STEAM-CRACKING: FROM MOLECULE TO INDUSTRIAL PROCESS

Kevin M. Van Geem and Guy B. Marin (keynote)
Laboratory for Chemical Technology
Steam cracking: hot section

Preheat feed and other utility streams

A: Radiation section
B: TLE
C: Steam drum
D: Convection section

Endothermic process 1050–1150 K
Developing a model for steam cracking

**Goal**
- Reactor geometry
- Operating conditions

**Feedstock properties** → **Simulation model** → **Product specs**

**Modeling**
- **Microkinetic model**
- **Reactor model**

- **Fundamental reactor model**
- **Detailed product composition**

**Detailed feedstock composition** → **Fundamental reactor model** → **Detailed product composition**
Outline

• Introduction
• Feedstock
• Kinetics
• Reactor
• Process
• Conclusions
Outline

• Introduction
• Feedstock: characterization
• Kinetics
• Reactor
• Process
• Conclusions
On-line GC × GC

GC × GC chromatogram: 2 parts
Conventional 1D part $\rightarrow$ C$_4$-
Comprehensive 2D part $\rightarrow$ C$_5$+

SIMCO: Maximization of Shannon Entropy

Feedstock properties
- Average molecular weight
- Elemental composition
- Specific density
- Global PINA analysis
- Boiling point data (e.g. D2887 simdist)
- Aromatic Sulfur

Detailed composition
- Species identity
- Mole or mass fractions

Feasible reconstruction maximization

Constraints from mixing rules (example):

\[
\sum_{i=1}^{N_M} \frac{y_i}{M_w} = \sum_{i=1}^{N_M} y_i M_w_i \\
\sum_{i=1}^{N_M} y_i = 1
\]

\[
\frac{d_{exp}}{d} = \frac{\sum_{i=1}^{N_M} y_i M_w_i}{\sum_{i=1}^{N_M} d_i \sum_{i=1}^{N_M} y_i M_w_i}
\]

\[
M_{w_{exp}} = \sum_{i=1}^{N_M} y_i M_w_i
\]

\[
S(y_i) = -\sum_{i=1}^{N_M} y_i \ln(y_i) \text{ with } \sum_{i=1}^{N_M} y_i = 1
\]

More than 100 unknown mole fractions

± 20 properties

S.P. Pyl et al., AIChE Journal, 56, 12, 3174-3188, 2010
SIMCO results: Hydrocarbons

- **n-paraffins**
  - Mass fraction (wt%) vs. Carbon number

- **i-paraffins**
  - Mass fraction (wt%) vs. Carbon number

- **Naphthenes**
  - Mass fraction (wt%) vs. Carbon number

- **Aromatics**
  - Mass fraction (wt%) vs. Carbon number
Outline

• Introduction
• Feedstock
• Kinetics
• Reactor
• Process
• Conclusions
CRACKSIM: steam cracking kinetics

**Goal**
- Reactor geometry
- Operating conditions
- Simulation model
- Feedstock properties
- Product specs

**Modeling**
- Microkinetic model: CRACKSIM
- Reactor model
- Fundamental reactor model
- Detailed feedstock composition
- Detailed product composition

13-Nov-17

8th Asian-Pacific Chemical Reaction Engineering (APCRE 2017) Symposium
East China University of Science and Technology, Shanghai, China, Nov. 12-15, 2017
Outline

• Introduction
• Feedstock
• Kinetics: reaction network
• Reactor
• Process
• Conclusions
Network generators
GENESYS: GENERation of reacting SYStems

Molecule Identifiers

Pattern Recognition

Reactant -> product

"Kinetics of Chemical Reactions: Decoding Complexity"
G.B. Marin and G.S. Yablonsky, Wiley-VCH Verlag, 446 pages, 2011

Vandewiele, N.M. et al., Chemical Engineering Journal, 207-208, 526-538, 2012
Families of elementary reactions

Bond dissociation and radical recombination

\[ R_1 - R_2 \rightleftharpoons R_1^\cdot + R_2^\cdot \]

Hydrogen abstraction (inter- and intramolecular)

\[ R_1 - H + R_2^\cdot \rightleftharpoons R_1^\cdot + R_2 - H \]

Radical addition and β-scission (inter- and intramolecular)

\[ R_1^\cdot + R_2 = R_3 \rightleftharpoons R_1 - R_2 - R_3^\cdot \]
CRACKSIM: $\mu$ and $\beta$ networks

**$\beta$ network**
Bi- and monomolecular reactions for $\beta$ radicals

\[
R_1 - R_2 \rightleftharpoons R_1 + R_2
\]
\[
R_1 - H + R_2 \rightleftharpoons R_1 + R_2 - H
\]
\[
R_1 + R_2 = R_3 \rightleftharpoons R_1 - R_2 - R_3
\]

