UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

Bridges in modelling and simulation of steam cracking: from fossil to renewable feedstock and from molecule to furnace

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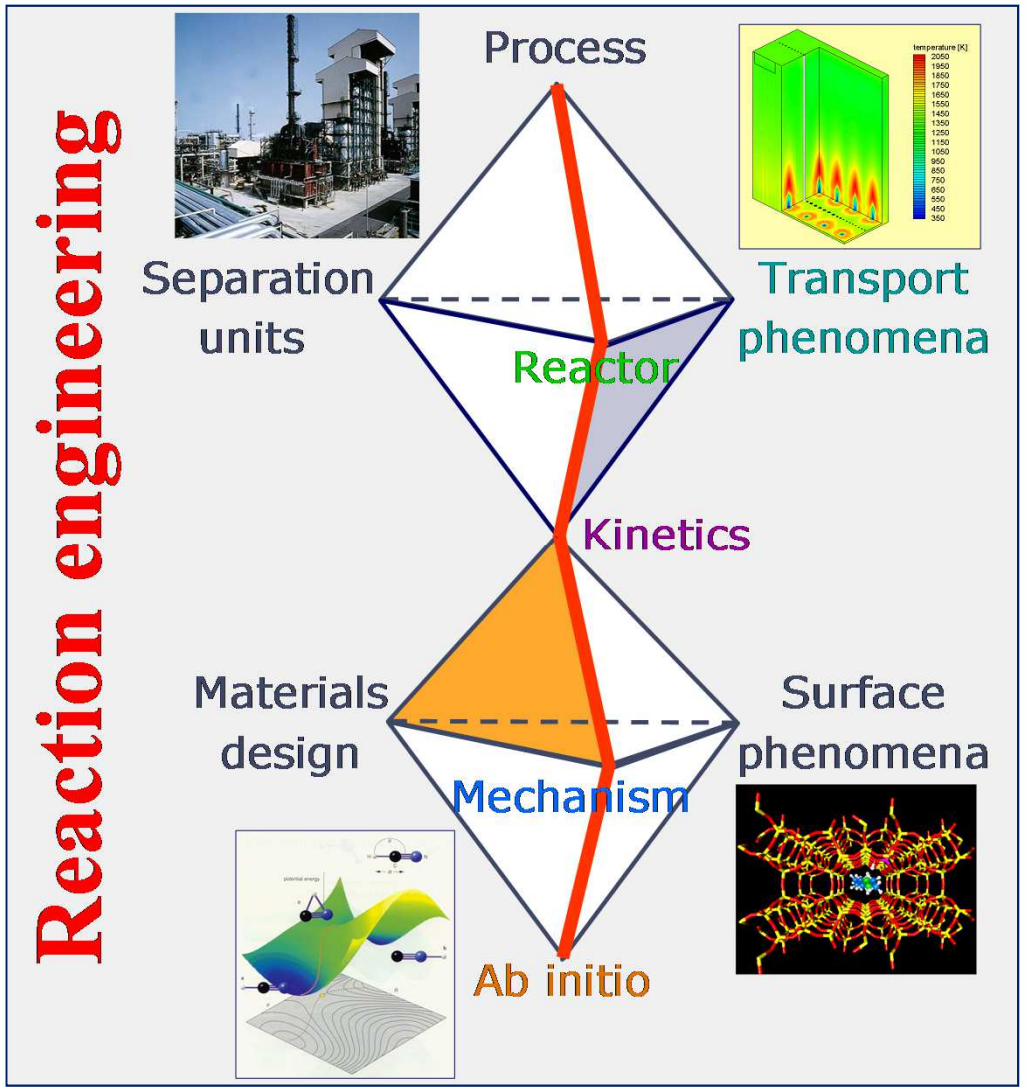
http://www.lct.UGent.be

66th Canadian Chemical Engineering Conference "Sustainability & Prosperity"
October 16-19 (2016) Québec City (Canada)

ERIC

From molecule to industrial plant



Process level

Molecular level

Steam cracking: from fossil to renewables

Crude oil

Natural gas

Bio-based feeds

Naphtha

Light gasoil

crude oil

Natural gas liquids

Gas-condensates

Hydrode-oxygenated FAME

Steam cracking

Ethene

Propene

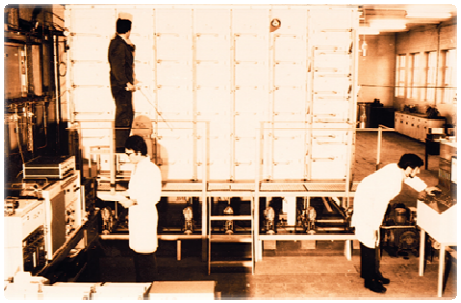
Butadiene

Aromatics

Consumer goods from chemical industry

atozforex.com; pnnl.org; districtenergy.org; scade.fr; schmidt-clemens.de; Linde Group

Steam cracking: Ghent University history



Pilot plant starts operation

First commercial license sold

Implementation of GCxGC

Pilot plant revamped

AVGI

1974 1976 1978 2001 2004 2006 2008 2010 2012 2015 2016

COILSIM3D, continuous expansion of kinetic network, …

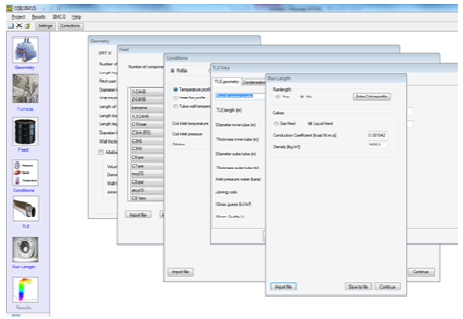
First simulations of steam cracking

First kinetics of coke formation

Large expansion of kinetic network

TLE model

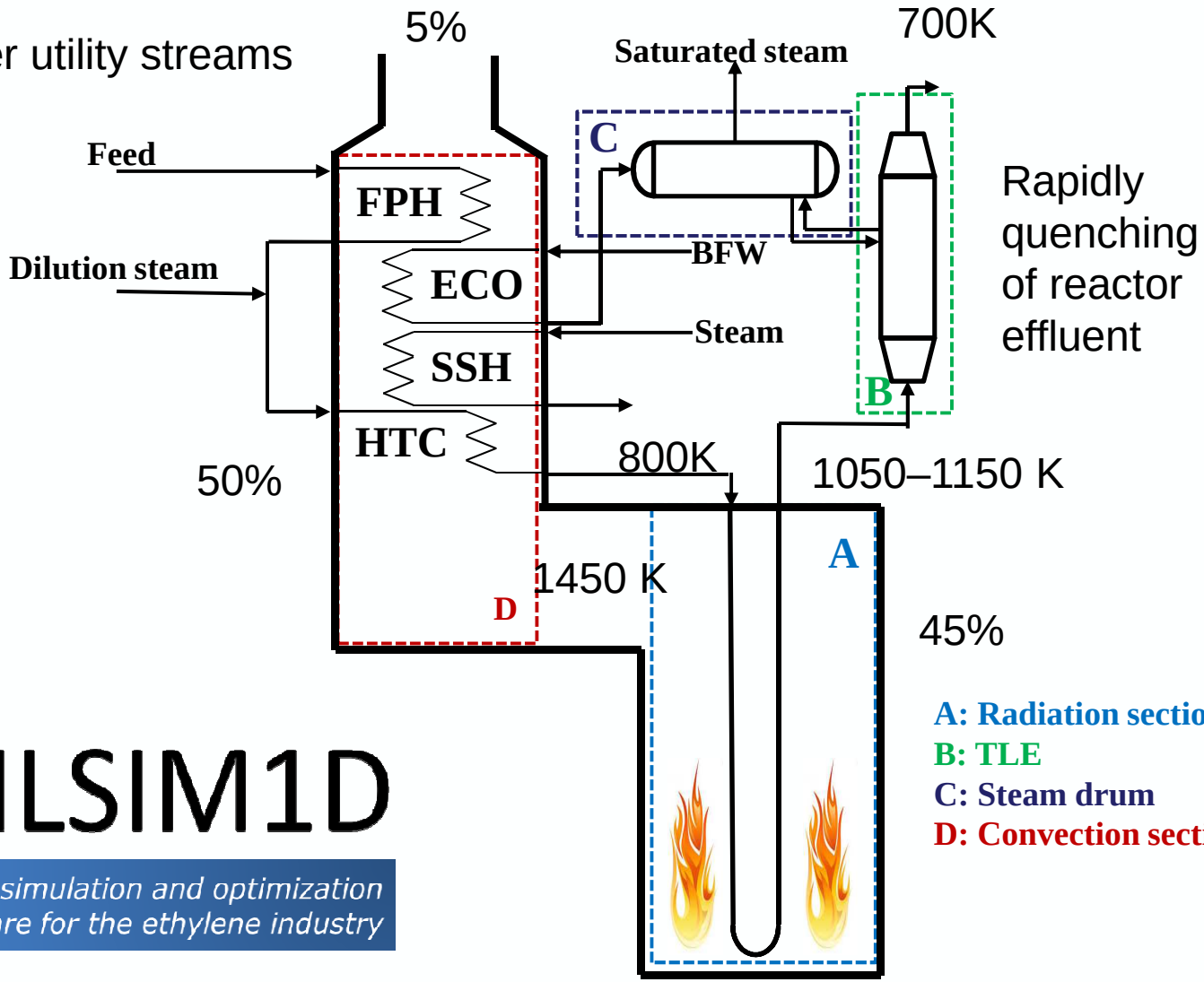
COILSIM1D's GUI implementation



Kinetic expansion; Firebox and convection models

Steam cracking: hot section

Preheat feed and other utility streams



Rapidly quenching of reactor effluent

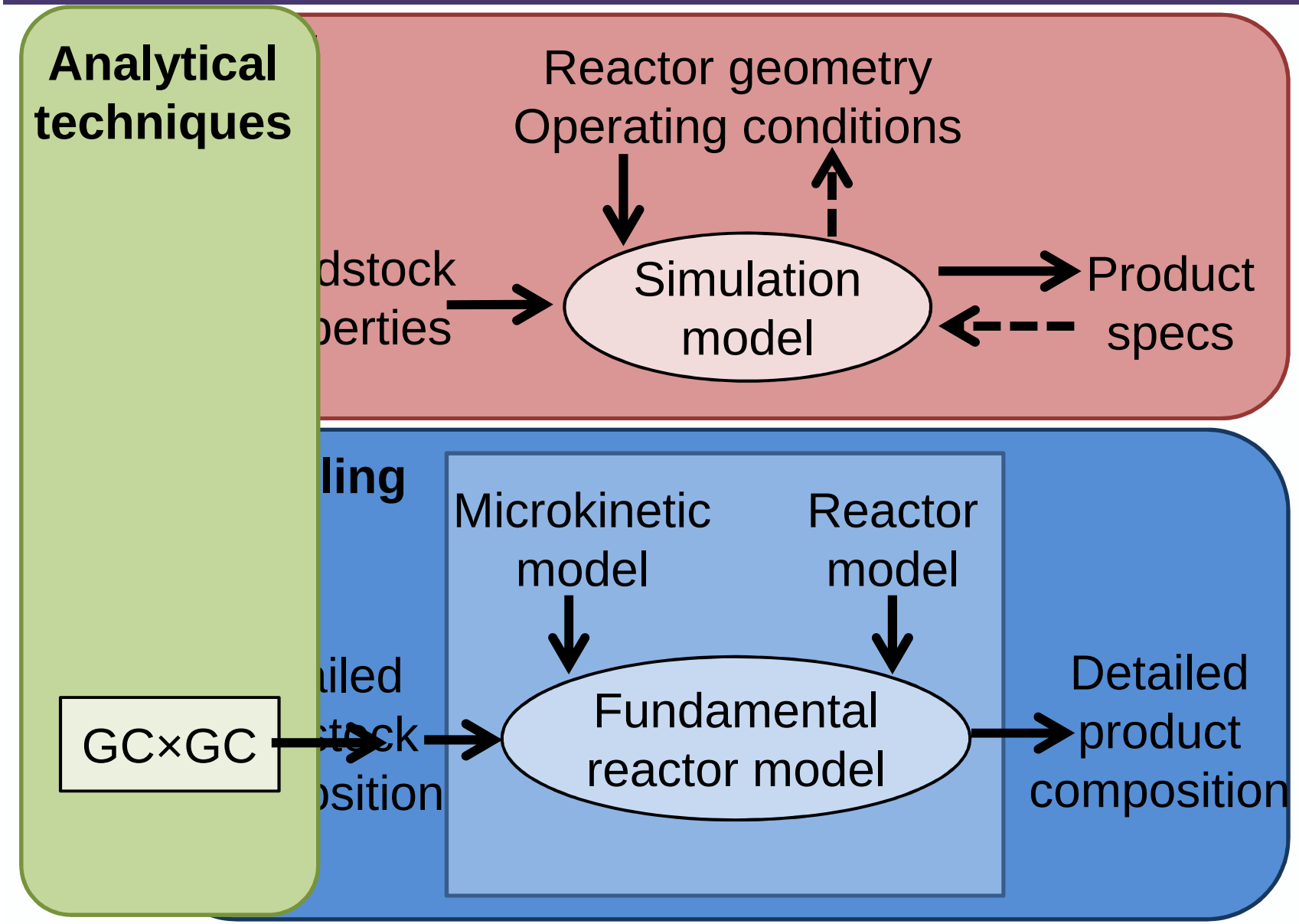
AVGI

COILSIM1D

The advanced simulation and optimization software for the ethylene industry

Endothermic process 1050–1150 K

Reaction and reactor model



Ristic, N.D. et al.,Journal of Visualized Experiments, Issue 114Toraman, H.E. et al., Journal of Chromatography A, 1460, 135-146, 2016

Outline

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

Outline

- Introduction
- Feedstock: characterization
- Kinetics
- Reactor
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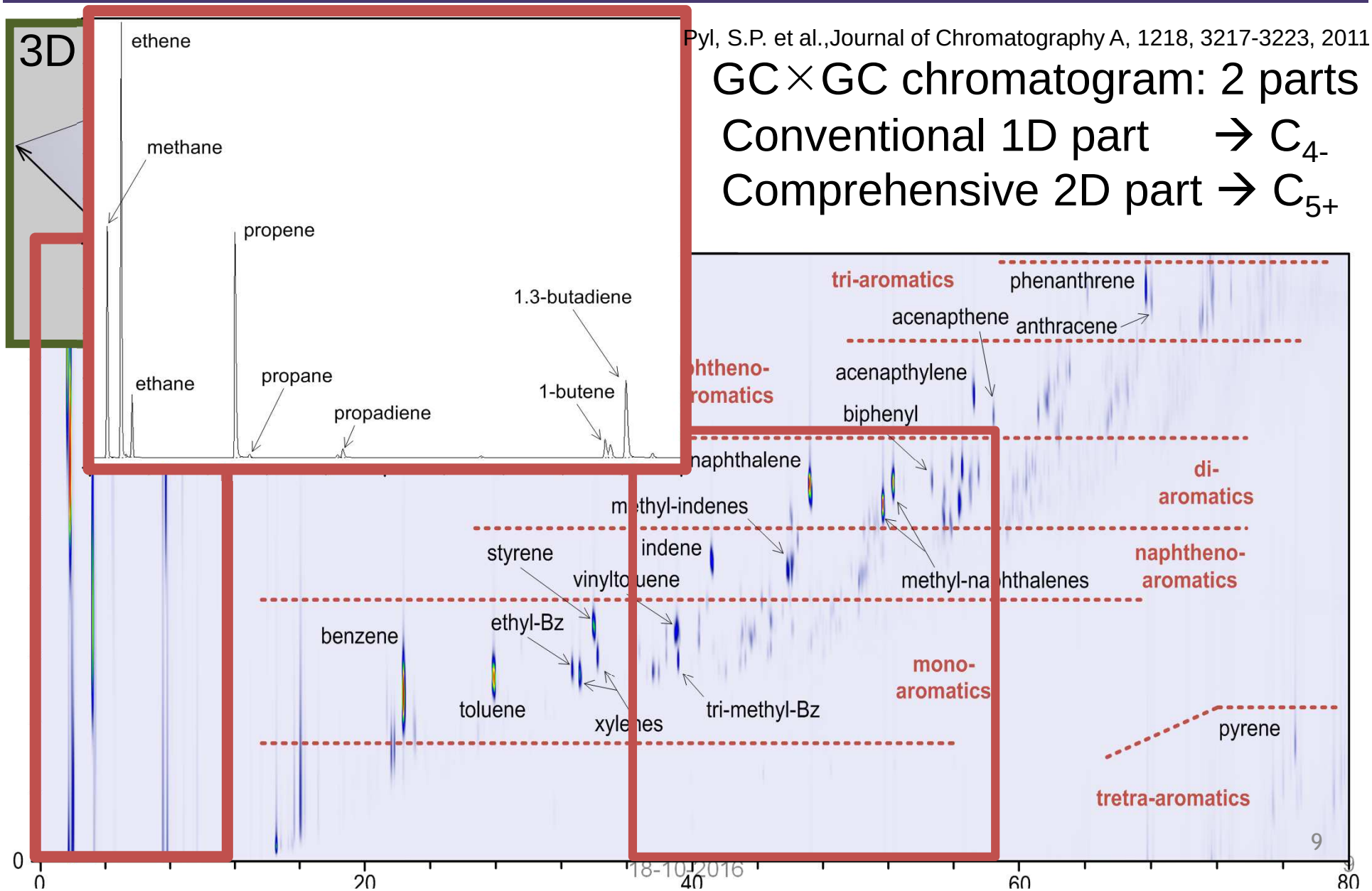
On-line GCxGC

