in the mixing region and detailed post-induction prediction are insensitive to initial chemical perturbations of intermediates present

- **Absolute time scale**
  - Computational time is zero at the mixing location
  - Can yield erroneous interpretation of results if perturbations exist in the mixing region

- **Initialization** (i.e. “Initial Conditioning”)
  - Applies in all cases, even if significant quantities of the initial reactants are consumed and/or perturbations from the intermediates formed in the mixing region are observed to affect downstream, post-induction chemistry
  - Uses measured stable species to compute full initialization of all species at an arbitrary axial location
Initial Mixing Effect on Overall Reaction Time

- Model reactor system as psr+pfr, i.e. \( \tau_{\text{reac}} = \tau_{\text{psr}} + \tau_{\text{pfr}} \)
- PSR-PFR simulation of \( \tau_{\text{reac}} \) for CO observations at different \( \tau_{\text{psr}} \) at 1165 K (Bendtsen et al., 2000).
- The change in \( \tau_{\text{psr}} \) affects absolute time scale of overall reaction, but each CO profile can be over-layered identically by time-shifting

\[
\frac{dY_A}{dx} = \left( \frac{\dot{\omega}_A M_A}{\rho u} \right) \tau_{\text{psr}} = 0
\]

\[
Y_A = Y_{A0} + \left( \frac{\dot{\omega}_A M_A}{\rho} \right) \tau_{\text{psr}}
\]

Conditions: Inlet gas composition of 2276 ppm CH4, 3.69 % O2 and 4 % H2O in N2 in the absence of NO from Zhao et al (2007)
Interpreting Data with Mixing Location as t=0

- Here we display the predicted CO mole fraction at the reactor exit at three different inlet temperatures as a function of $\tau_{psr}$.
- Comparing predictions assuming an absolute reaction time scale with the position of mixing as t=0 can lead to misinterpretations of results.

Conditions: Inlet gas composition of 2276 ppm CH4, 3.69 % O2 and 4 % H2O in N2 in the absence of NO, Total reaction time = 249.6 sK/T

from Zhao et al (2007)
Interpreting Reactivity Observations

- Similar care must be taken in comparing Reactivity experimental observations with predictions because of non plug flow effects in the reactor mixing region

from Zhao et al (2007)
Surrogate Mixture Validation Database

- Experimental data covering the range of pressures, temperatures, and equivalence ratios needed for:
  - Each component to develop and validate component models
  - For component mixtures to develop and validate component model interactions
  - For real fuels to test concepts for surrogate mixture target matching and testing surrogate mixture models
- The following slides provide examples of the above for developing n-heptane/iso-octane/toluene surrogate mixtures for gasoline, for understanding cetane improver effects on diesel surrogates and diesel fuel, and for producing high temperature models for the oxidation of large carbon number alkanes (>C₁₀)
• Extent of oxidation measured by conversion to CO and CO₂
• Order of reactivity (both low and intermediate temperature conditions): n-alkanes > branched alkanes > aromatics.
PRF + Toluene Two Stage Ignition Properties

- Much higher “hot-ignition” temperature for toluene.
- Addition of toluene to 87% iso-octane/13% n-heptane (ON87 PRF) mixture increases “hot-ignition” temp. and decreases low-T reactivity.

\[
\begin{align*}
 p &= 12.5 \text{ atm} \\
 \phi &= 1.0 \\
 X_{O_2,i} &= 0.015 \\
 \tau &= 1.8 \text{ sec}
\end{align*}
\]
PRF+1 Model Validation against Binary Mixtures

- PRF+1 model predictions against *n*-heptane/toluene and *iso*-octane/toluene reactivity data collected in the VPFR.
  - Major species, the NTC region is properly reproduced
- Characteristic reaction time scales and dependences on equivalence ratio also properly captured by the model (not shown)

From Chaos et al. (2007)
Model Validation
VPFR – PRF+1 Emulation of a Gasoline with ON of 87

- The PRF+1 Model was developed by validation against pure components, binary, and ternary component mixtures, and the prediction results are compared here against real gasoline data having an (R+M)/2 Octane Number of 87
  - An empirical method for comparing the gasoline autoignition properties with the an appropriate ternary mixture was developed as part of this research

Princeton VPFR (12.5 atm, φ =1, 740 ppm)

from Chaos et al. (2007)
Validation Data for Cetane 45 Reference Mixture

(P = 12.5 atm, Φ = 1.0, τ = 1.8 sec, 1% Carbon)

n-hexadecane and heptamethyl-nonane mixture

ΔT

O₂

CO

CO₂

Note the heat release accompanying the low and intermediate temperature reaction below the hot ignition temperature

from SAE1999-01-1504
Prior Research on Cetane Improvers (2-EHN)

- Blends of ternary component mixtures constructed to develop Cetane scale
- Blends + 2-EHN compared with cetane changes.

Cetane Numbers for Surrogate Diesel Autoignition Ternary Mixtures
(Measured in a Cetane Engine 3/31/99)

<table>
<thead>
<tr>
<th>SAMPLE #</th>
<th>144,944-1</th>
<th>144,944-2</th>
<th>144,944-3</th>
<th>144,944-4</th>
<th>144,944-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexadecane %</td>
<td>23.3</td>
<td>23.3</td>
<td>33.3</td>
<td>33.3</td>
<td>43.3</td>
</tr>
<tr>
<td>Decalin %</td>
<td>30.0</td>
<td>30.0</td>
<td>30.0</td>
<td>30.0</td>
<td>30.0</td>
</tr>
<tr>
<td>1-Methylnaphthalene %</td>
<td>46.7</td>
<td>46.7</td>
<td>36.7</td>
<td>36.7</td>
<td>26.7</td>
</tr>
<tr>
<td>2-Ethylhexyl nitrate</td>
<td>0</td>
<td>4 mL</td>
<td>0</td>
<td>4 mL</td>
<td>0</td>
</tr>
<tr>
<td>Cetane Number 1</td>
<td>35.3</td>
<td>45.6</td>
<td>45.5</td>
<td>52.4</td>
<td>54.0</td>
</tr>
<tr>
<td>Cetane Number 2</td>
<td>35.8</td>
<td>45.9</td>
<td>45.3</td>
<td>52.7</td>
<td>53.6</td>
</tr>
<tr>
<td>Ave. Cetane Number</td>
<td>35.6</td>
<td>45.8</td>
<td>45.4</td>
<td>52.6</td>
<td>53.8</td>
</tr>
</tbody>
</table>

from SAE1999-01-1504
Baseline Diesel Surrogate Blends

- The reactivity of the surrogate diesel mixtures are consistent CN 45 Reference fuel mixture of n-hexadecane and heptamethyl-nonane
- Comparison of the reactivity data for 35, 45, and 55 Cetane surrogate mixtures show that both the low temperature and the intermediate temperature chemical rate of conversion of the fuel increase with increasing Cetane number
- Low temperature and intermediate temperature kinetics are shown to be exothermic, causing auto-thermal acceleration of the chemical conversion when “hot ignition” occurs

(P= 12.5 atm, $\Phi = 1.0$, $\tau = 1.8$ sec, 1% Carbon)

from SAE1999-01-1504
Initial Plans for VPFR MURI Experiments

- Two stage and high temperature oxidation data for higher carbon number alkanes, alkane isomers needed (>C_{10}) at high pressures
- Pyrolysis and oxidation data for cyclo alkanes, n-propyl benzene, tri methyl pentanes, and mixtures at all pressures
- 1-Methyl Napthalene for P>1 atm
- Representative jet fuels

from Zeppieri et al. (2005)
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