1324 reversible reactions
51 molecules
43 radicals

**$\mu$ network**
Monomolecular reactions for $\mu$ radicals

\[
R_1 - R_2 \rightarrow R_1 + R_2
\]
\[
R_2 - R_1 - H \rightleftharpoons H - R_2 - R_1
\]
\[
R_1 + R_2 = R_3 \rightarrow R_1 - R_2 - R_3
\]
\[
R_1 - R_2 = R_3 \rightleftharpoons R_1 \equiv R_2 - R_3
\]

13584 schemes
676 molecules
Outline

- Introduction
- Feedstock
- Kinetics: ab initio
- Reactor
- Process
- Conclusions
Kinetics: computational approach

Conventional Transition State Theory (high pressure limit)

\[ A + B \rightleftharpoons [AB]^\ddagger \rightleftharpoons C \]

Transition state

\[ k_\infty (T) = \kappa (T) \frac{k_B T}{h} \frac{q_\ddagger}{q_A q_B} V_m e^{\frac{-\Delta E_0}{RT}} \]

Electronic barrier \( \Delta E_0 \)
The CBS-QB3 ab initio method is used.

Partition functions \( q \)
- Ideal gas approximation
- Hindered Rotor (1D-HR)

Tunneling coefficient \( \kappa \)
- Eckart
Objective: data base

Reactor simulation for hydrocarbon radical chemistry

- Reactor model
  - Solver
- Reaction network
  - Kinetic and thermodynamic data

Develop a consistent data set based on ab initio calculations

using group additivity

Van de Vijver, R. et al., Chemical Engineering Journal, 278, 385–393, 2015
From small to large species with group additivity

2-methoxy-2-methylbut-3-enoic acid

Group additivity

Additivity

Atoms in large molecules

Atoms in small molecules with similar surroundings

Additive groups:
- $C_d-(H)_2$
- $C_d-(C)(H)$
- $C-(C)(C)(O)(CO)$
- $O-(C)_2$
- $C-(O)(H)_3$
- $C-(C)(H)_3$
- $CO-(C)(O)$
- $O-(CO)(H)$


8th Asian-Pacific Chemical Reaction Engineering (APCRE 2017) Symposium
East China University of Science and Technology, Shanghai, China, Nov. 12-15, 2017
Kinetics: data base of $\Delta GAV^o$

Hydrogen abstraction (ethyl + ethenyl methylether)

$$E_a(T) = E_{a,\text{ref}}(T) + \Delta GAV^o_{E_a}(C_1) + \Delta GAV^o_{E_a}(C_2) + \Delta GAV^o_{E_a}(X_1) + \Delta GAV^o_{E_a}(Y_1) + \Delta E_{a,\text{res}}$$

$E_{a,GA} = 62.6$ kJmol$^{-1}$

$E_{a, \text{ab initio}} = 62.0$ kJmol$^{-1}$

$\log(A_{GA}/m^3 \text{ mol}^{-1} \text{ s}^{-1}) = 5.095$

$\log(A_{\text{ab initio}})/m^3 \text{ mol}^{-1} \text{ s}^{-1}) = 5.203$

8th Asian-Pacific Chemical Reaction Engineering (APCRE 2017) Symposium
East China University of Science and Technology, Shanghai, China, Nov. 12-15, 2017
Kinetics: validation of group additivity

![Graph showing log(k)/log(k_Al) at 1000 K](image)

- H additions
- H β scission
- C addition
- C β scission
- H-abstraction

Outline

• Introduction
• Feedstock
• Kinetics
• Reactor
• Process
• Conclusions
Steam Cracking Pilot Plant

- Gas-Fired Furnace + Reactor
- High temperature sampling system
- Online Analysis Section
- Control “Room”

HC Feed → H2O

8th Asian-Pacific Chemical Reaction Engineering (APCRE 2017) Symposium
East China University of Science and Technology, Shanghai, China, Nov. 12-15, 2017
Pilot results: $C_1/C_2/C_3/C_4$

<table>
<thead>
<tr>
<th>Process conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>COT</td>
</tr>
<tr>
<td>COP</td>
</tr>
<tr>
<td>Steam dilution</td>
</tr>
</tbody>
</table>

without a single adjusted parameter
Industrial ethane/propane cracker

Satisfactory agreement for all major product yields, based on ab initio data only.
Outline

• Introduction
• Feedstock
• Kinetics
• Reactor: 3D alternatives
• Process
• Conclusions
Coke formation