Pyl, S.P. et al.,Journal of Chromatography A, 1218, 3217-3223, 2011

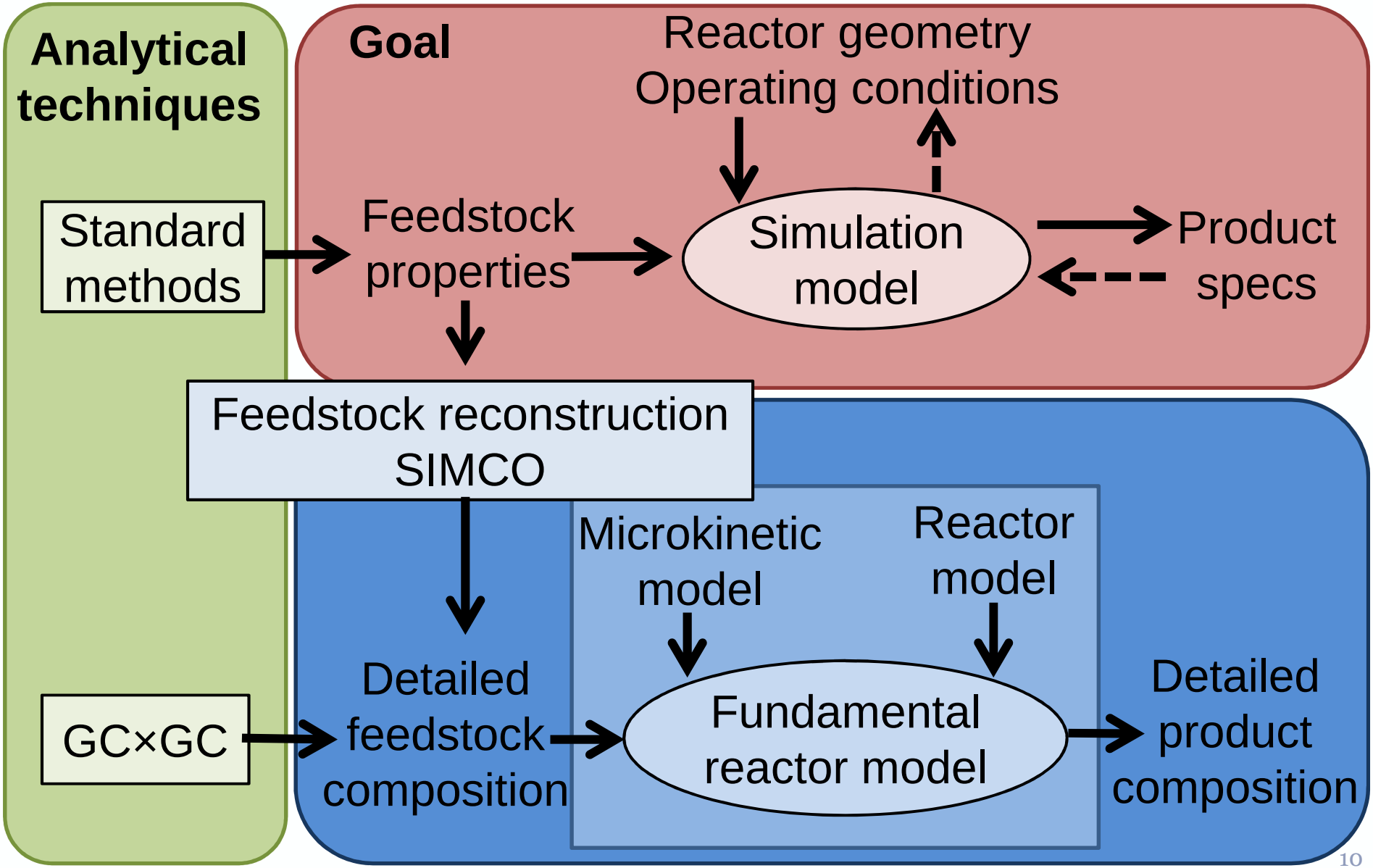
GC×GC chromatogram: 2 parts

Conventional 1D part → C_{4-}

Comprehensive 2D part → C_{5+}



SIMCO: ANN or Shannon entropy



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

Feedstock reconstruction

Shannon entropy maximization

Detailed composition

- Species identity
- Mole or mass fractions

$$\text{MAX} \quad S(y_i) = -\sum_{i=1}^{N_M} y_i \ln(y_i) \qquad \text{with} \quad \sum_{i=1}^{N_M} y_i = 1$$

± 20 properties

Constraints from mixing rules (example):

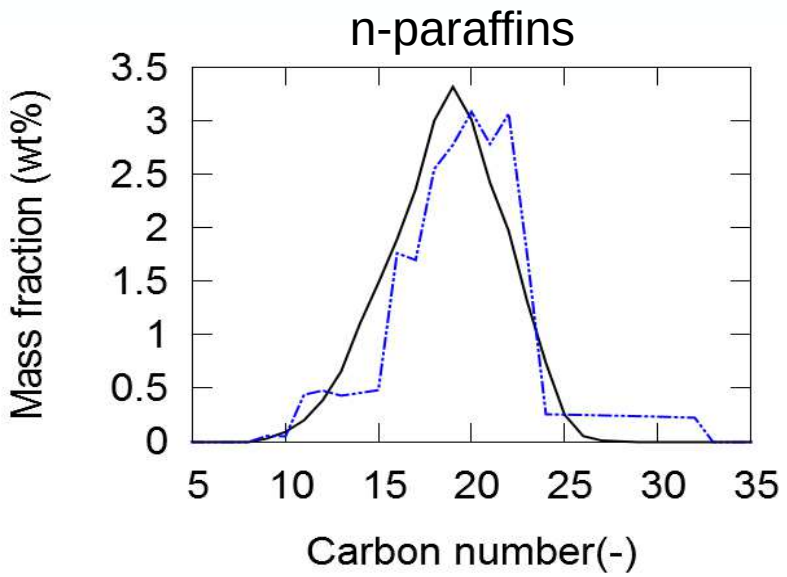
$$\frac{1}{\mathrm{d}_{\exp}} = \sum_{i=1}^{N_M} \frac{y_i \mathrm{Mw}_i}{\mathrm{d}_i \sum y_i \mathrm{Mw}_i}$$

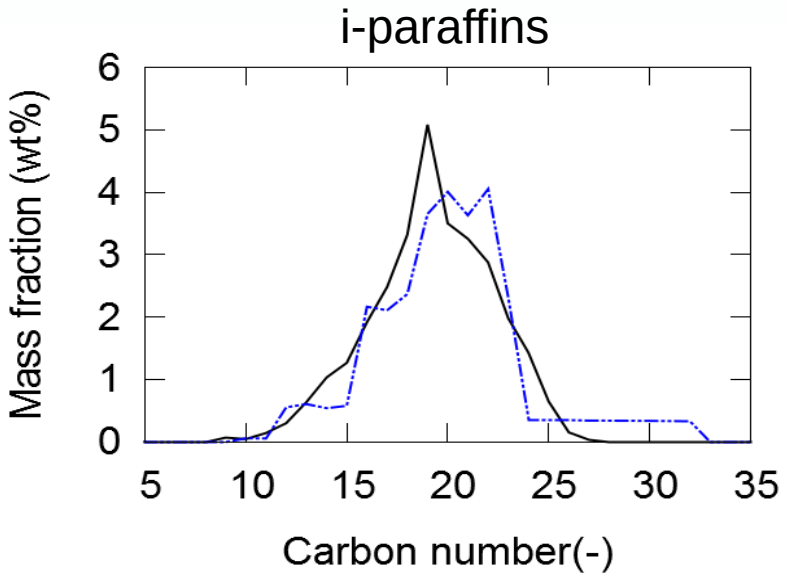
More than 100 unknown mole fractions

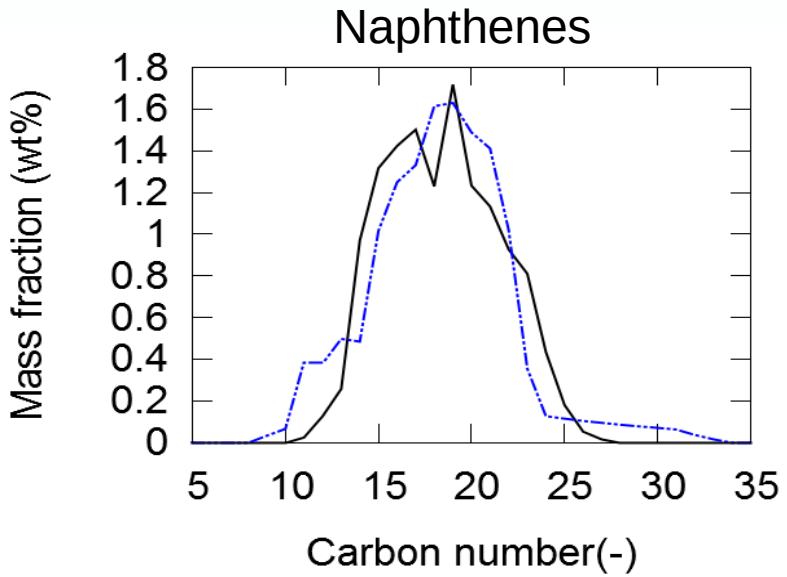
$$\mathrm{Mw}_{\exp} = \sum_{i=1}^{N_M} y_i \mathrm{Mw}_i$$

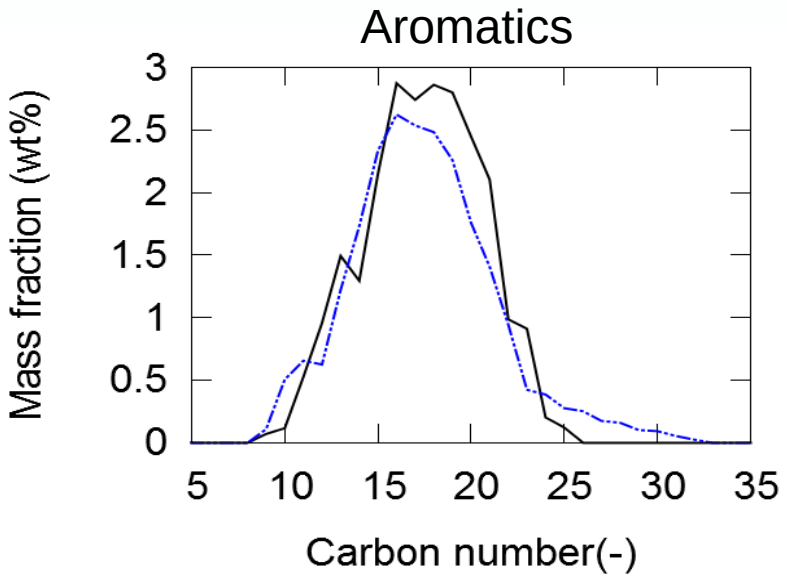
S.P. Pyl et al., AIChE Journal, 56, 12, 3174-3188, 2010

SIMCO results: Hydrocarbons









Outline

- Introduction
- Feedstock: renewables
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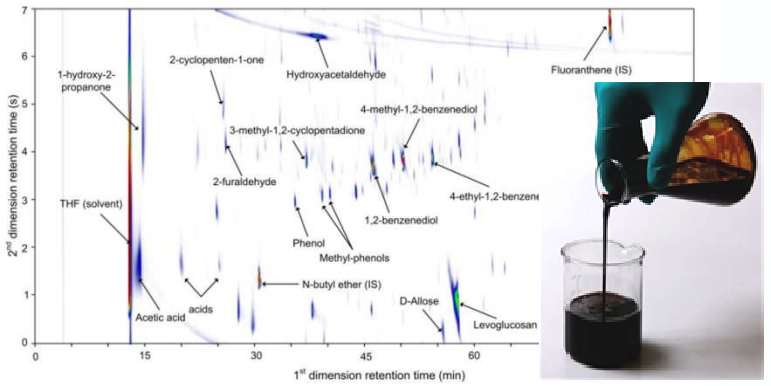
Thermochemical conversion of biomass

GAS

CO H_2 NH_3 CO_2 CH_4 H_2O C_2H_4 HCN

BIO-OIL



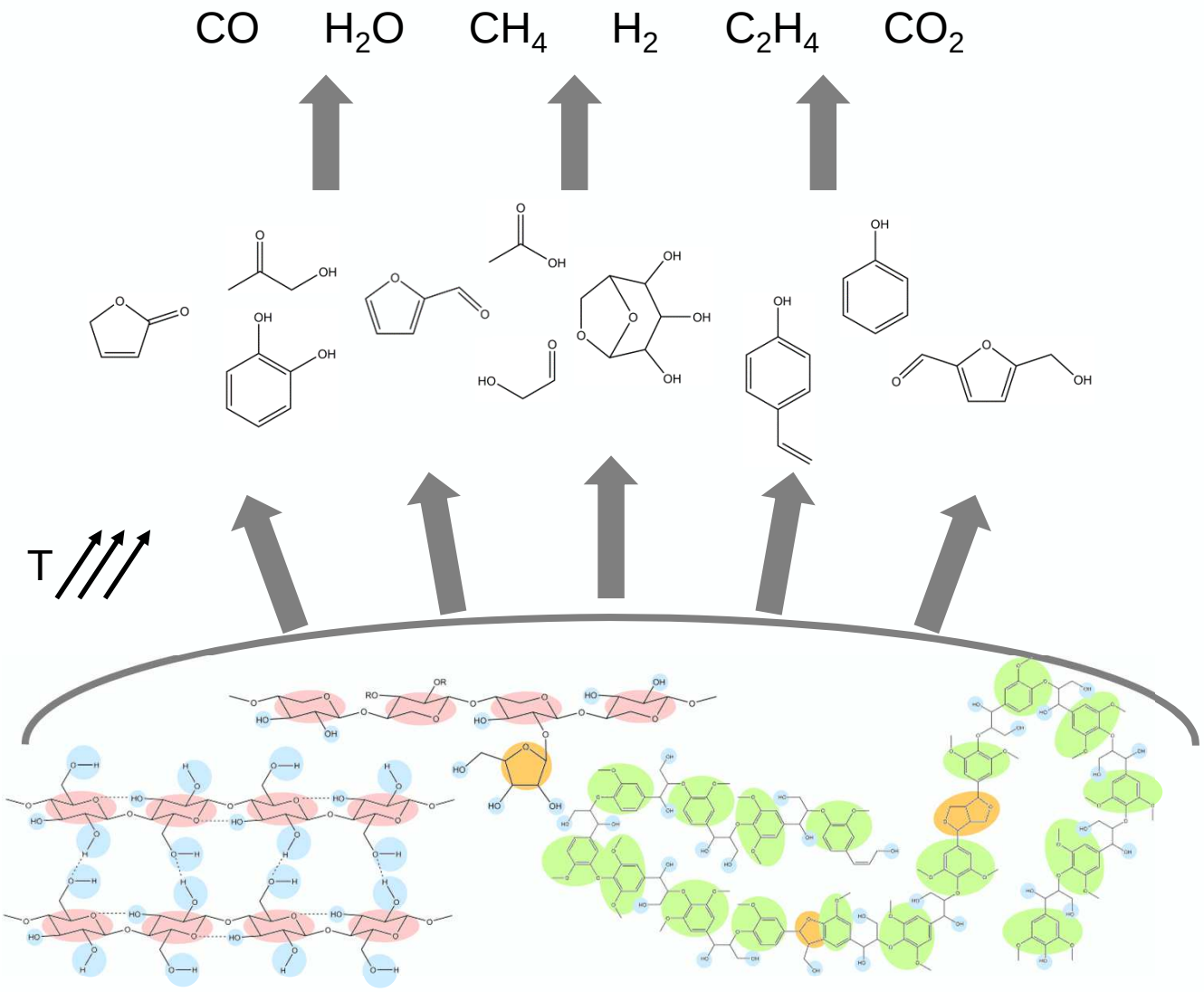
CHAR

5wt%	Torrefaction	20wt%
35wt%	Slow pyrolysis	30wt%
13wt%	Fast pyrolysis	75wt%
85wt%	Gasfication	5wt%
		75wt%
		35wt%
		12wt%
		10wt%

LIGNOCELLULOSIC BIOMASS

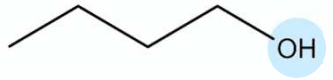
Toraman, H.E.et al.,Bioresource Technology, 207, 229-236, 2016

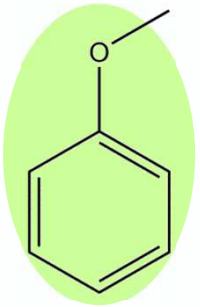
Model components for biomass pyrolysis



Study molecules with structural moieties found in biomass

For example:

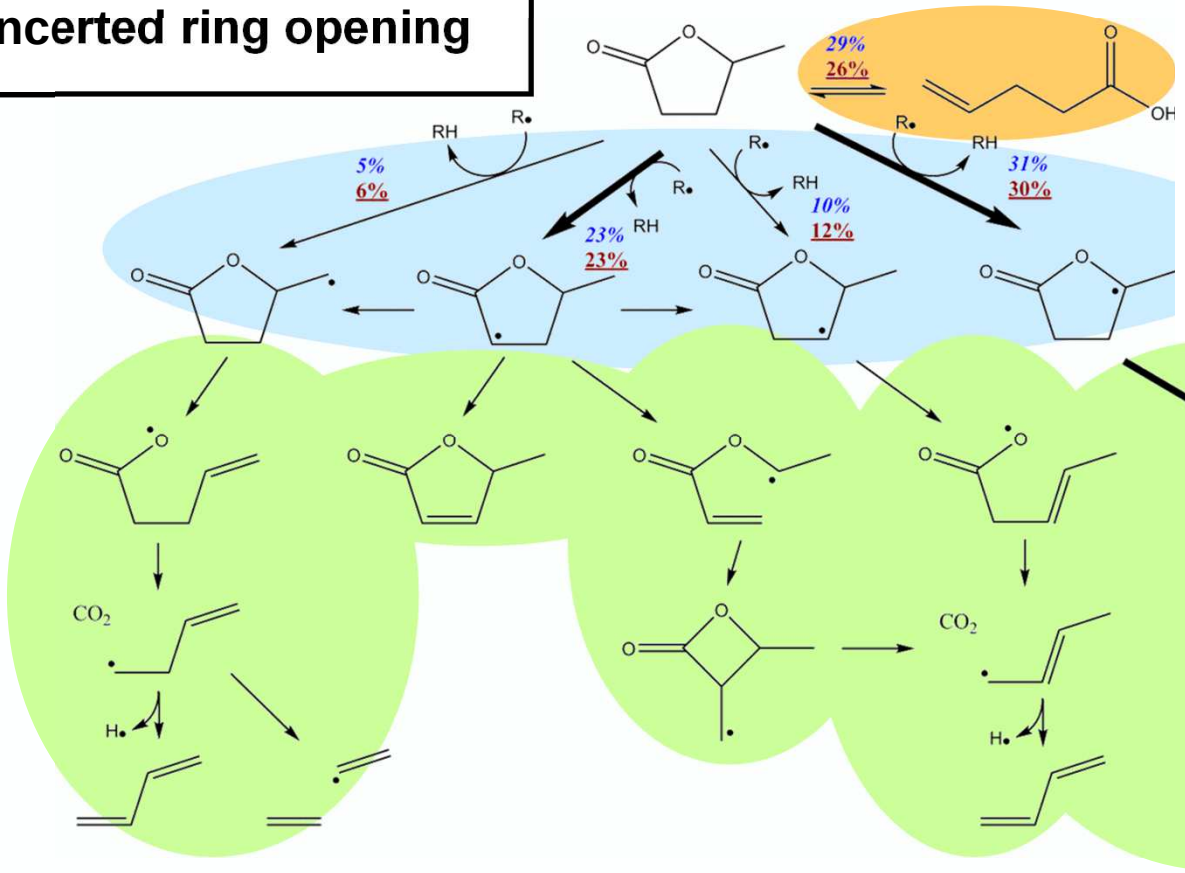


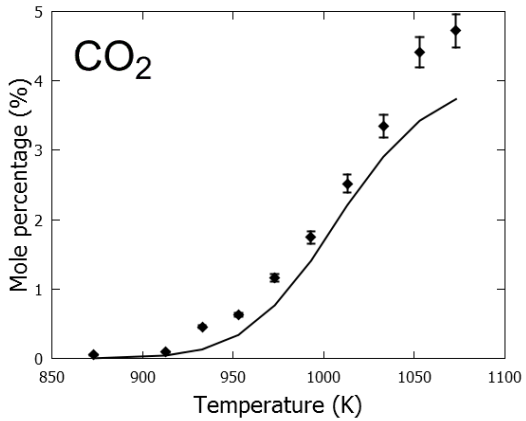


aleroLactone (GVL) pyrolysis

Reaction families

1) Scission
2) Hydrogen abstraction
3) β-scission/addition
4) Concerted ring opening





