Pentanol: A Promising Fuel and Petrochemical Building Block

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Current energy industry

• Combustion is the main source of energy
• Combustion fuels from fossil resources
• Global energy demand and use keep increasing

Primary energy consumption by fuel

Source: BP Energy Outlook
Source: EIA, 2016
Current energy industry

- Combustion is the main source of energy
- Combustion fuels from fossil resources
- Global energy demand and use keep increasing

- Greenhouse gas emissions
- Small particles formation

Source: globalclimate.ucr.edu
Source: NASA Earth Observatory
Current energy industry
• Combustion is the main source of energy
• Combustion fuels from fossil resources
• Global energy demand and use keep increasing

False Greenhouse gas emissions
False Soot particles formation

→ Need for alternatives, i.e. bio-derived resources
→ Need for better understanding
  → Underlying combustion/pyrolysis chemistry
  → Engine/reactor technology
Introduction

Why use pentanol?
- Higher energy content
- Higher boiling point
- Less hygroscopic
- Several possible production processes

This study
- Pyrolysis of pentanol in flow reactor
- Kinetic model building using Genesys
- Reactor simulations and model validation
Most important aspects:

- Tubular reactor: $L = 1.5m$, $D = 0.006m$, Incoloy HT
- Analysis equipment: GCxGC-FID/(TOF-MS) Light Oxygenates Analyser Refinery Gas Analyser
- Conditions: $T = 913 - 1073K$; $P = 0.17$ MPa

- Pentanol flow rate $1.3-3.3 \times 10^{-2} \text{ g s}^{-1}$
- Pentanol inlet mole fraction $0.2-0.5$
Kinetic model generation

Microkinetic model
- Only includes elementary steps
- The number of species and reactions can become very large
- Manual generation nearly impossible
→ Use of automatic kinetic model generation software
Kinetic model generation: Genesys

Use of chemoinformatics
- Molecular representation
- Graph and group theory
- Not tailored to specific applications

Molecules
- Unique Representation
- Thermo-dynamics

Reaction families
- Reaction Identification
- Kinetic Parameters

Reaction rules
- Kinetic model enlargement
- Termination criterion

OpenBabel

CDK
Kinetic model generation: Termination

**Rule-based**

- No reactor simulations
- No dependence on rate coefficients
- Constraints can be defined at several levels (atoms, functional groups, reactants, products), i.e. wide applicability

- Too many unimportant reactions in final model
- Need for user expertise

**Rate-based**

- Only include important reactions
- More accurate final model

- Dependent on kinetics, thus need for accurate rate coefficients
- Edge can become very large: computational limitations (memory)

Genesys uses a combination of both

- Keeps size of edge manageable through constraints
- Accurate rate coefficients via group additivity from CBSQB3 calculations
- No inclusion of redundant pathways
Thermodynamic data

2-methylnonane

Atoms in large molecules

Group additivity

Atoms in small molecules with similar surroundings

**Group** definition based on surroundings (ligands)

**Additivity:**

\[
\begin{align*}
\text{>Additivity:} & \quad \text{[Diagram]} \\
& = 1 \text{ green} + 6 \text{ blue} + 3 \text{ orange}
\end{align*}
\]
Kinetic data

**Rate coefficients**

Arrhenius equation

\[ k(T) = \kappa n_e \tilde{A} \exp \left( -\frac{E_a}{RT} \right) \]

Group additivity for Arrhenius parameters

\[ E_a = E_{a,\text{ref}} + \sum_{i=1}^{n} \Delta GAV^{0}_{Ea}(X_i) \]

\[ \log \tilde{A} = \log \tilde{A}_{\text{ref}} + \sum_{i=1}^{n} \Delta GAV^{0}_{\log \tilde{A}}(X_i) \]

\[ \kappa = 1 + \left( \frac{162}{T} \right)^{3} \cdot E_{a,exo} + 2.71 \cdot 10^{-6} \cdot \exp \left( -\frac{T - 300}{26} \right) \cdot E_{a,exo}^{4} \]

\[ n_e = \frac{n_{opt, \dagger \dagger}}{\prod_{r} \sigma_{r}} \cdot \prod_{r} \sigma_{r} \]

**ΔGAV° Library**

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<th>C_1</th>
<th>log(A)</th>
<th>E_a</th>
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<td>S-(C)</td>
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**Reference reaction**

\[ \text{CH}_3\text{S}^* + \text{CH}_4 = \text{CH}_3\text{SH}^* + \text{CH}_3 \]

\[ \log(A) = 7.970 \quad 107.6 \]

\[ \Delta GAV° \text{ Library} \]

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<tr>
<th>SMARTS C_1</th>
<th>log(A)</th>
<th>E_a</th>
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<td>C-(H)_{3}(C)</td>
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<td>C-(C)_{2}(H)</td>
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<td>C-(H)_{2}</td>
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<td>C_{r}(C)</td>
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Pentanol kinetic model generation

Hydrogen abstractions

\[
R_1 H + \dot{R}_2 \rightarrow \dot{R}_1 + R_2 H
\]

\[
H R_1 \rightarrow R_2 \rightarrow R_1 \rightarrow R_2 H
\]

Beta-scissions

\[
\begin{align*}
\cdot & R_2 R_3 \rightarrow R_1 = R_2 + \dot{R}_3 \\
\cdot O & R \rightarrow O=\dot{C} + \dot{R}
\end{align*}
\]

Alpha-scissions

Base mechanism from literature
Initial homolytic bond scissions from literature
Final Model

- 448 species
- 4752 reactions
Additional \textit{ab initio} calculations

\textbf{KinBot}

Code for automatically exploring a Potential Energy Surface (PES)
Identifies stationary points directly using 3D coordinates of atoms
Reactions are searched for via possible transformations programmed in the code

- Systematic and exhaustive searches
- On-the-fly coupling with Gaussian
- Off-line coupling with MolPro and Master Equation codes
- Both for uni- and bimolecular reactions
Additional *ab initio* calculations

C₅H₁₁O PES

Automatically explored using the KinBot software

Geometry optimization
M062X/6-311++G(d,p)

Energy calculation
UCCSD(T)-F12/cc-pVTZ-F12

1D hindered rotors

Rate coefficients from master equation calculations
Reactor modeling

1. Conversion [%] vs Temperature [K]
2. Ethene mass fraction [%] vs Conversion [%]
3. Methane mass fraction [%] vs Conversion [%]
4. CO mass fraction [%] vs Conversion [%]

Graphs showing the relationship between various masses and conversions.

References:
Wang et al. Combust Flame. 2015;162(9):3277-3287
Rate of production analysis

Initial chemistry

Radical chemistry
Pentanol as biofuel or chemical building block?

- Many reaction pathways for pyrolysis or combustion
- Use of Genesys for kinetic model construction
- Additional ab initio calculations for the C$_5$H$_{11}$O reactions
- Promising model validation, but more experimental data is also needed
- Combustion behaviour
Acknowledgements

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