Molecular-level Kinetics in Chemical Engineering: From Chemical to Mathematical Modeling

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Outline

• Chemical Modeling
• Elements of Chemical Modeling
  ▪ Structure
  ▪ Reaction Paths and Kinetics
  ▪ Detailed Kinetic Modeling Approaches
• Computational Tools
• A Practical Hybrid Approach
• Conclusions
Chemical Modeling Complements Real System Experiments

The direct and practical approach to obtaining chemical information:

Real Experiment

- Generally Whole-feed (e.g., Resid, Coal, Lignin) Experiments
- Pilot Plant or Lab Scale
- Global feed, Global Product Measurements
- Lumped Model

Limitations of Lumped Models

- Absence of chemical structure
- Consequence: absence of properties beyond definition of lump
- Conflict: new questions of unprecedented molecular detail
  - performance
  - environmental
  - reactivity
- Motivates molecular-level modeling
Chemical Modeling Complements Real System Experiments

Accurate Chemical Modeling Requires Rigorous Mapping Steps

\[ CM = \text{Chemical Modeling} \]
\[ ME = \text{Model System Experiment} \]
\[ CM^{-1} = \text{Inverse Chemical Modeling Transform} \]

Elements of Chemical Modeling

- Simulation of Structure: CME
- Optimization of 10K+ Molecular Composition: CME
- Network Analysis: DelPlots
- LFER Analysis: Organization of 10K+ Rate, Adsorption and Thermodynamic Parameters
- Extrinsic Effects: Kinetic Coupling; Solvent Effects; Phase Behavior, Transport
- Novel Reactors

- 10K+ Multifunctional Molecules: Implicit Equations via Monte Carlo Simulation of Kinetics
- Equation Generation: NetGen, OdeGen
- Kinetic Coupling: Accounting for Interactions; Optimal System Design
- Transport: Molecule vs. Moiety; Size and Matrix Effects
- ARM: Modeling \( N \) molecules with fewer than \( N \) equations
Basic DelPlot Analysis (9/8/15)

Object is to determine the rank* of each product

*Generations removed from reactant
Second-rank DelPlot Exposes Generations

\[ k_1/\text{min}^{-1} = 1, \; k_1/\text{min}^{-1} = 2, \; \text{and} \; k_3/\text{min}^{-1} = 4. \]

Extended DelPlot Analysis

\[ R = r, \; R < r, \; R > r \]
Elements of Chemical Modeling

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Reaction Families Organize Pathways and Kinetics*

• Reaction Family: a set of reactions having similar transition states

\[
\begin{align*}
\Delta(S^\circ) &\equiv 0 \quad \text{or} \quad \Delta(S^\circ) \neq \Delta(H^\circ) \\
\Delta(G^\circ) &\neq \Delta(H^\circ) \\
\ln k & = a + bRI , \quad \text{where } RI \text{ is reactivity index}
\end{align*}
\]

• Reaction Families:
  – Allow for computer-generated reaction paths
  – Allow for massive parameter reduction via LFER organization

*9/22/15
Geometric Rationalization of LFER

- Physical picture of hypothetical reaction:
  \[ \text{Na} + \text{RCl} \rightarrow \text{NaCl} + \text{R}^\bullet \]
- Variation of R gives Reaction Family

\[ \Delta E^* \]

\[ \Delta q = \alpha' \text{RI} \]

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The kinetics of hydrogen abstraction provide the probe of the mechanism.

The options for hydrogen abstraction:

\[ \beta + A \rightarrow^{11} \beta H + \mu' \]
\[ \beta + XD \rightarrow^{12} \beta D + X' \]
\[ X' + A \rightarrow^{21} XH + \mu \]

Consequences:
- \( \beta D \) favored as XD/A \( \rightarrow \infty \)
- \( \beta D/(\beta D + \beta H) = DI \rightarrow 1.0 \) as XD/A \( \rightarrow \infty \)
- Kinetics analysis shows \( XH = \beta D \)
Free-Radical Pyrolysis of PDD