De Bruycker, R. et al., Combustion and Flame, 164, 183-200, 2016
De Bruycker, R. et al.,Proceedings of the Combustion Institute, 35, 515-523, 2015

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- Kinetics
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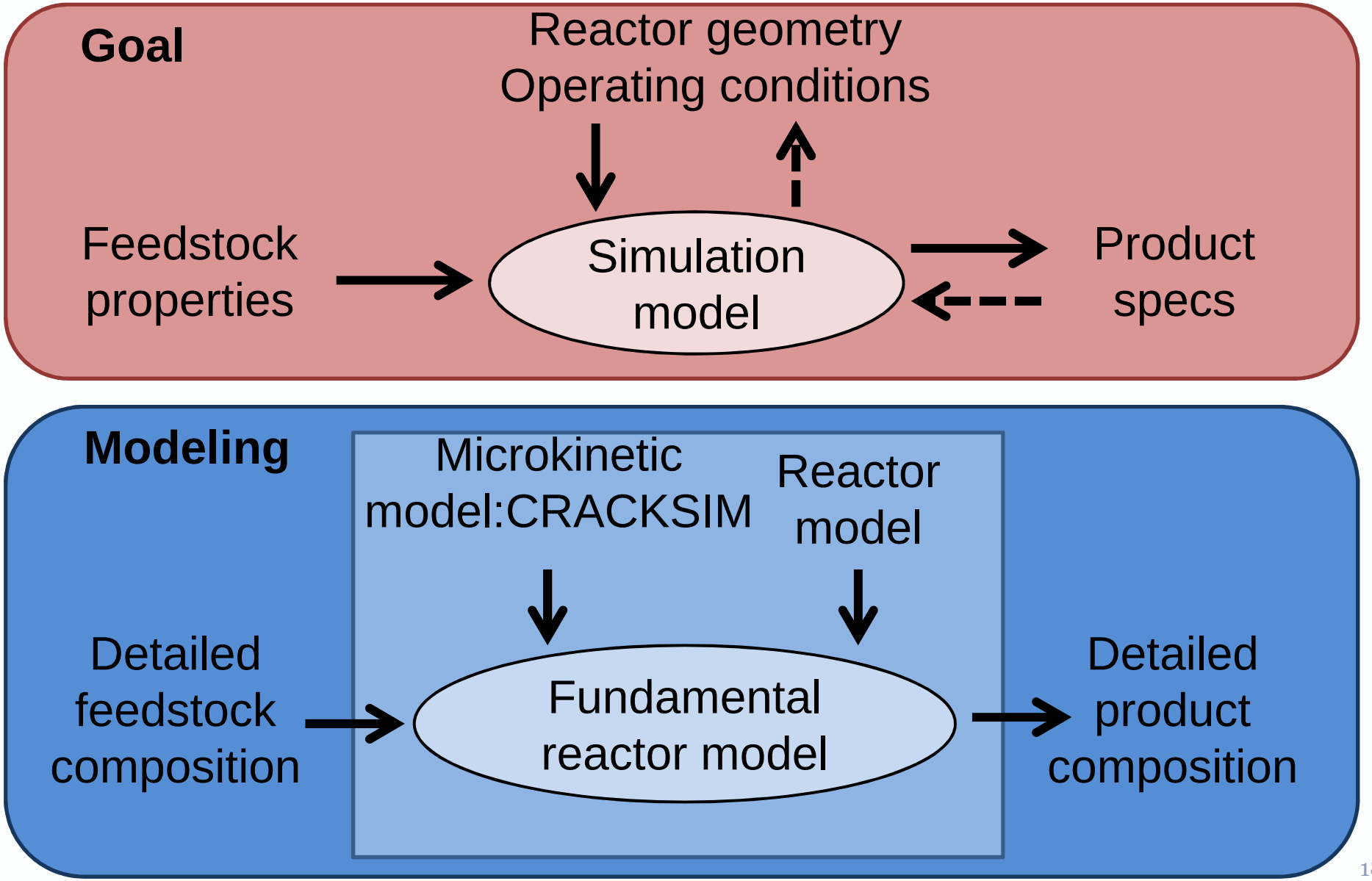
CRACKSIM: steam cracking kinetics



Outline

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- Kinetics: reaction network
- Reactor
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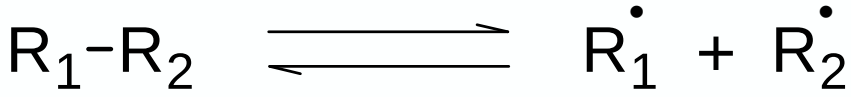
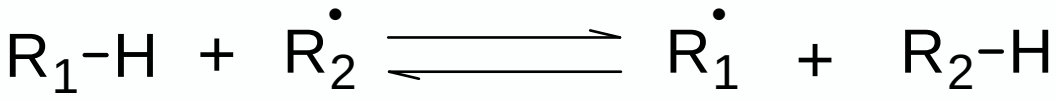
Families of elementary reactions

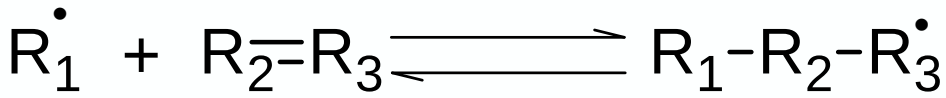
Bond dissociation and radical recombination



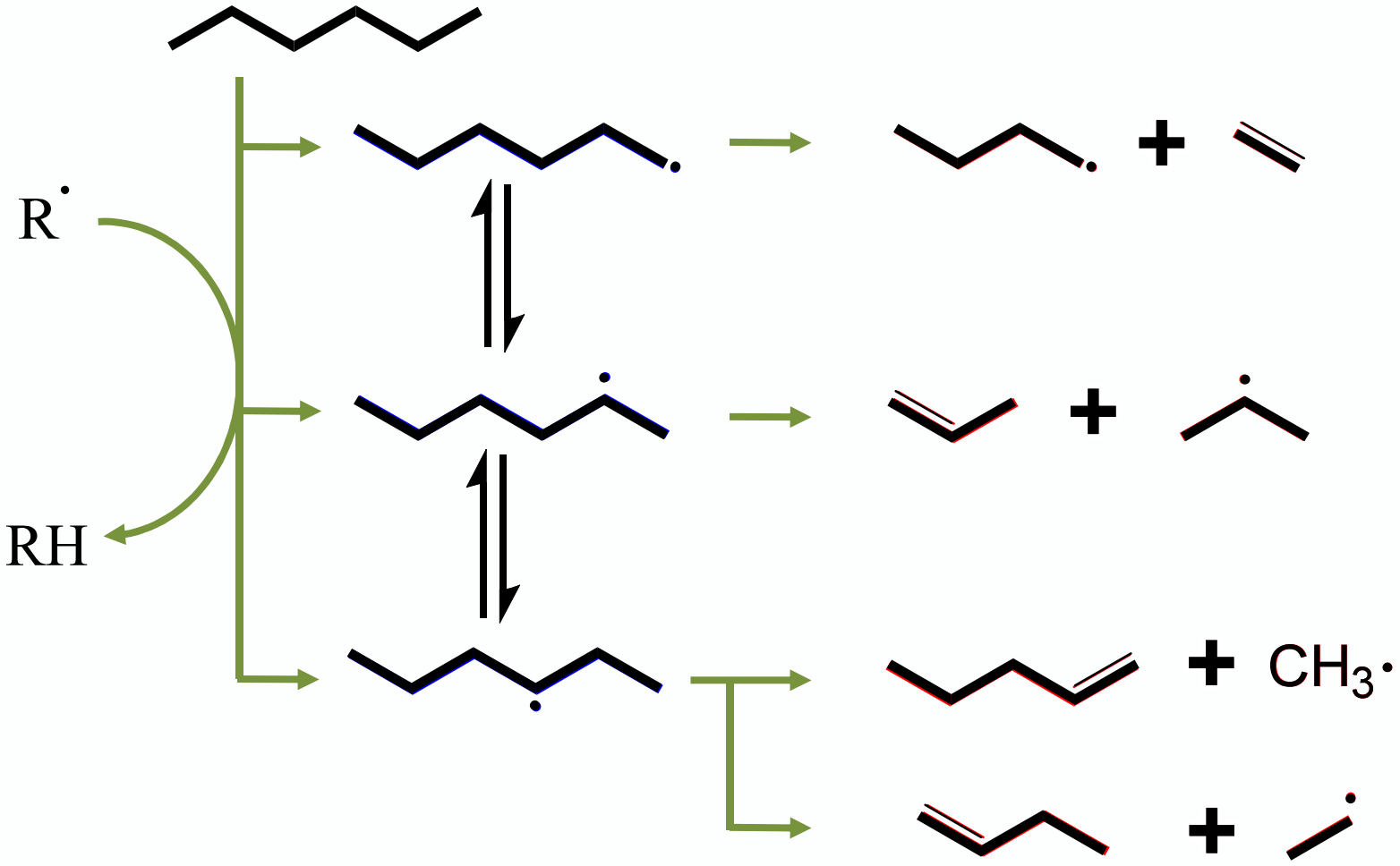
Hydrogen abstraction (inter- and intramolecular)



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



Decomposition scheme: n-hexane



β species

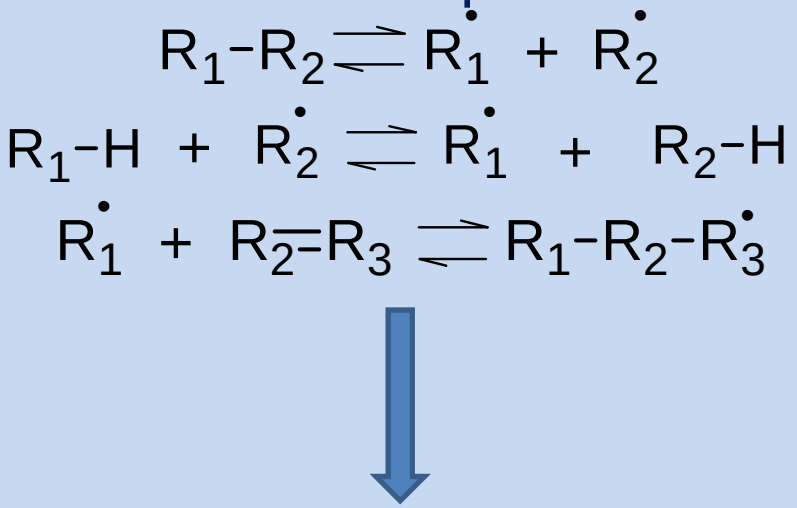
PSSA to μ radicals

μ and β networks: CRACKSIM

CRACKSIM

β network

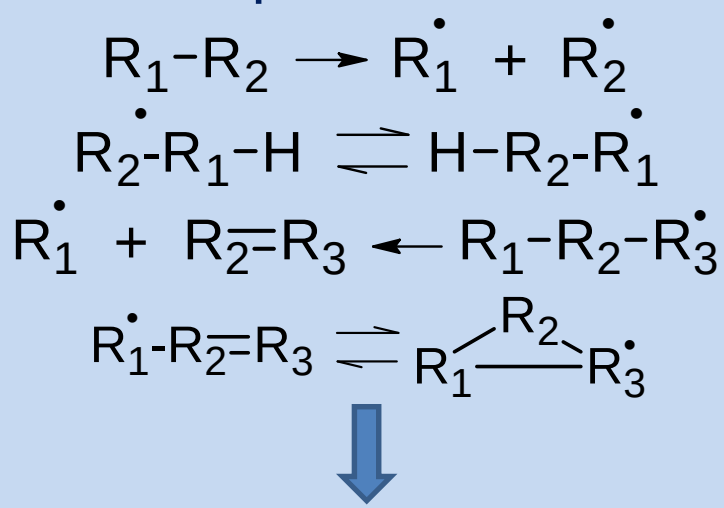
Bi- and monomolecular reactions for β radicals



1324 reversible reactions
51 molecules
43 radicals

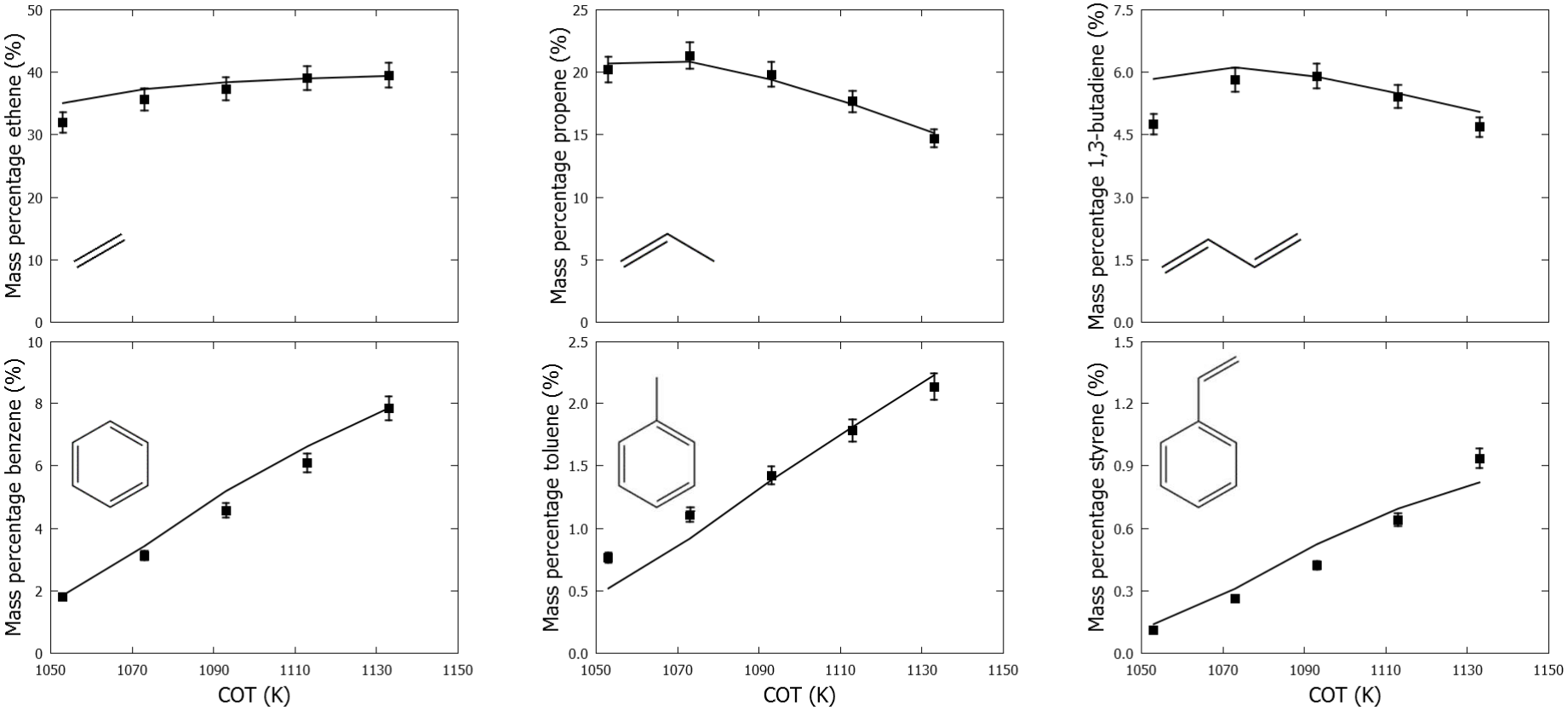
μ network

Monomolecular reactions for μ radicals



13584 schemes
676 molecules

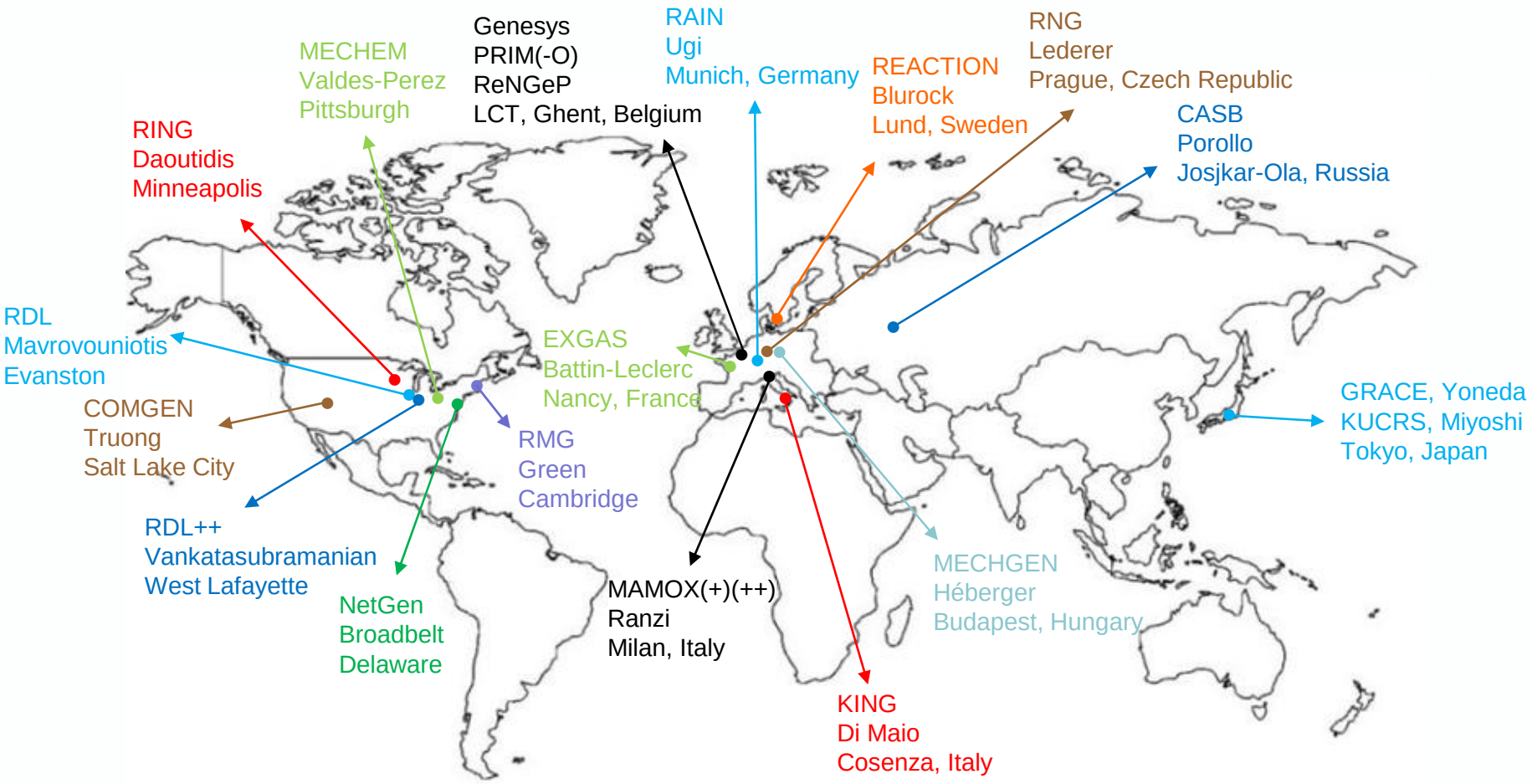
Validation



- **Experimental yields during steam cracking of bio-derived hydrocarbons**
  Feedstock composition: $MW_{average}$ = 230g/mol 51wt% normal alkanes – 49wt% branched alkanes
  $F_{HC,0}$ = 0.04 g/s, $F_{H2O,0}$ = 0.02 g/s, P = 0.17 MPa