Deposition of a carbon layer on the reactor surface

- Thermal efficiency
- Product selectivity
- Decoking procedures

Estimated annual cost to industry: $2 billion

Optimization by
- Feed additives
- Metallurgy & surface technology
- 3D reactor technology

Coke formation: 3D reactor technologies

Cokes formed here
T \uparrow \Rightarrow \text{ coking rate } \uparrow \uparrow

Reduce convective heat resistance

Increase surface area

Better mixing

~ 15 °C

~600 °C

T \uparrow \Rightarrow \text{ coking rate } \uparrow \uparrow

*Borealis.com, kubota.com, Technip.com

8th Asian-Pacific Chemical Reaction Engineering (APCRE 2017) Symposium
East China University of Science and Technology, Shanghai, China, Nov. 12-15, 2017
CFD and Coking kinetics: Coke layer growth

SOR (0 hrs)  SOR

48 hrs  10 days

8th Asian-Pacific Chemical Reaction Engineering (APCRE 2017) Symposium
East China University of Science and Technology, Shanghai, China, Nov. 12-15, 2017
Millisecond propane cracker

- Feedstock: 118.5 kg/h propane
- Propane conversion: 80.15% (± 0.05%)
- Steam dilution: 0.326 kg/kg
- CIT: 904°C
- COP: 170 kPa

- Different geometries simulated
- Same reactor volume
- Same axial length
- Same minimal wall thickness

Bare Fin c-Rib
Millisecond propane cracker: run length simulation

Increasing run length

Axial position [m]

Heat flux [W m⁻²]

SOR 48h 96h
Tube Metal Temperature

Thermal resistance coke layer $\rightarrow$ Max. TMT increases
Outline

- Introduction
- Feedstock
- Kinetics
- Reactor
- Process
- Conclusions
Outline

• Introduction
• Feedstock
• Kinetics
• Reactor
• Process: furnace
• Conclusions
Coupled reactor-furnace simulation

External coil temperature

Convergence

Reactor (COILSIM1D) \[\rightarrow \text{convergence} \rightarrow\] Furnace simulation

Heat flux to reactors

Hu, G. et al., Industrial & Engineering Chemistry Research, 54 (9), 2453-2465, 2015
Full furnace simulation

**Ultra Selective Conversion (USC)**

- 100% floor burner
- Fuel composition mol%: CH₄ (89%) - H₂ (11%)
- U coil
- Feedstock: Naphtha

**Coupled modeling**

- 3D CFD furnace model
- 1D reactor model (COILSIM1D)
- Detailed cracking kinetics (CRACKSIM)

Zhang, Y. et al., AIChE Journal 61 (3), 936-954, 2015
Flue gas: velocity and concentration fields

- Detailed case
  - Stronger turbulence
  - Faster reaction

Methane mole fraction

detailed  simplified

Zhang, Y. et al., AIChE Journal 61 (3), 936-954, 2015
Tube wall temperature field: local hot spots

This information is key for run length
Outline

• Introduction
• Feedstock
• Kinetics
• Reactor
• Process
• Conclusions
Conclusions

• Shannon Entropy maximization to reconstruct feedstocks in terms required for a microkinetic model (SIMCO)
• Consistent data set for thermochemistry and kinetics of hydrocarbon radical chemistry (CRACKSIM)
• Ab initio simulation of steam cracking of C$_2$/C$_3$/C$_4$
• Emergence of 3D reactor technologies: CFD as tool
• Integration of reactor/convection section/furnace (COILSIM1D)

Integration of computational chemistry methods with engineering tools, e.g. CFD, at larger time and length scales and experimental validation provides a powerful tool for the optimization and/or design of industrial units
Acknowledgments

• Profs. Marie-Françoise Reyniers, Maarten Sabbe, Feng Qian (ECUST)

• Drs. Steven Pyl, Nick Vandewiele, Thomas Dijkmans, Paschalis Paraskevas, Marko Djokic, Ruben Van de Vijver, David Van Cauwenberge, Andres Munoz (AVGI), Yu Zhang (ECUST)

• PhD students Pieter Reyniers, Laurien Vandewalle, Nenad Ristic, Florence Vermeire, Moreno Geerts, Aleksandar Bojkovic, Muralikrishna Khandavilli
GLOSSARY

• SFT: Swirl Flow Tube, a tube with a helicoidal centerline. The helix amplitude is smaller than or equal to the tube radius.
• Swirl flow: a whirling or eddying flow of fluid.
• Swirl number: ratio of tangential over axial momentum transfer
• Wall shear stress: component of stress parallel with the wall. It is the product of the viscosity and the derivative of axial velocity with respect to the radial coordinate.