Experimental Example of Kinetic Coupling

DBE enhanced with PPE

PPE impeded with DBE
Two-Component Rice-Herzfeld Pyrolysis

\[
A_1 \xrightarrow{\alpha_1} 2 \beta_1 \\
\beta_1 + A_1 \xrightarrow{k_{11}} P_1 + \mu_1 \\
\mu_1 \xrightarrow{k_1} \beta_1 + Q_1 \\
A_2 \xrightarrow{\alpha_2} \beta_2 \\
\beta_2 + A_2 \xrightarrow{k_{22}} \mu_2 + P_2 \\
\mu_2 \xrightarrow{k_2} \beta_2 + Q_2 \\
\beta_1 + A_2 \xrightarrow{k_{12}} \mu_2 + P_1 \\
\beta_2 + A_1 \xrightarrow{k_{21}} \mu_1 + P_2 \\
\beta_1 + \beta_1 \xrightarrow{\alpha_{11}} \beta_1 + \mu_1 \\
\beta_1 + \mu_1 \xrightarrow{\alpha_{11}} \beta_1 + \mu_1 \\
\mu_1 + \mu_1 \xrightarrow{\alpha_{11}} \mu_1 + \mu_1
\]

Rate Laws for Coupled Binary Systems

\[
r_1(A_1, A_2) = \\
k_{11}A_1\left(\frac{\alpha_1 A_1}{\alpha_1 A_1}\right)^{\frac{1}{2}} \left(1 + \theta_1 \hat{k}_1 S_1\right) \left(1 + \theta_2 \hat{k}_2 S_2\right) \\
\left[1 + y_1^{\frac{1}{2}} M_1 \left(1 + \theta_1 \hat{k}_1 S_1\right) + y_2^{\frac{1}{2}} \hat{k}_2 S_2 \left(1 + \theta_1 \hat{k}_1 S_1\right) \left(1 + \theta_2 \hat{k}_2 S_2\right)\right] \\
\left[1 + n_1 + \frac{n_1}{\theta_1 \hat{k}_1 S_1}\right] \\
\left[1 + \theta_1 \hat{k}_1 S_1 + \frac{n_1}{\theta_1 \hat{k}_1 S_1}\right] \left(1 + \theta_2 \hat{k}_2 S_2\right) \\
\left[1 + n_1 + \frac{n_1}{\theta_1 \hat{k}_1 S_1}\right] \\
\left[1 + \theta_2 \hat{k}_2 S_2 + \frac{n_1}{\theta_1 \hat{k}_1 S_1}\right] \\
\left[1 + n_1 + \frac{n_1}{\theta_1 \hat{k}_1 S_1}\right] \\
\left[1 + \theta_2 \hat{k}_2 S_2 + \frac{n_1}{\theta_1 \hat{k}_1 S_1}\right]
\]

\[
r_2(A_1, A_2) = \\
k_{21}A_2\left(\frac{\alpha_2 A_2}{\alpha_2 A_2}\right)^{\frac{1}{2}} \left(1 + \theta_1 \hat{k}_1 S_1\right) \left(1 + \theta_2 \hat{k}_2 S_2\right) \\
\left[1 + y_1^{\frac{1}{2}} M_1 \left(1 + \theta_1 \hat{k}_1 S_1\right) + y_2^{\frac{1}{2}} \hat{k}_2 S_2 \left(1 + \theta_1 \hat{k}_1 S_1\right) \left(1 + \theta_2 \hat{k}_2 S_2\right)\right] \\
\left[1 + n_1 + \frac{n_1}{\theta_1 \hat{k}_1 S_1}\right] \\
\left[1 + \theta_1 \hat{k}_1 S_1 + \frac{n_1}{\theta_1 \hat{k}_1 S_1}\right] \left(1 + \theta_2 \hat{k}_2 S_2\right) \\
\left[1 + n_1 + \frac{n_1}{\theta_1 \hat{k}_1 S_1}\right] \\
\left[1 + \theta_2 \hat{k}_2 S_2 + \frac{n_1}{\theta_1 \hat{k}_1 S_1}\right] \\
\left[1 + n_1 + \frac{n_1}{\theta_1 \hat{k}_1 S_1}\right] \\
\left[1 + \theta_2 \hat{k}_2 S_2 + \frac{n_1}{\theta_1 \hat{k}_1 S_1}\right]
\]
**Chain Transfer Limiting Case**