—— **calculated**

Network generators



A new program for kinetic model construction

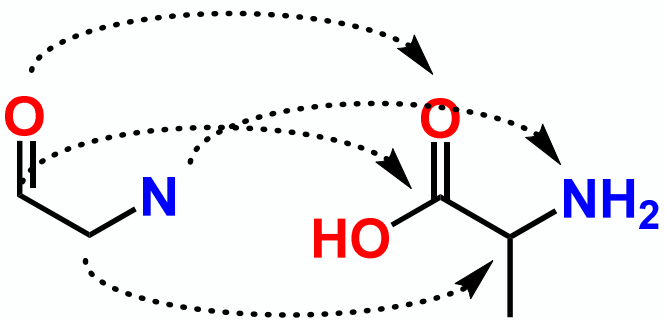
GENESYS - GENEration [of reacting] SYStems

Genesys: Kinetic model construction using chemo-informatics
Vandewiele, N.M.; Van Geem, K.M.; Reyniers, M.-F.; Marin, G.B.
Chemical Engineering Journal, 207-208, 526-538, 2012

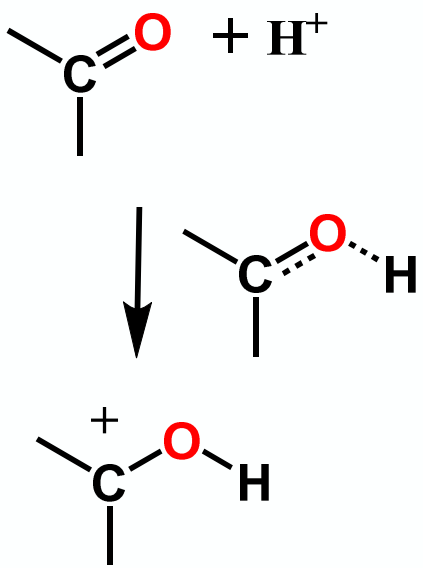
Van de Vijver, R. et al. International Journal of Chemical Kinetics, 47 (4), 199-231, 2015

Graph theory yields powerful algorithms

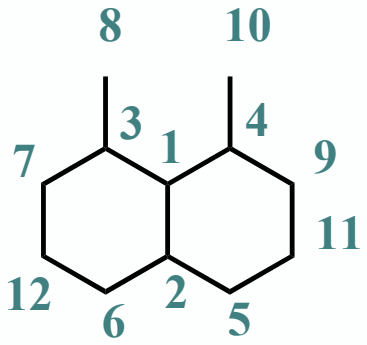
Pattern Recognition

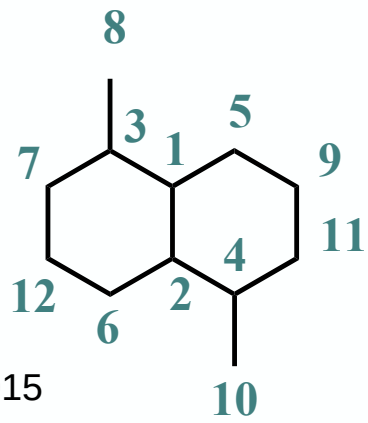


Reactant -> product



Molecule Identifiers





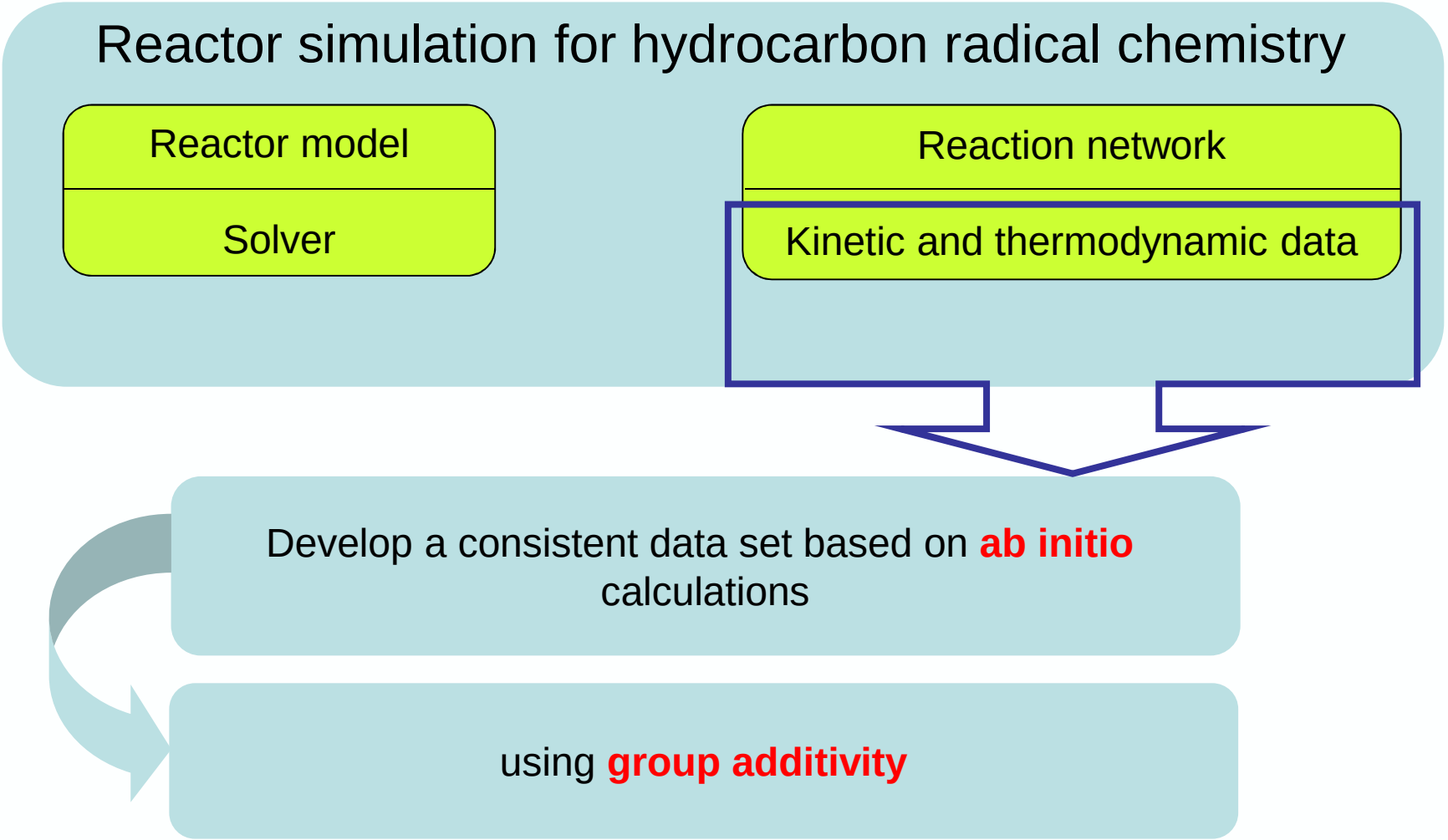
"Kinetics of Chemical Reactions : Decoding Complexity"
G.B. Marin and G.S. Yablonsky,Wiley-VCH Verlag, 446 pages, 2011

Vandewiele, N.M. et al., Journal of Computational Chemistry, 36 (3), 181-192, 2015

Outline

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

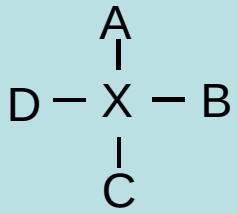
Objective: data base



Van de Vijver, R. et al., Chemical Engineering Journal, 278, 385–393, 2015

Benson's group additive method

Benson group



Notation: X-(A)(B)(C)(D)

X: Central atom

Valence ≥ 2

{ C, C_d, O, CO, CCO, C•, C_d• }

A, B, C, D: Ligand

H, C, C_d , O, CO, CCO,
C•, C_d•, O•,CO•,CCO•

Group additivity for thermochemistry

$$f = \sum_i GAV_f(\text{group}_i) + \sum_j NNI_j$$

$$f = \Delta_f H°, S°_{\text{int}}, C°_p \qquad S°_{\text{int}} = S° + R\ln\left(\frac{\sigma}{n_{\text{opt}}}\right)$$

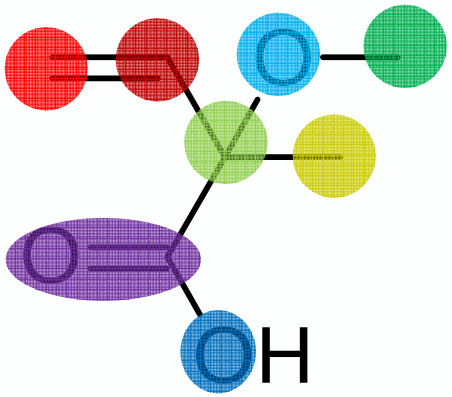
Group additive values (**GAV**)

Corrections for non-nearest-neighbor interactions (**NNI**)

- ✓ hydrogen bonds
- ✓ gauche interactions
- ✓ other interactions

From small to large species with group additivity

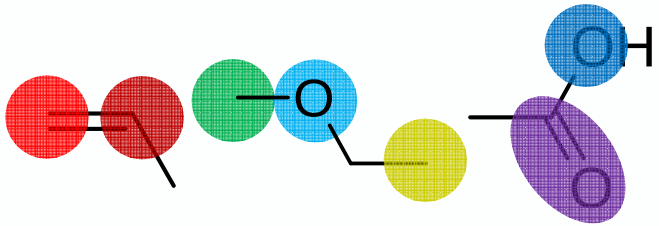
2-methoxy-2-methylbut-3-enoic acid



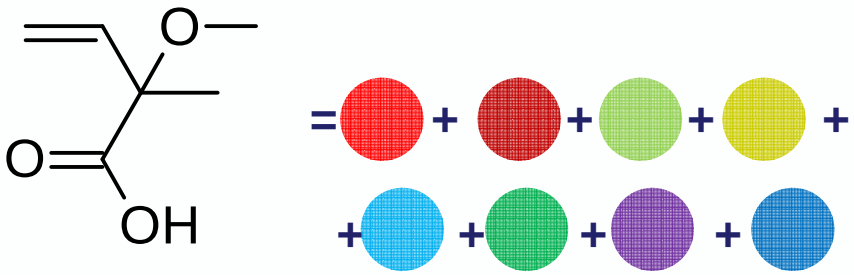
Atoms in large molecules

Group additivity

Atoms in small molecules with similar surroundings



Additivity



additive groups

- C_d-$(H)_2$
- C_d-(C)(H)
- C-(C)(C_d)(O)(CO)
- O-$(C)_2$
- C-(O)$(H)_3$
- C-(C)$(H)_3$
- CO-(C)(O)
- O-(CO)(H)

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Ince, A.et al. AIChE Journal, 61 (11), 3858–3870, 2015

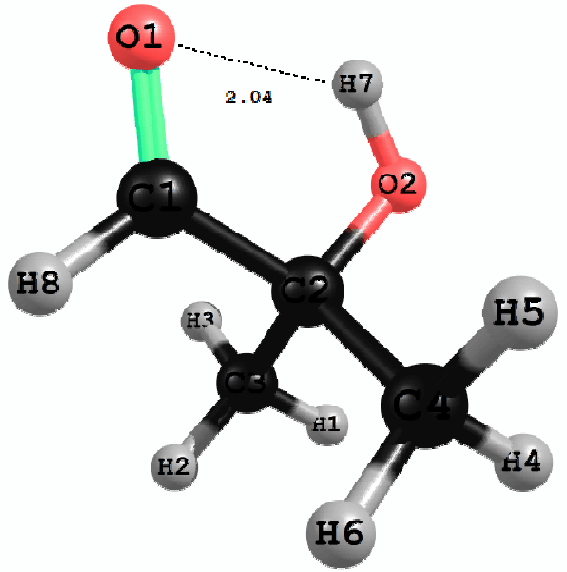
Thermo e.g. for oxygenates: GAV data base

Database of thermodynamic data, $\Delta_f H°$, $S°$ and $C_p°$ (300 K-1500 K)

- 450 oxygenate compounds
- CBS-QB3 methodology
- 1D-HR approximation for all internal rotors

- 157 GAVs using Benson's GA method
- 26 NNI corrections (mainly hydrogen bonds)
- 77 HBIs for the thermochemistry of radicals

2-hydroxy-2-methyl-propanal



NNI8 Hbr_H-O-C-CO

Outline

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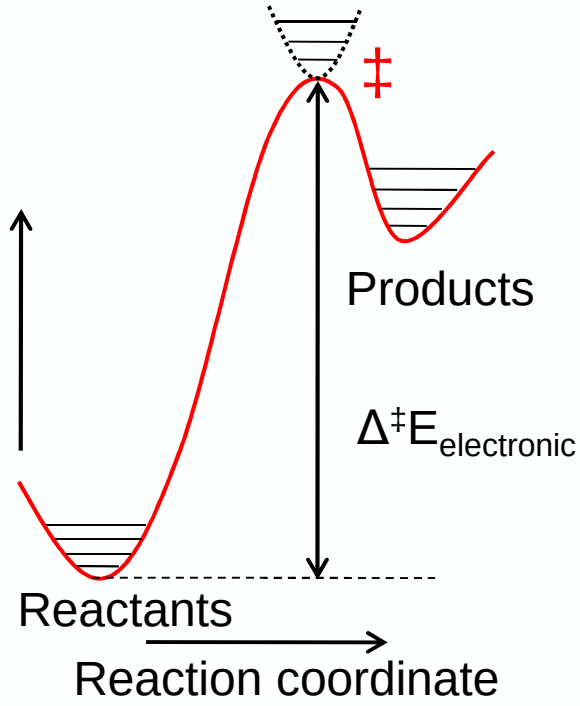
Kinetics: computational approach

Conventional Transition State Theory (high pressure limit)

A + B $\rightleftharpoons$ **[AB]**‡ $\rightleftharpoons$ **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 ΔE_0

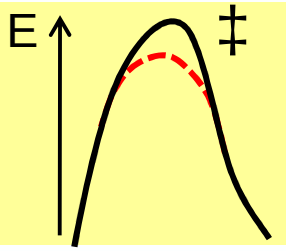
The CBS-QB3 ab initio method is used.