**One Component Pyrolysis**

\[ A_1 \xrightarrow{a_1} 2 \beta_1 \]

\[ \beta_1 + A_1 \xrightarrow{k_{11}} \beta_1H + \mu_1 \]

\[ \mu_1 \xrightarrow{k_2} \beta_1 + Q_1 \]

\[ 2 \beta_1 \xrightarrow{a_2} \text{Products} \]

**Additional Reactions with Solvent**

\[ \beta_1 + A_2 \xrightarrow{k_{12}} \beta_1H + \mu_2 \]

\[ \mu_2 + A_1 \xrightarrow{k_{13}} \beta_2 + \mu_1 \]

\[ \beta_1 + \mu_2 \xrightarrow{a_3} \text{Products} \]

\[ \mu_1 + \mu_2 \xrightarrow{a_4} \text{Products} \]

---

**Pyrolysis with Chain Transfer Solvent**

**Volcano Curve for Pyrolysis with Chain Transfer Solvent**

Fixing species 1 \( [d^0(\beta_1-H)] \) and \( d^0(\mu_1-H) \)
Coal Liquefaction Efficiency

An-H2  Py-H2  Phen-H2
AceN  Tet  Ind  Me-N

Bond Dissociation Energy / kcal mol$^{-1}$

Coal Conversion to THF Solubles

UD Computational Tools*

- Develop usable approaches and software tools for molecule-based kinetic modeling of complex feeds
- *Maintain fundamental chemistry as the primary focus*
- Link quantum and engineering levels
- Produce models that are compatible across a process (e.g., refinery)
- Deliver in a user-friendly format

*10/13, 15, 20 and 11/22
UD Software Tools

Experimental Data on Feedstock

Composition Model Editor
• Optimizes mole fractions using experimental data

Interactive Network Generator
• Automatically builds reaction network based on feedstock molecules, reaction chemistries, and reaction rules

Feedstock Molecules

Feedstock Mole Fractions

Kinetic Model Editor
• Builds and solves kinetic model
• Optimizes kinetic parameters using reactor experimental data

Experimental Data on Reactor

Total Molecular Footprint Molecule Reactivity

UD Software Tools

Composition Model Editor

Kinetic Model Editor

Interactive Network Generator

CMB2A

26
UD Supporting Apps and Tools

**Composition Model Editor**
- **CME-2.4**

**Kinetic Model Editor**
- **Kom**

**Universal Sampling Builder**
- Estimates physical properties of molecules
- Sampling protocol between structural attribute pdfs and molecular compositions

**CME-Plastics**
- Light-weight CME applied to linear polymers

**HOUGen**
- Creates molecular identities of general hydrocarbon mixtures

**CoreGen**
- Creates core structures

**INGen Network Merge**
- Merges reaction networks, removes duplicates

**PropGen**
- Creates core structures

**CoreGen**
- Creates core structures

**Reaction Network Visualizer**
- Visualizes reaction networks

**Interaction Model Visualizer**
- Bulk Properties
1. Composition Models: CME
   - Measurements (GS-MS, NMR, etc.)
   - Modeling: Properties -> Molecular Structure

2. Reaction Network Modeling: INGen
   - $N < N_c$: "Conventional" deterministic methods
   - $N > N_c$: Hybrid methods, e.g., The Attribute Reaction Model

3. Reaction Modeling: KME
   - Model parser and solver in various engineering modes
   - Order 10 $O(10)$ LFER’s for every process chemistry

4. Property Estimation: CME
   - Molecular Structure -> Properties
   - End-use and internal-use properties
2. Optimization of Probability Distributions:
   - Initially uniform probability
   - Minimization of objective function