Partition functions *q*

- Ideal gas approximation
- Hindered Rotor (1D-HR)

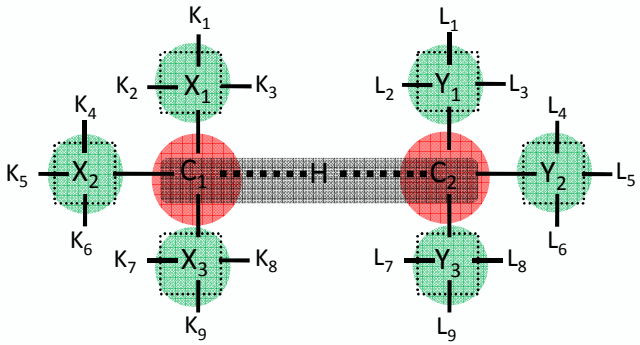
Tunneling coefficient κ

- Eckart



Group additivity for kinetics:data base of ΔGAV°

Transition state for hydrogen abstraction



Arrhenius equation

$$k = Ae^{-\frac{E_a}{RT}}$$

$$k = \kappa_{Eckart} n_e k_{GA} = \kappa n_e \tilde{A} e^{-\frac{E_a}{RT}}$$

Number of single events

$$n_e = \frac{n_{opt,\ddagger}}{\prod_j n_{opt,j}} \frac{\prod_j \sigma_j}{\sigma_\ddagger}$$

Group additivity for Arrhenius parameters

Primary **Secondary** **Tertiary**

$$E_a(T) = E_{a,ref}(T) + \sum_{i=1}^{2} \Delta GAV^{\circ}_{E_a}(C_i) + \sum_{i=1}^{3} \Delta GAV^{\circ}_{E_a}(X_i) + \sum_{i=1}^{3} \Delta GAV^{\circ}_{E_a}(Y_i) + \Delta E^{\circ}_{E_{a,res}}$$

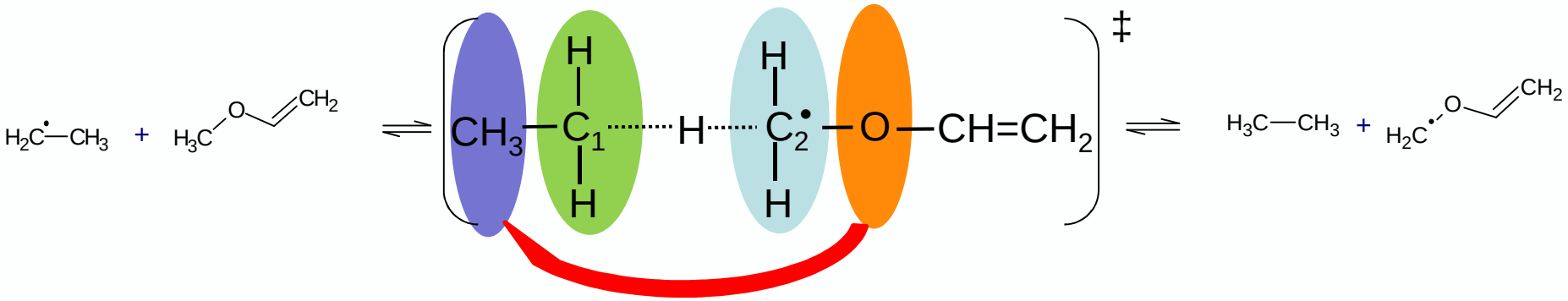
$$\log \tilde{A}(T) = \log \tilde{A}_{ref}(T) + \sum_{i=1}^{2} \Delta GAV^{\circ}_{\log \tilde{A}}(C_i) + \sum_{i=1}^{3} \Delta GAV^{\circ}_{\log \tilde{A}}(X_i) + \sum_{i=1}^{3} \Delta GAV^{\circ}_{\log \tilde{A}}(Y_i) + \Delta \log \tilde{A}^{o}_{res}$$

Proposed by Saeys et al. for activation energies (*AIChE J.* **2004,** *50* (2), 426-444.)
Extended by Sabbe et al. for pre-exponential factors (*Phys. Chem. Chem. Phys.* ***2010***, *12*, 1278-1298)

Kinetics: data base of ΔGAV°

Hydrogen abstraction (*ethyl* + ethenyl methylether)

Paraskevas, P. et al.,Journal of Physical Chemistry A, 119 (27), 6961-6980, 2015



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

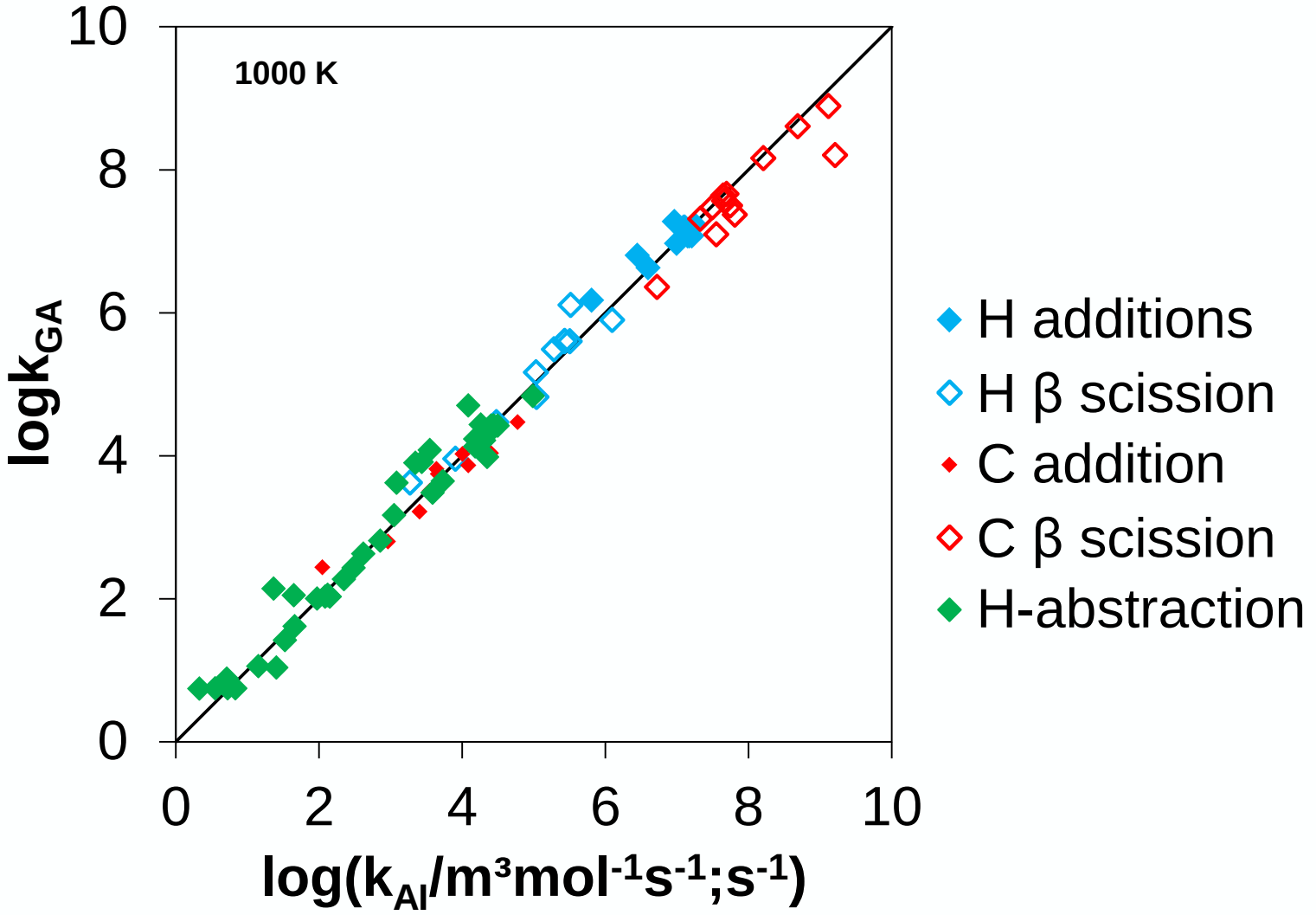
$CH_3 + CH_4$	C_1-(C)(H)$_2$	C_2-(O)(H)$_2$	C-(C_1)(H)$_3$	O-(C_2)(C_d)	
69.7 kJmol^{-1}	+4.7 kJmol^{-1}	-18.2 kJmol^{-1}	+0 kJmol^{-1}	+6.8 kJmol^{-1}	-0.4 kJmol^{-1}

$E_{a,GA}$ = 62.6 kJmol^{-1} ⟺ $E_{a,\ ab\ initio}$ = 62.0 kJmol^{-1}

$CH_3 + CH_4$	C_1-(C)(H)$_2$	C_2-(O)(H)$_2$	C-(C_1)(H)$_3$	O-(C_2)(C_d)	
5.268	-0.866	-0.512	+0	+0.480	-0.053

$\log(A_{GA}/m^3\ mol^{-1}s^{-1})$ = 5.095 ⟺ $\log A_{ab\ initio}$ = 5.203

Kinetics: validation of group additivity



Sabbe et al. *ChemPhysChem* **2008,** *9* (1), 124-140
Sabbe et al. *ChemPhysChem*, **2010**, 11(1), 195-210
Sabbe et al. *PhysChemChemPhys,* **2010**, 12 (6), 1278-1298

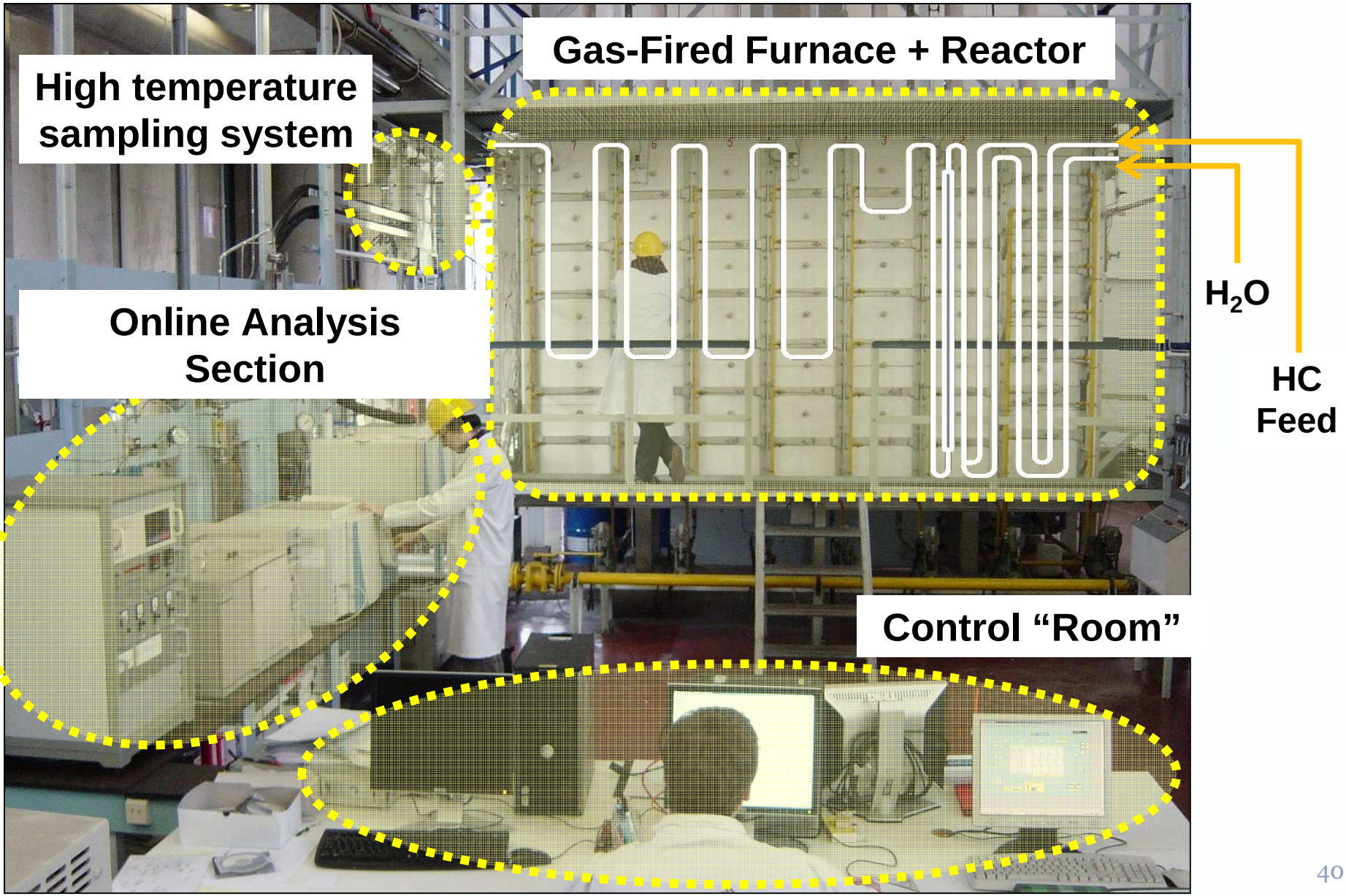
Outline

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

Outline

- Introduction
- Feedstock
- Kinetics
- Reactor : pilot scale
- Process
- Conclusions

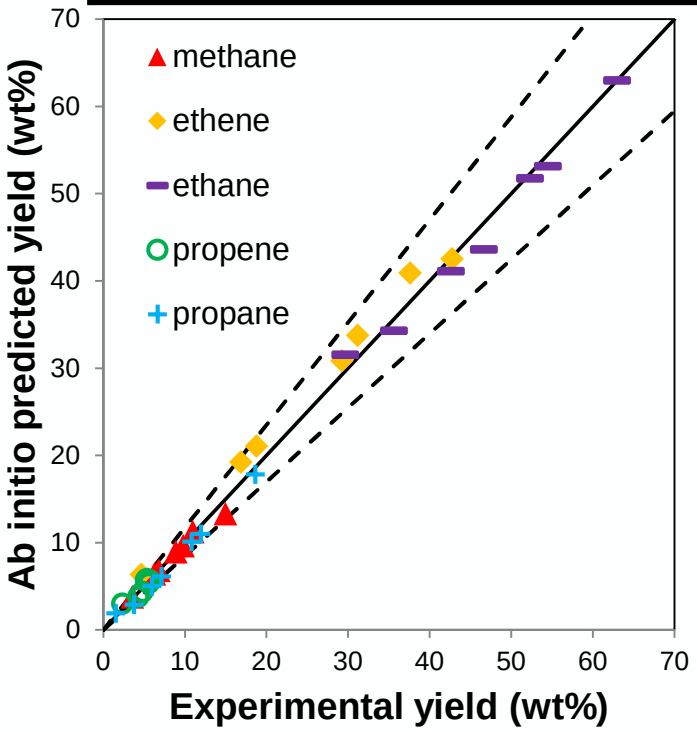
Steam Cracking Pilot Plant

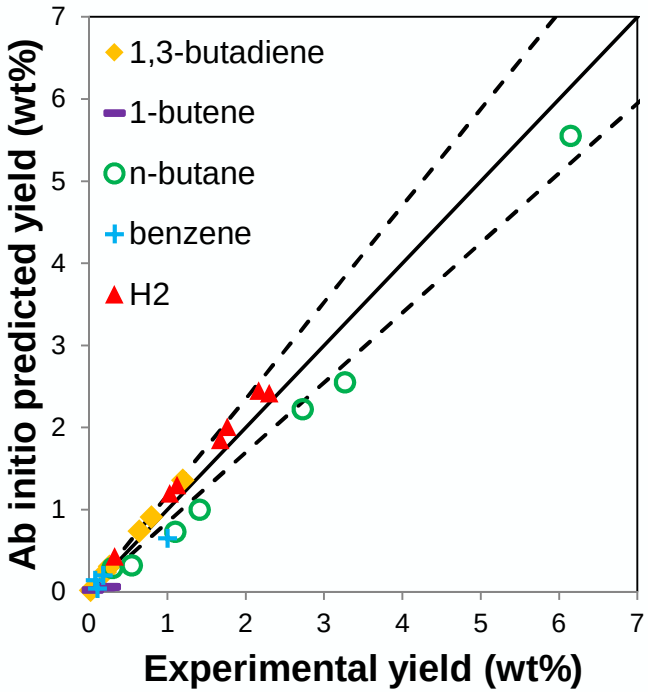


Pilot results: $C_1/C_2/C_3/C_4$

Process conditions	
Feed	3 wt% C_1 67 wt% C_2 22 wt%C_3 8 wt% C_4
COT	1005-1119 K
COP	0.152-0.157 MPa
Steam dilution	0 kg/kg

without a single adjusted parameter





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

[Muñoz, 2013]

Estimated annual cost to industry: $ 2 billion

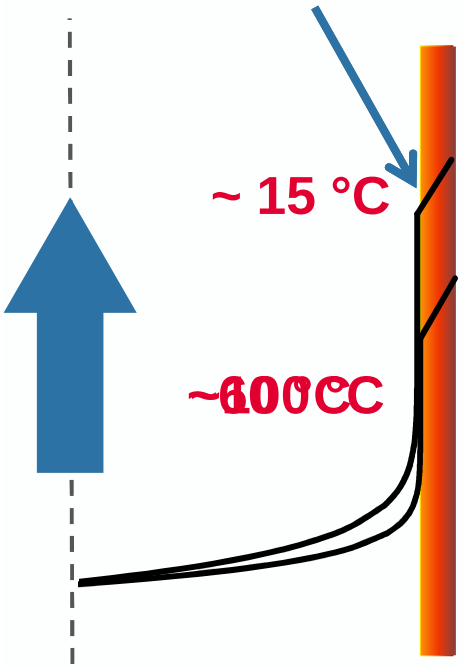
Mitigation by

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

[2]L. Benum, "Achieving Longer Furnace Runs at NOVA Chemicals," in AIChE Spring National Meeting, 14th Annual Ethylene Producers' Conference, New Orleans, Louisiana, 2002.