Molecular-level Modeling Requirements

1. Composition Models: CME
   - Measurements (GS-MS, NMR, etc.)
   - Modeling: Properties -> Molecular Structure

2. Reaction Network Modeling: INGen
   - \( N < N_c \): "Conventional" deterministic methods
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3. Reaction Modeling: KME
   - Model parser and solver in various engineering modes
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4. Property Estimation: CME
   - Molecular Structure -> Properties
   - End-use and internal-use properties
Equivalent Computational Representations

**Bond Electron Matrix**

```
   O O O O O O O O O O O O O O O O
   O O O O O O O O O O O O O O O O
   O O O O O O O O O O O O O O O O
   O O O O O O O O O O O O O O O O
   C1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
   C2 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
   H1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
   H2 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
```

**Adjacency List**

```
//pentane
17
0 8 C : (1, 1), (5, 1), (6, 1), (7, 1);
1 8 C : (0, 1), (2, 1), (4, 1), (9, 1);
2 8 C : (0, 1), (1, 1), (10, 1), (11, 1);
3 8 C : (2, 1), (4, 1), (13, 1), (15, 1);
4 8 C : (3, 1), (14, 1), (15, 1), (16, 1);
5 8 H : (2, 1);
6 8 H : (9, 1);
7 8 H : (9, 2);
8 8 H : (9, 2);
9 8 H : (9, 3);
10 8 H : (9, 3);
11 8 H : (9, 4);
12 8 H : (9, 4);
13 8 H : (9, 5);
14 8 H : (9, 5);
15 8 H : (9, 5);
16 8 H : (9, 5);
```

**String Code**

```
C(C(C(H3)H2)C(C(H3)H2)H2)
```

**SMILES Code**

```
CCCCC
```

---

Chemical Reaction as a Matrix Operation

```
\[ \begin{array}{c}
\text{C}_1 \\
\text{C}_2 \\
\text{H}_1 \\
\text{H}_2 \\
\end{array} + \begin{array}{c}
\text{H}_1 \\
\text{H}_2 \\
\end{array} \rightarrow \begin{array}{c}
\text{C}_1 \\
\text{C}_2 \\
\text{H}_1 \\
\text{H}_2 \\
\end{array} \]
```

Reduced Reactant Matrix \( M_A \)

```
\[ \begin{array}{cccc}
0 & 1 & 0 & 0 \\
1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 \\
0 & 0 & 1 & 0 \\
\end{array} \]
```

Reaction Matrix \( M_R \)

```
\[ \begin{array}{cccc}
0 & -1 & 1 & 0 \\
-1 & 0 & 0 & 1 \\
1 & 0 & 0 & -1 \\
0 & 1 & -1 & 0 \\
\end{array} \]
```

Reduced Product Matrix \( M_B \)

```
\[ \begin{array}{cccc}
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
\end{array} \]
```
**Network Building Algorithm**

1. **Graph of reactant molecule** => **Input**
2. Determine species type
3. Determine reaction sites and apply reaction matrices
4. Determine connected components
5. Determine products uniqueness (isomorphism) if unique, add to unreacted species list
6. Add reaction expression to the list
7. Obtain species from unreacted list
8. **Structure/Reactivity parameters**
9. Determine Reactivity Index (CQC, GA, Data Base, etc.)
10. Rate law parameters