Coke formation: 3D reactor technologies

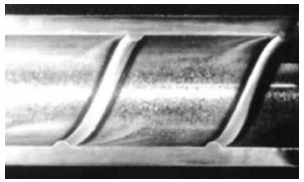
Cokes formed here
T ↑ ➔ coking rate ↑↑



Reduce convective heat resistance

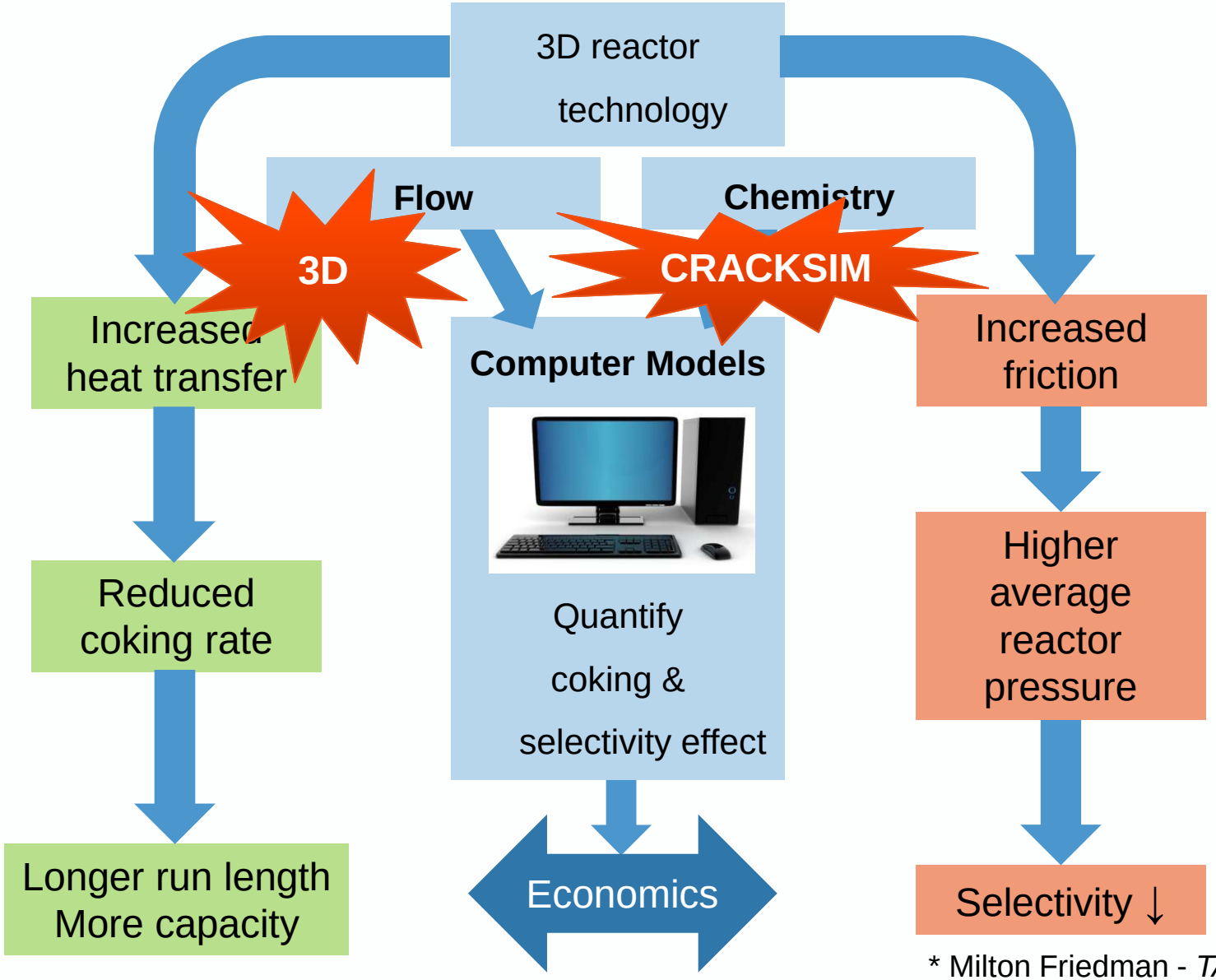
Increase surface area

Better mixing



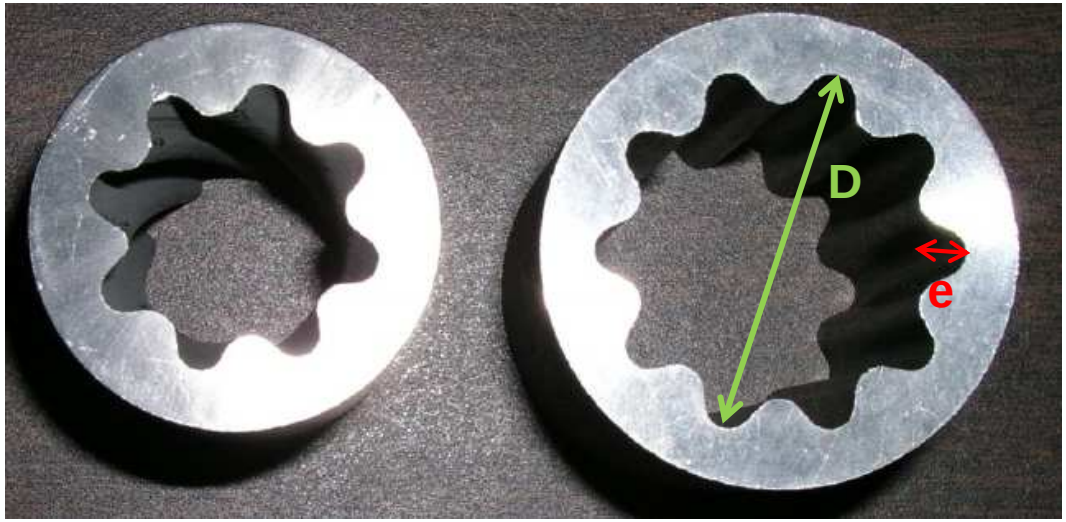
*Borealis.com, kubota.com, Technip.com

"There ain't no such thing as a free lunch"

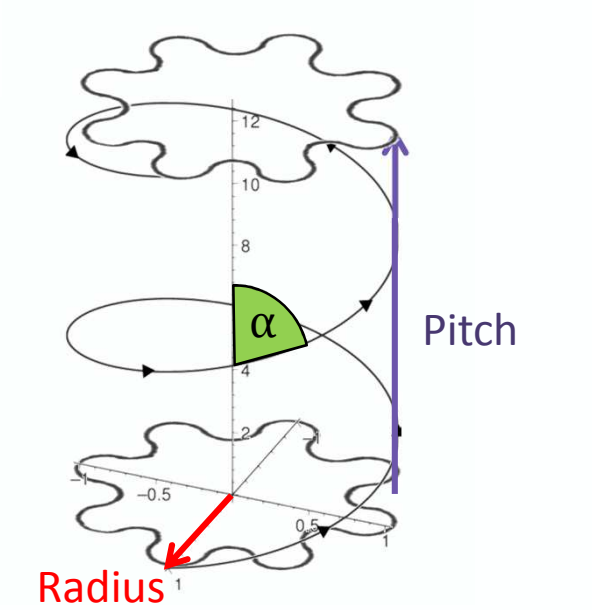


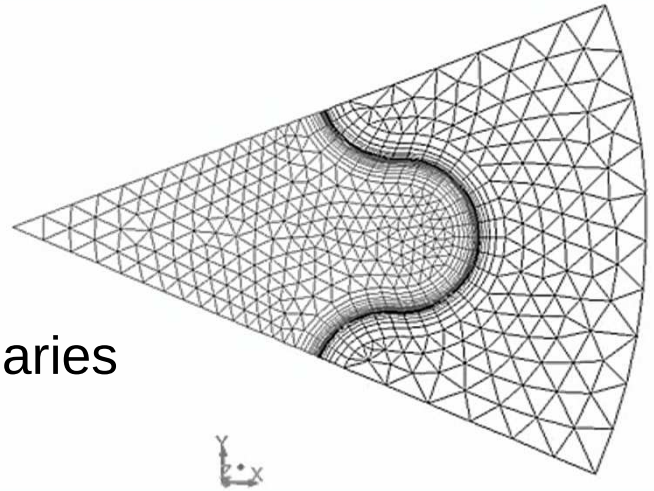
* Milton Friedman - *TANSTAAFL*

Helicoidal finned tubes



Radiant coils in Borealis Furnace, KBR



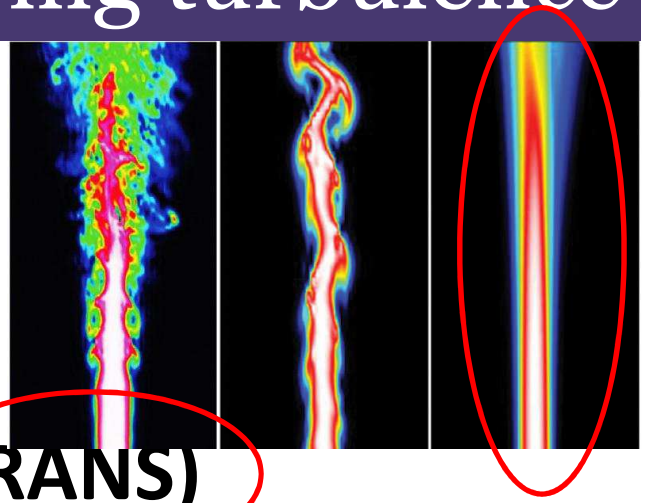


Computational domain: 1 fin with periodic boundaries

Outline

- Introduction
- Feedstock
- Kinetics
- Reactor : CFD models
- Process
- Conclusions

Resolving turbulence



Reynolds-Averaged Navier-Stokes (RANS)

Single model for all scales, additional equations to provide closures

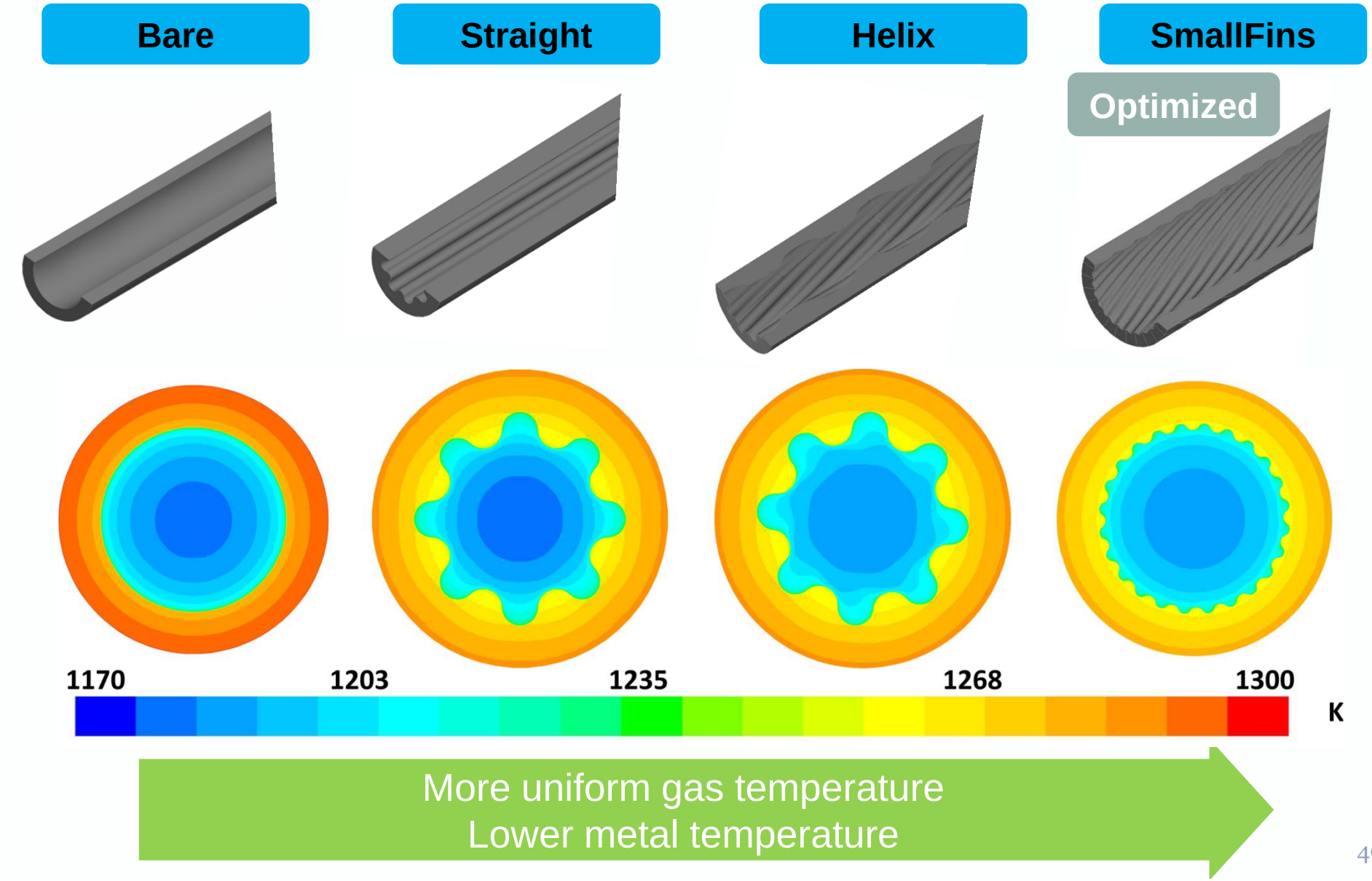
Large Eddy Simulation (LES)

Resolve relevant energy containing scales, model the smaller energy dissipating eddies

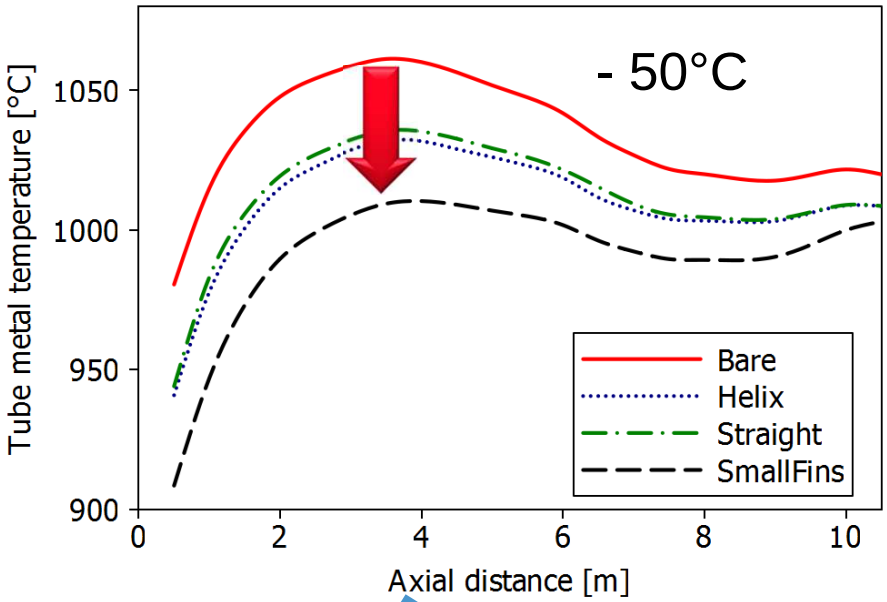
Direct Numerical Solution (DNS)

Fully resolve all time and length scales

Radial temperature profiles

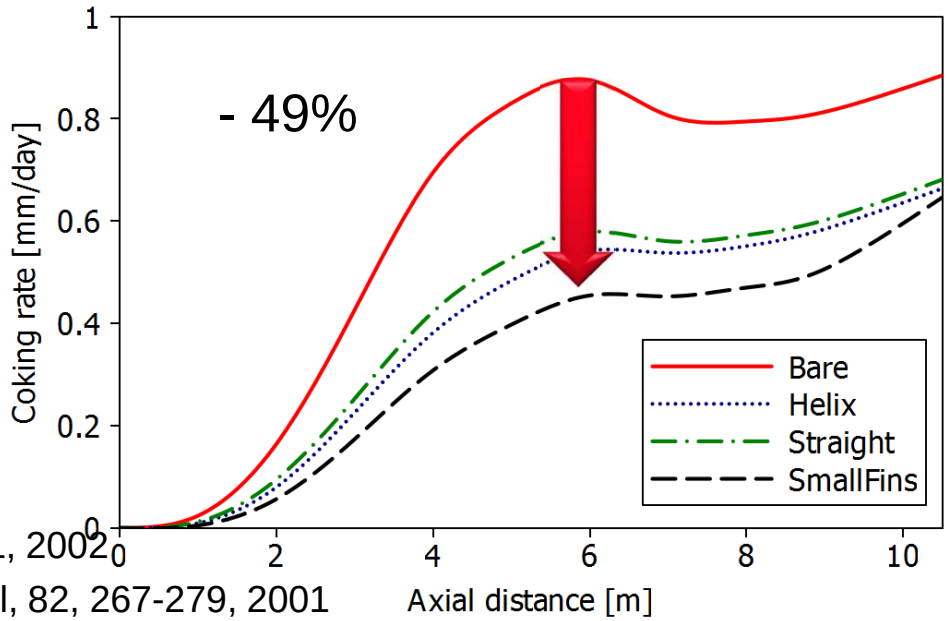


Axial wall temperature and coking profile



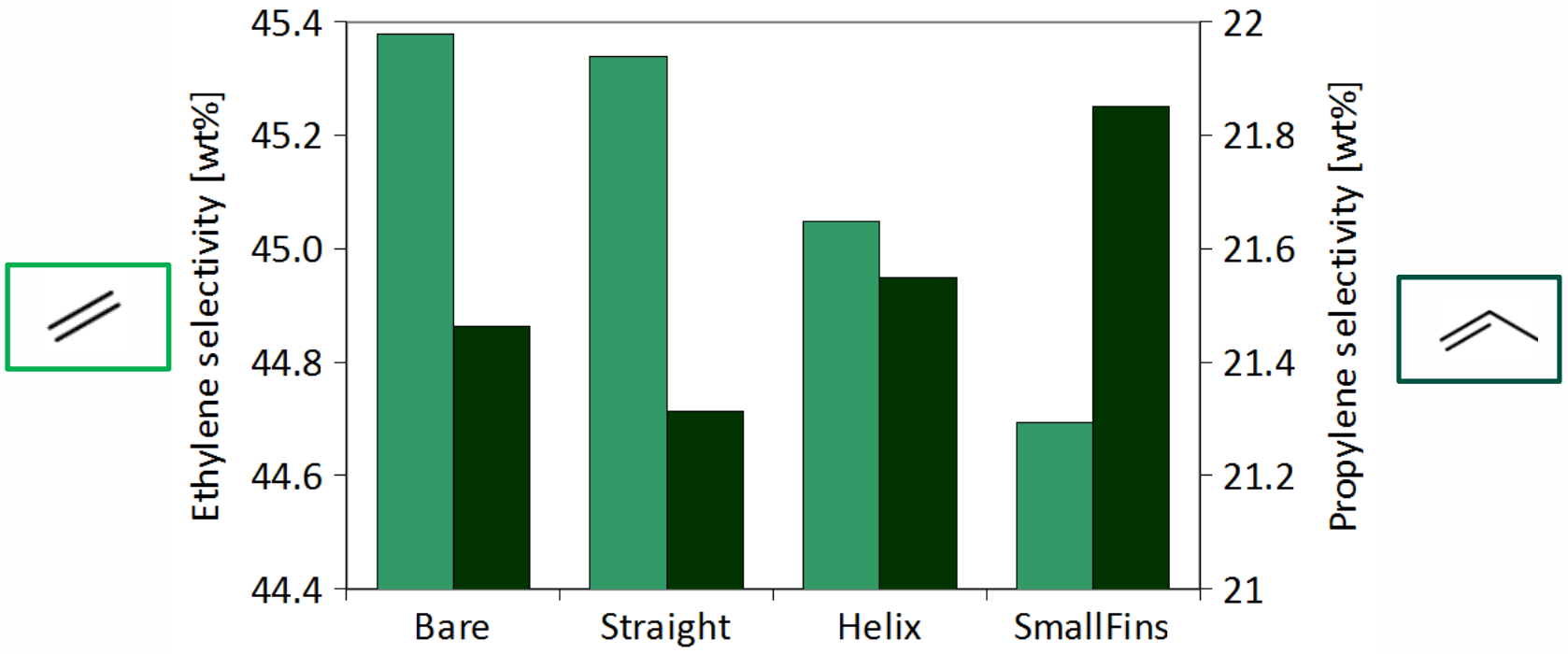
Cracking reaction model
26 components
13 radical species
212 elementary reactions

Coke model



S. Wauters and G.B. Marin, IEC Research, 41, 2379-2391, 2002
S. Wauters and G.B. Marin; Chemical Engineering Journal, 82, 267-279, 2001