**INGen Output: Species Analysis**

<table>
<thead>
<tr>
<th>Species</th>
<th>Rank</th>
<th>MW</th>
<th>Type</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species1</td>
<td>2</td>
<td>2.016</td>
<td>2 undetermined</td>
<td>phenanthrene</td>
</tr>
<tr>
<td>Species2</td>
<td>278.224</td>
<td>24</td>
<td>20 A2-9H0-N9-H0-S6N0-S6N0-R2-arom</td>
<td>1,1,3-trimethyl-2,3-dihydro-1H-indene</td>
</tr>
<tr>
<td>Species3</td>
<td>160.26</td>
<td>12</td>
<td>18 A1-9H0-N9-H0-S5N0-R3-naphthalene</td>
<td>1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene</td>
</tr>
<tr>
<td>Species4</td>
<td>174.287</td>
<td>13</td>
<td>18 A1-9H0-N9-H0-S5N0-R3-naphthalene</td>
<td>1,1,2,3-dimethyl-1,2,3,4-tetrahydronaphthalene</td>
</tr>
<tr>
<td>Species5</td>
<td>182.266</td>
<td>14</td>
<td>14 A2-9H0-N9-H0-S5N0-R2-arom</td>
<td>ethene-1,1-dichlorobenzene</td>
</tr>
<tr>
<td>Species6</td>
<td>160.26</td>
<td>12</td>
<td>16 A1-9H0-N9-H0-S5N0-R3-naphthalene</td>
<td>1,2,3-trimethyl-2,3-dihydro-1H-indene</td>
</tr>
<tr>
<td>Species7</td>
<td>184.282</td>
<td>14</td>
<td>16 A2-9H0-N9-H0-S5N0-R4-arom</td>
<td>2,3-dimethyl-1,2,3,4-tetrahydronaphthalene</td>
</tr>
<tr>
<td>Species8</td>
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<td>12</td>
<td>18 A1-9H0-N9-H0-S5N0-R9-arom</td>
<td>1,2,3,4-tetrahydronaphthalene</td>
</tr>
<tr>
<td>Species9</td>
<td>148.249</td>
<td>11</td>
<td>16 A1-9H0-N9-H0-S5N0-R5-arom</td>
<td>2,3-dimethyl-1,2,3,4-tetrahydronaphthalene</td>
</tr>
<tr>
<td>Species10</td>
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<td>11</td>
<td>16 A1-9H0-N9-H0-S5N0-R5-arom</td>
<td>2,3-dimethyl-1,2,3,4-tetrahydronaphthalene</td>
</tr>
<tr>
<td>Species11</td>
<td>156.228</td>
<td>12</td>
<td>12 A2-9H0-N9-H0-S5N0-R5-arom</td>
<td>2,3-dimethyl-1,2,3,4-tetrahydronaphthalene</td>
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<tr>
<td>Species12</td>
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<td>14</td>
<td>16 A2-9H0-N9-H0-S5N0-R4-arom</td>
<td>2,3-dimethyl-1,2,3,4-tetrahydronaphthalene</td>
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<tr>
<td>Species14</td>
<td>170.253</td>
<td>13</td>
<td>14 A2-9H0-N9-H0-S5N0-R3-arom</td>
<td>2,3-dimethyl-1,2,3,4-tetrahydronaphthalene</td>
</tr>
<tr>
<td>Species15</td>
<td>170.253</td>
<td>13</td>
<td>14 A2-9H0-N9-H0-S5N0-R3-arom</td>
<td>2,3-dimethyl-1,2,3,4-tetrahydronaphthalene</td>
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<td>162.276</td>
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<td>12</td>
<td>12 A2-9H0-N9-H0-S5N0-R2-arom</td>
<td>2,3-dimethyl-1,2,3,4-tetrahydronaphthalene</td>
</tr>
</tbody>
</table>
Co-Processing of BPO & HGO

Biomass → Pyrolysis Unit → BPO (Biomass Pyrolysis Oil) → Hydrotreating Unit → Commodity Chemicals & Fuels

HGO (Heavy Gas Oil) → Hydrogen

BPO (Biomass Pyrolysis Oil) → 1-α

Water → α

INGen Output: Network

KME Compatible Network

Reaction Family
Lignin Monomers

\[ \text{\(p\)-coumaryl alcohol} \quad \text{Coniferyl alcohol} \quad \text{Sinapyl alcohol} \]

Freudenberg Lignin Model as a String

The computer “knows” Lignin as its SMILES code

Substituents: 39 Attributes
Cores: 19 Attributes
63 Connections:
Pyrolysis Reaction Chemistry

- β-O-4 Ether Cleavage Reactions
- β-O-4 Ether Dehydration
- α-O-4 Ether Cleavage
- Vinyl Degradation Pathways

Model Results

- INGen Results: beta and alpha linkage reactions on adapted molecule
- 1851 reactions
- 295 species