Effect on start of run yields



- 0.7 wt%

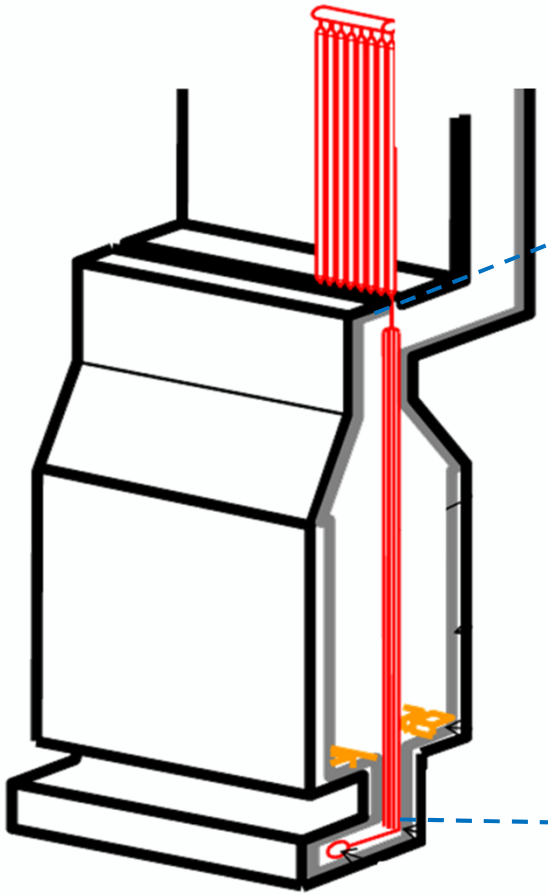
+ 0.3 wt%

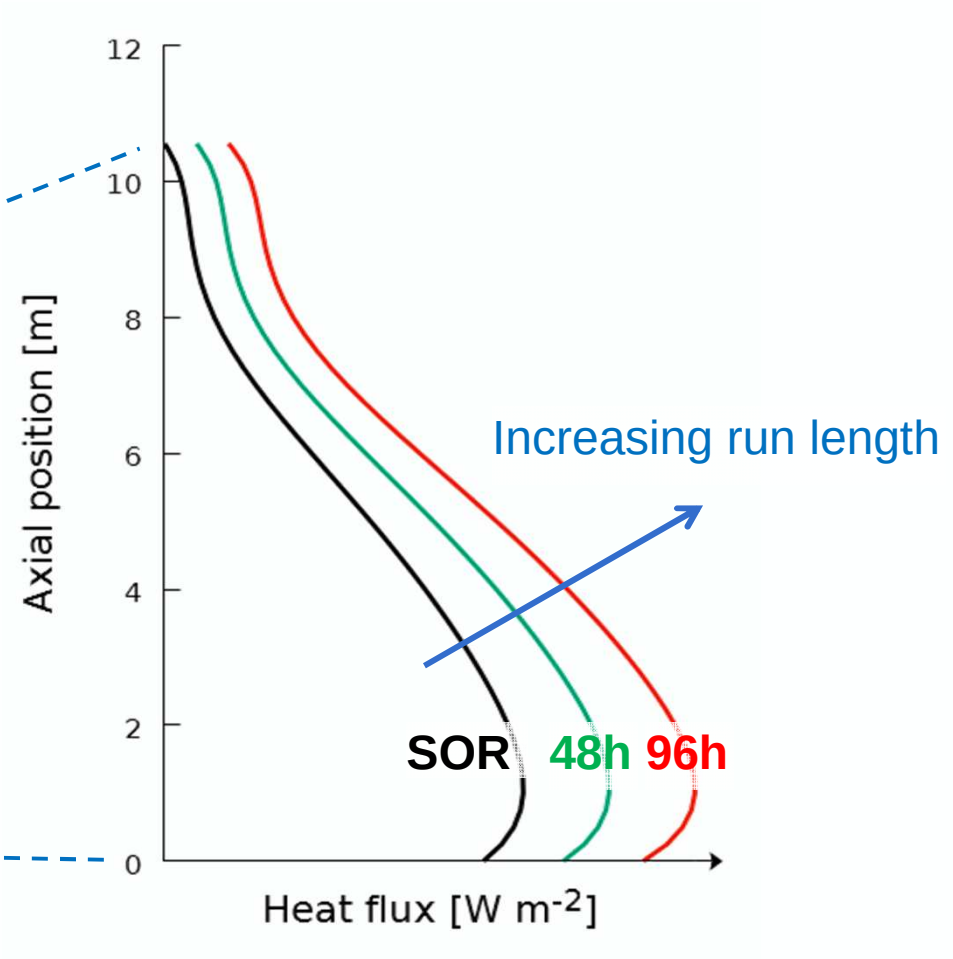
Radical reaction model
26 components
13 radical species
212 elementary reactions

Outline

- Introduction
- Feedstock
- Kinetics
- Reactor: "run length"
- Process
- Conclusions

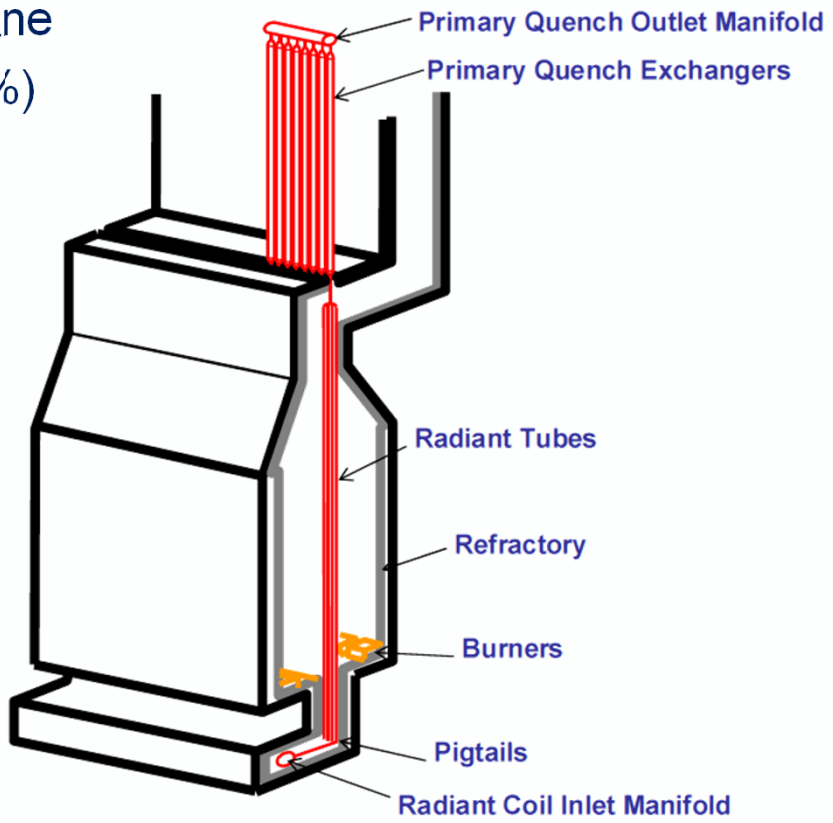
Run length simulation





Millisecond propane cracker

- Feedstock 118.5 kg/h propane
- Propane conversion 80.15 % (± 0.05%)
- Steam dilution 0.326 kg/kg
- CIT 903.7 °C
- COP 170 kPa

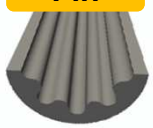


Different geometries simulated

- Same reactor volume
- Same axial length
- Same minimal wall thickness

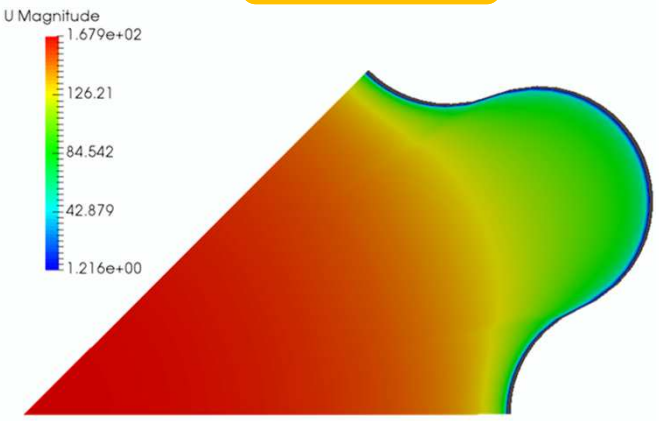
Non-uniform coke layer growth

Fin

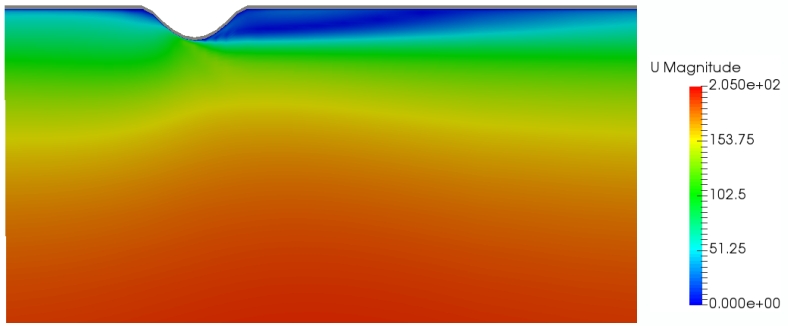


c-Rib

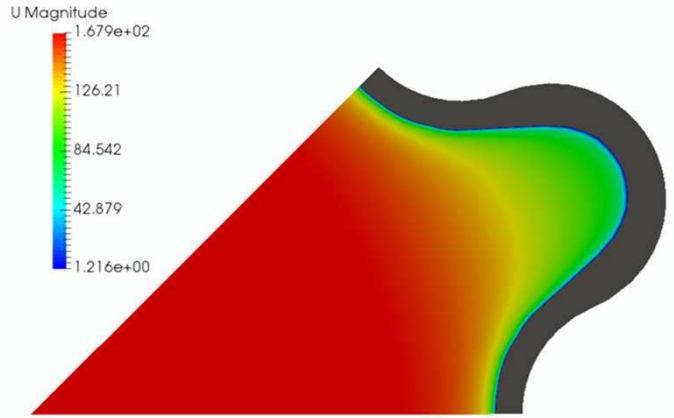
SOR (0 hrs)