<table>
<thead>
<tr>
<th>Carbon #</th>
<th>Cleavage Reacting</th>
<th>Reaction #</th>
<th>Species #</th>
<th>Total RXN #</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>5</td>
<td>8</td>
<td>9</td>
<td>1851</td>
</tr>
<tr>
<td>20</td>
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</tr>
<tr>
<td>30</td>
<td>15</td>
<td>622</td>
<td>278</td>
<td>2473</td>
</tr>
<tr>
<td>40</td>
<td>31</td>
<td>1654</td>
<td>784</td>
<td>3565</td>
</tr>
<tr>
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<tr>
<td>60</td>
<td>50</td>
<td>9941</td>
<td>2314</td>
<td>11792</td>
</tr>
</tbody>
</table>

- Kinetic Model Solution Time
  - C#=30, 2-3 minutes
  - C#=60, 1 hour
Attribute Reaction Modeling

Reduction the Freudenberg Lignin into its Attributes
Attribute Reaction Model Equations

- Reducible Molecule Reaction Submodel

\[
\frac{d\text{Core}}{dt} = \sum_{i, \text{reactions}} \tilde{v}_i \times \text{rate}_i \\
\frac{d\text{IL}}{dt} = \sum_{i, \text{reactions}} \tilde{v}_i \times \text{rate}_i \\
\frac{d\text{SC}}{dt} = \sum_{i, \text{reactions}} \tilde{v}_i \times \text{rate}_i
\]

- Irreducible Molecule Reaction Submodel

Juxtaposition Tracks Molecules

Cores Inter-unit Links Side Chains
Model Results

- Parity plot comparison with literature data
- Once-through solution time: 5 seconds

### Computational Issues

- Conventional Model
  - More than 2000 species (equations) and 10,000 reactions
  - Solution time: minutes to hours depending on complexity
- Attribute Reaction Model
  - Less than 100 equations and hundreds of reactions
  - 5 second solution time

| Table 1: Vinyl Graft Degradation Reactions based on a carbon skeleton |
|-----------------------------|-------------|-------------|-------------|
| Carbon #<br>Products from Linkage | Cleavage Reaction | Reaction # | Species # | Total RXN # (+1881) |
|-----------------------------|-------------|-------------|-------------|
| 10 | 5 | 18 | 1899 |
| 20 | 10 | 44 | 33 | 1895 |
| 30 | 15 | 622 | 278 | 2473 |
| 40 | 31 | 1,644 | 584 | 3325 |
| 50 | 41 | 2,251 | 739 | 4115 |
| 60 | 50 | 9,961 | 2314 | 13,792 |
Co-Processing of BPO & HGO

HGO Composition

- Aromatic species
  - Cores
  - Substituents
    - Substituents are further divided into side chains and inter-core linkages
- Paraffins
  - C5-C25 \(n\)-Paraffins
  - C4-C15 2-methyl and 3-methyl Paraffins
### Hydrotreating Reaction Families*

<table>
<thead>
<tr>
<th>Reaction Family</th>
<th>log A</th>
<th>$E_0^*$</th>
<th>$E_0$</th>
<th>$E_0$</th>
<th>$E_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-O Hydrogenolysis</td>
<td>10</td>
<td>21</td>
<td>$H_2$</td>
<td>$H_2$</td>
<td>$H_2$</td>
</tr>
<tr>
<td>Dealkylation</td>
<td>10</td>
<td>25</td>
<td>$H_2$</td>
<td>$H_2$</td>
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*10/22/15

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### Hydrotreating Reaction Network

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<th>Reaction Family</th>
<th>BPO</th>
<th>HGO</th>
<th>Sum of Models</th>
<th>Combined Model</th>
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<td>Decarboxylation-Oxygen</td>
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<td>Total</td>
<td>1,747</td>
<td>475</td>
<td>2,222</td>
<td>2,178</td>
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</table>

*541*
Profile Plot of Major Species

PFR, 1,000 atm pressure, 800 K

Preliminary Status

• Quantitative organization of science and engineering knowledge base
• Identified some key technology gaps, science needs
  • Petroleum was inherently profitable, which allowed for 100+ years of technology development
  • Biomass not inherently competitive, issues need to be addressed
    • $H_2$ consumption: expensive
    • $H_2$ consumption: $CO_2$ footprint
    • $H_2O$ release
      • $O$ rejection as $H_20$ or $CO_2$?
    • Energy density
Conclusions

- Irreducible complexity, as measured by model parameters:
  - Structure: $O(10)$ 5-10 pdf’s $\times$ 2-3 parameters each
  - Reactivity: $O(10)$ 10 LFER’s $\times$ 2 parameters each
  - Reaction Families: $O(10)$ Reaction Matrices
- Rigorous kinetics can model interactions and competitions
- Net reduction of complexity: $O(10^5 \times 10^5)$ parameters reduced to $O(30)$
- Combinatorial detail easily handled by
  - INGen
  - KME
  - CME

CME Converts Measurements to Molecules

Available Measurements  \[\text{CME} \quad \text{Simulated Compositions} \quad \text{Molecules}\]

- Attribute PDFs
- Simulated Properties
- Sample
- PropGen
- Adjust
2. Optimization of Probability Distributions:
   • Initially uniform probability
   • Minimization of objective function

Molecular-level Modeling Requirements

1. Composition Models: CME
   – Measurements (GS-MS, NMR, etc.)
   – Modeling: Properties -> Molecular Structure

2. Reaction Network Modeling: INGen
   – N < N_C: "Conventional" deterministic methods
   – N > N_C: Hybrid methods, e. g., The Attribute Reaction Model

3. Reaction Modeling: KME
   – Model parser and solver in various engineering modes
   – Order 10 [O(10)] LFER’s for every process chemistry

4. Property Estimation: CME
   – Molecular Structure -> Properties
   – End-use and internal-use properties
Lignocellulosic Biomass

Adapted Freudenberg Structure

- Formed from three monolignols
- Phenolic copolymer linkages
  - \(\alpha\)-O-4 linkages
  - \(\beta\)-O-4 linkages
- There is a propensity toward the \(\beta\)-O-4 linkage forming with it comprising upwards of 50-70% of linkages of the lignin [1]

Exhaustive Method Reaction Network

- Seven degradation pathways and many reactive sites on the lignin macromolecule create a combinatorial problem.
  - Within INGen the amount of species reaches a computational limit due to the amount of memory required to store species information.
- Two separate reaction networks were created for linkage and vinyl cleavages respectively and merged to create an overall network.

Probability Distributions to Mole Fractions

- Benzene
  \[ \text{Mole Fraction} = X_1 \cdot P(\bigodot) \cdot P(\bigtriangleup) \cdot P(\bigtriangleup) \cdot P(\bigtriangleup) = X_1 \cdot 0.25 \cdot 0.35 \cdot 0.35 \]

- Diphenyl Methane
  \[ \text{Mole Fraction} = X_2 \cdot P(\bigodot) \cdot P(\bigtriangleup) \cdot P(\bigtriangleup) \cdot P(\bigtriangledown) \]
### Reactions between Attributes

- Inter-core Linkages cleave to two side chains
- Side chains react to form smaller side chains and irreducible molecules
- Cores can break down to form smaller cores and irreducible molecules
- Char formation

![Chemical structures](image)

### BPO Composition: Major Species

<table>
<thead>
<tr>
<th>#</th>
<th>Major Species Name</th>
<th>ChemDraw Name</th>
<th>Network Species #</th>
<th>Mole Fraction</th>
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<td>5</td>
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<tr>
<td>7</td>
<td>4-methylguaiacol</td>
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### Effect of Catalyst on BPO Composition

#### Fast Pyrolysis

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<th>wt%</th>
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<td>3</td>
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#### Catalyzed Pyrolysis

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<td>70</td>
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### HGO Composition: Cores

#### Aromatic Cores

#### Sulfur-containing Cores

#### Nitrogen-containing Cores
HGO Composition: Substituents

Side Chains

Inter-Core Linkages

Attribute Juxtaposition Details
Monomers & dimers
Coordination number: 4