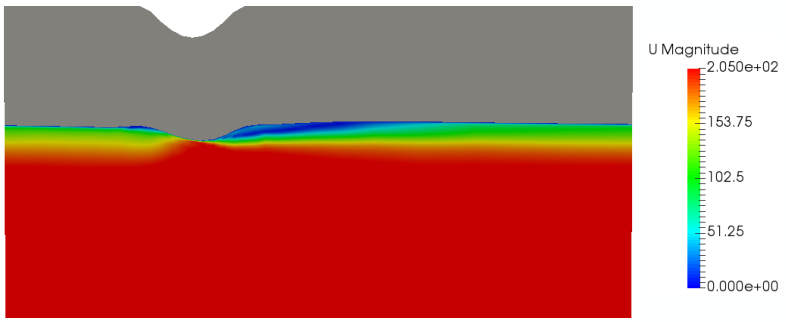
SOR



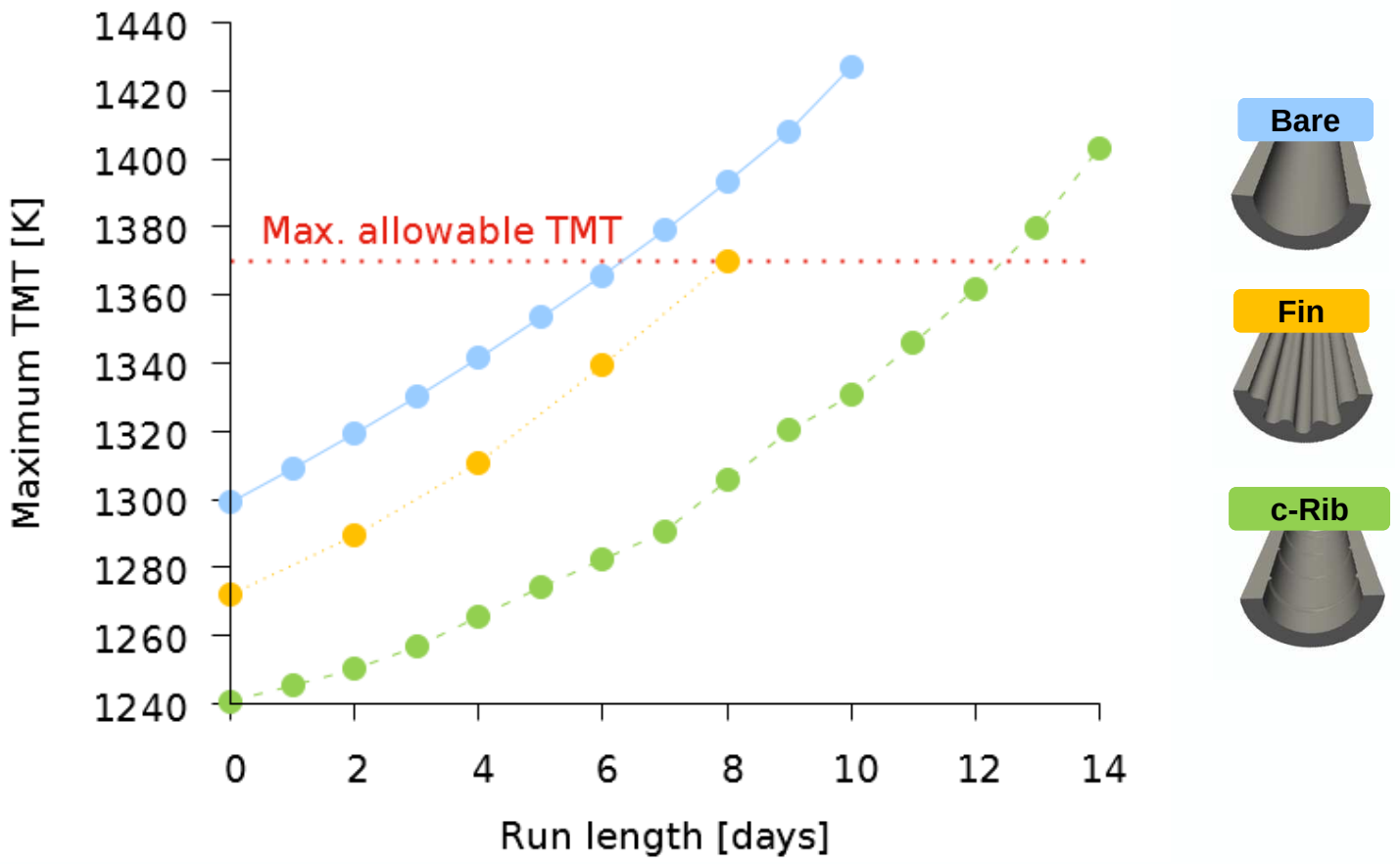
48 hrs



10 days

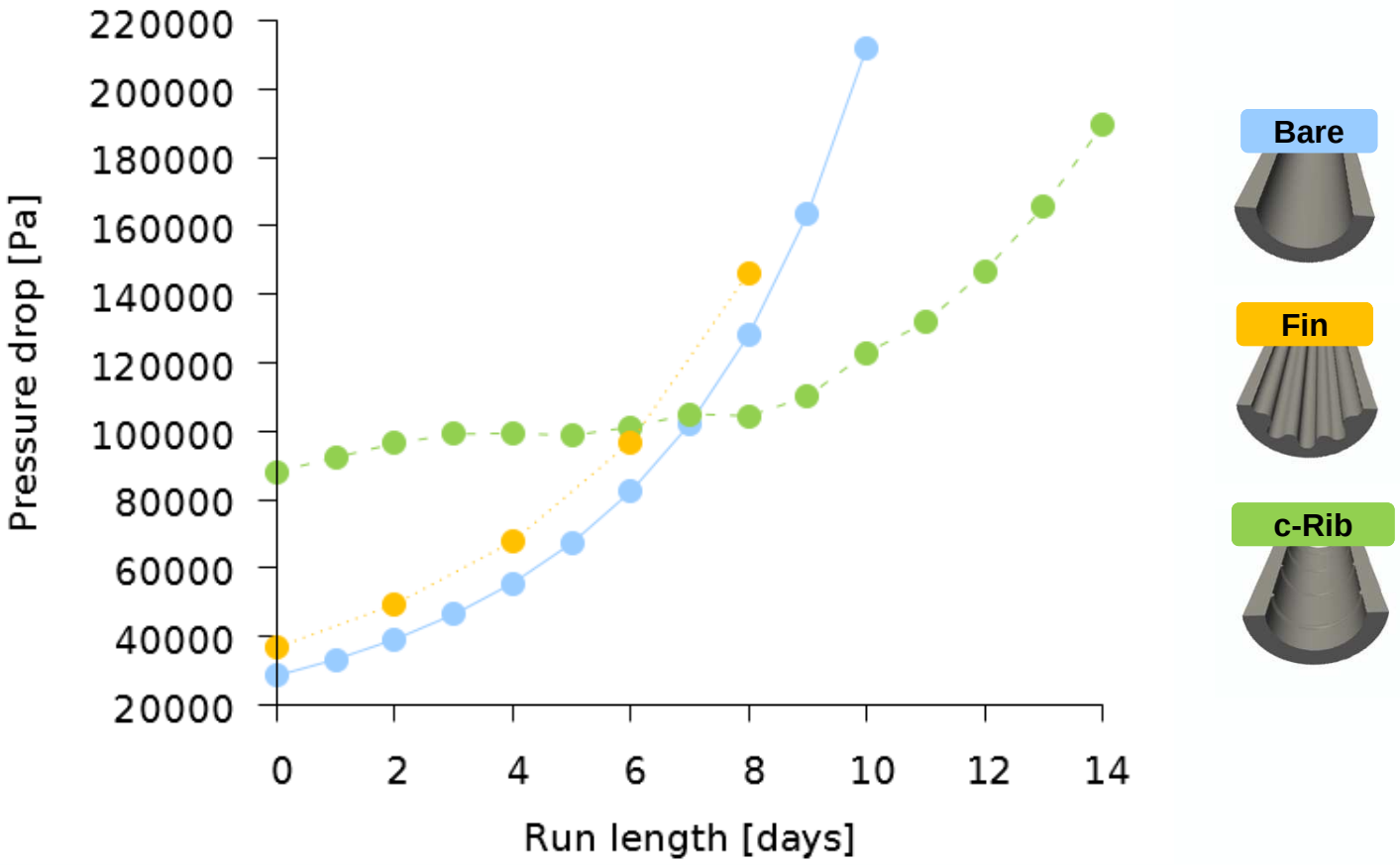


Tube Metal Temperature



Thermal resistance coke layer → Max. TMT increases

Pressure drop



Cross-sectional flow area decreases due to coke → Pressure drop increases

Outline

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Outline

- Introduction
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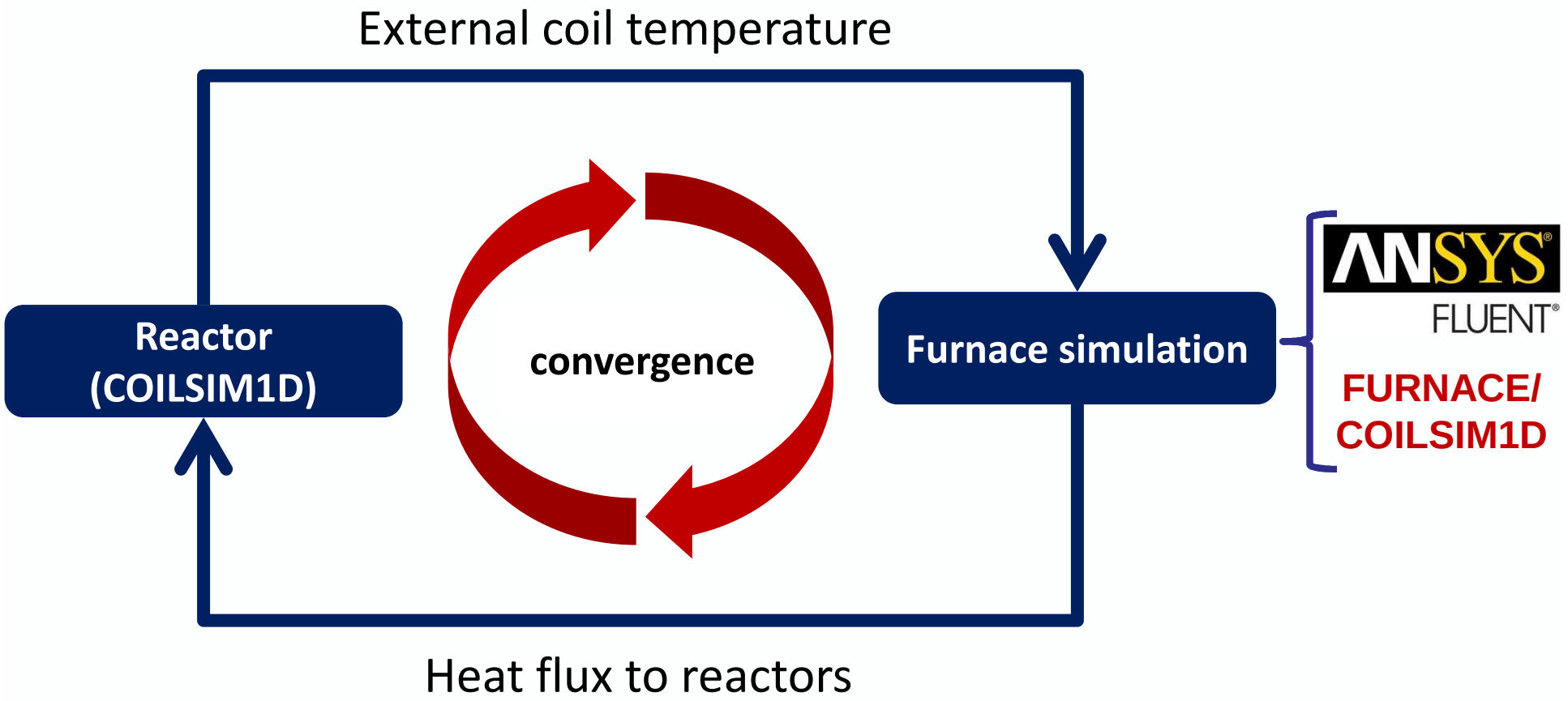
- Kinetics
- Reactor
- Process: fire box
- Conclusions

Coupled reactor-furnace simulation



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

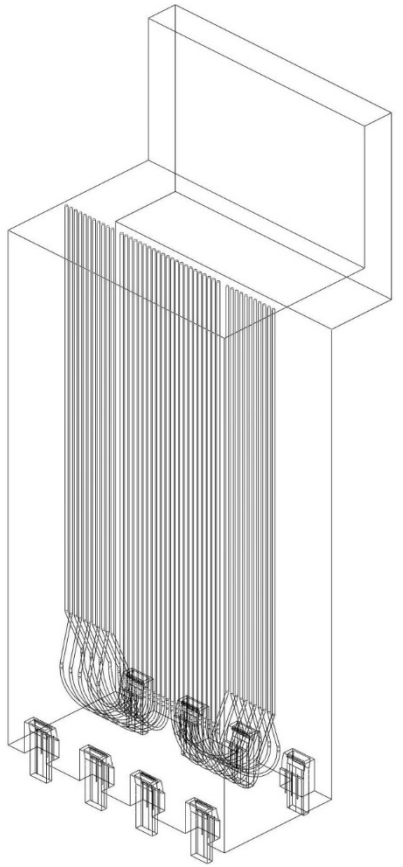
Full furnace simulation

Ultra Selective Conversion (USC)

- 100% floor burner
- Fuel composition mol%: CH_4(89%)-H_2(11%)
- U coil
- Feedstock: Naphtha

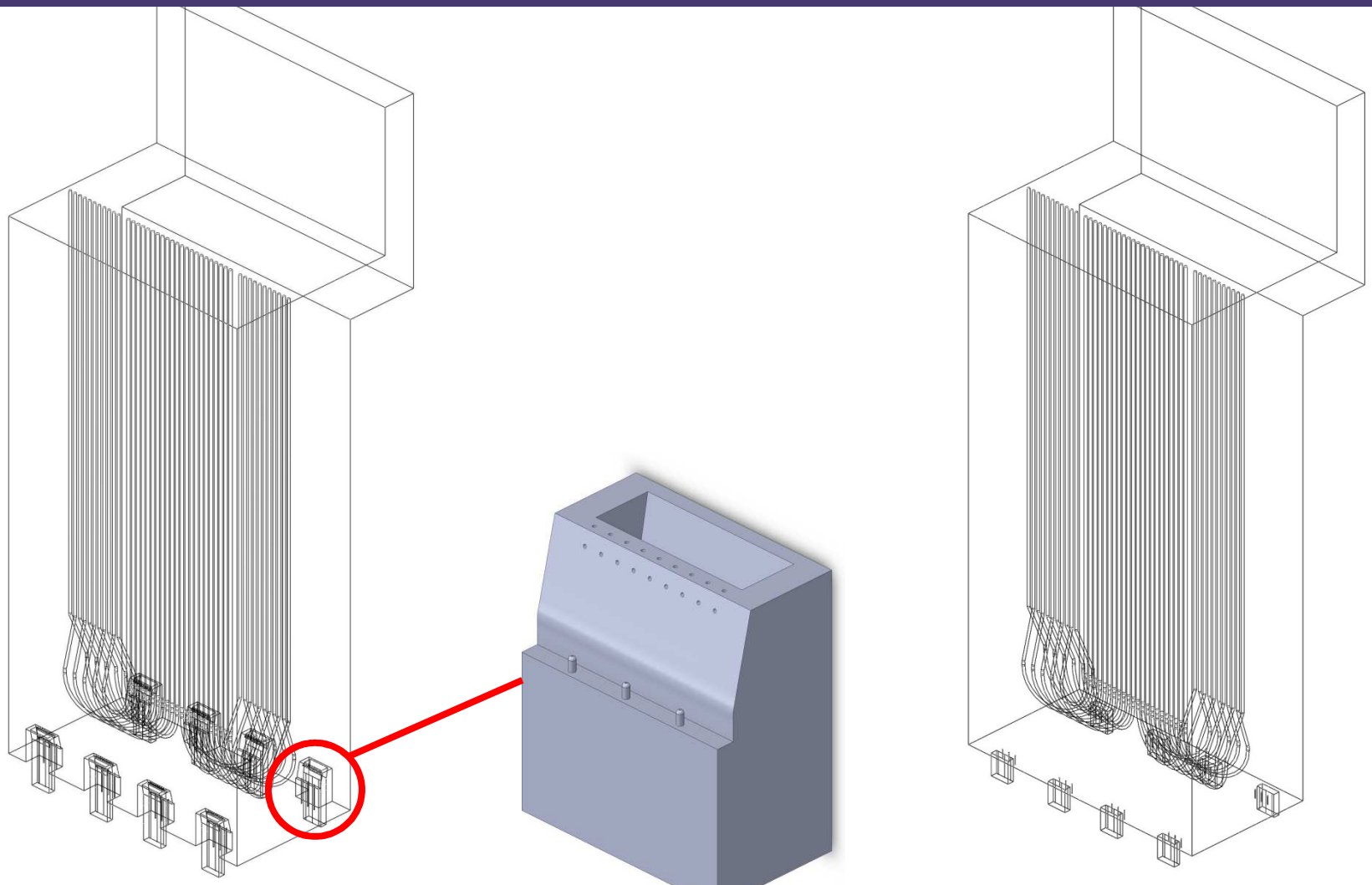
Coupled modeling

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



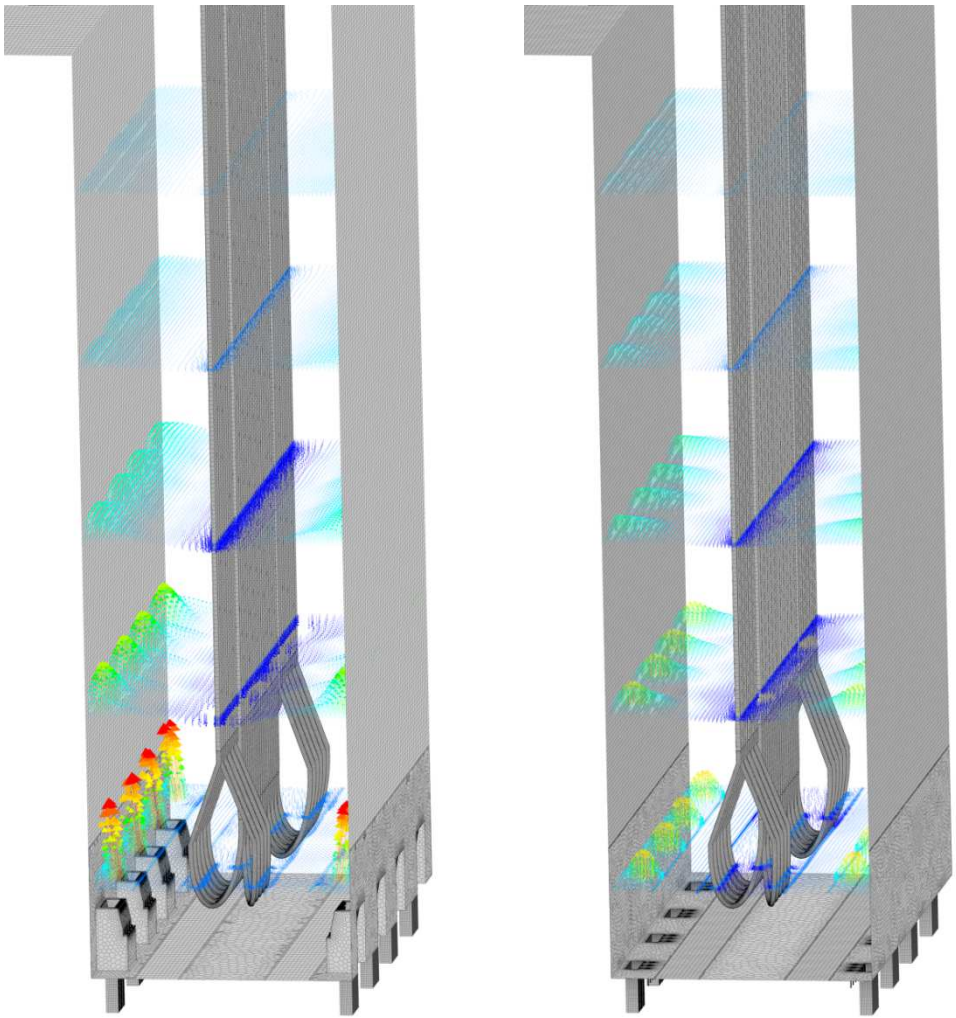
Zhang, Y. et al.,AIChE Journal 61 (3), 936-954, 2015

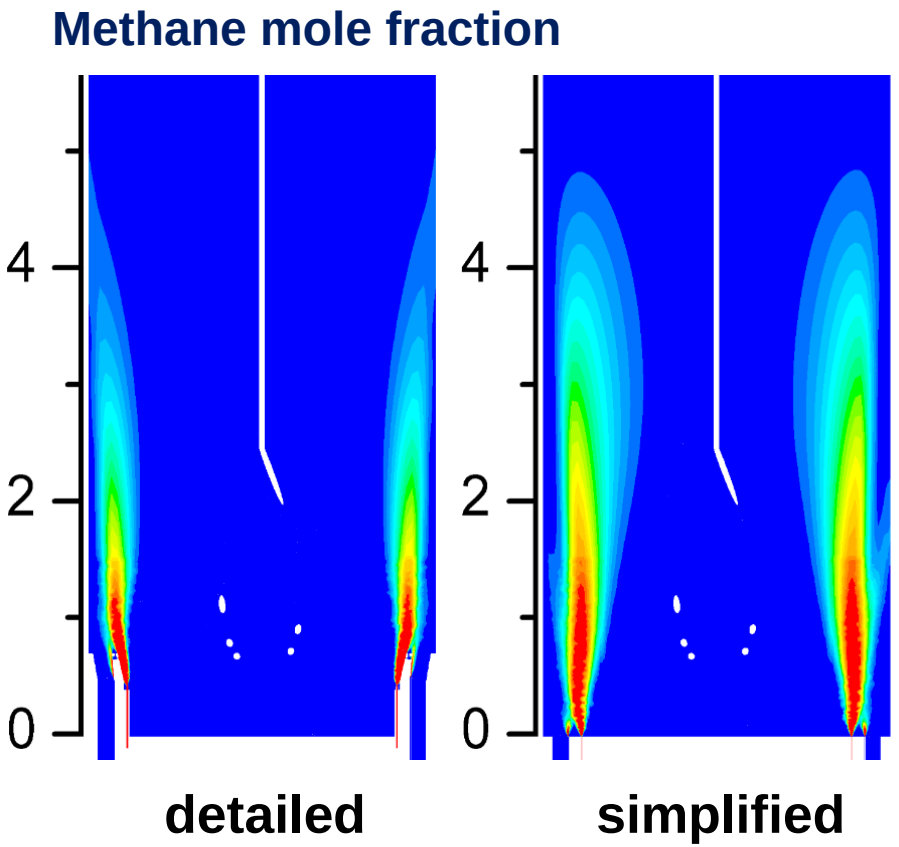
Detailed : long flame burners



detailed **simplified**

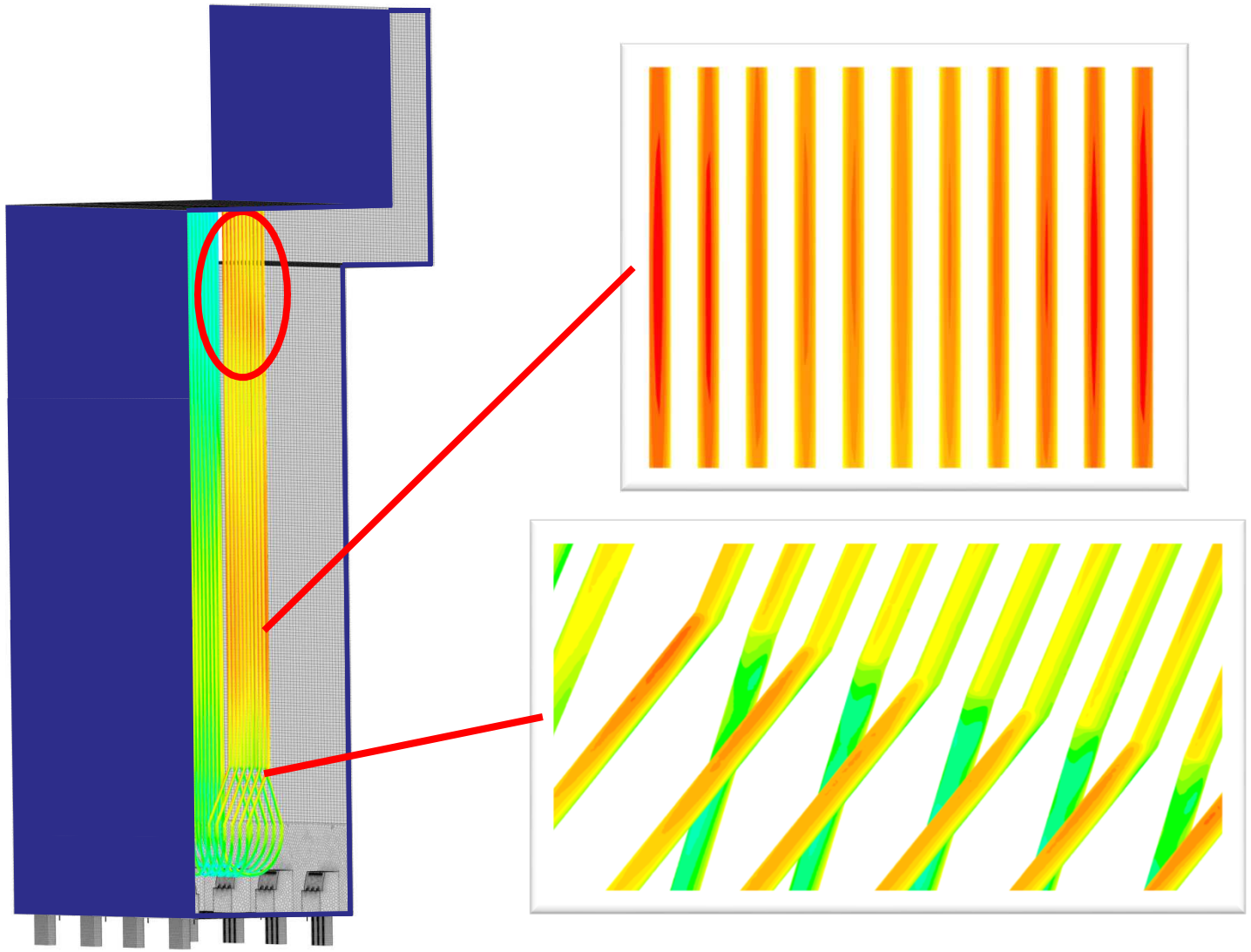
Flue gas: velocity and concentration fields





- **Detailed case**
  - Stronger turbulence
  - Faster reaction

Tube wall temperature field: local hot spots



This information is key for control

Outline

- Introduction
- Feedstock
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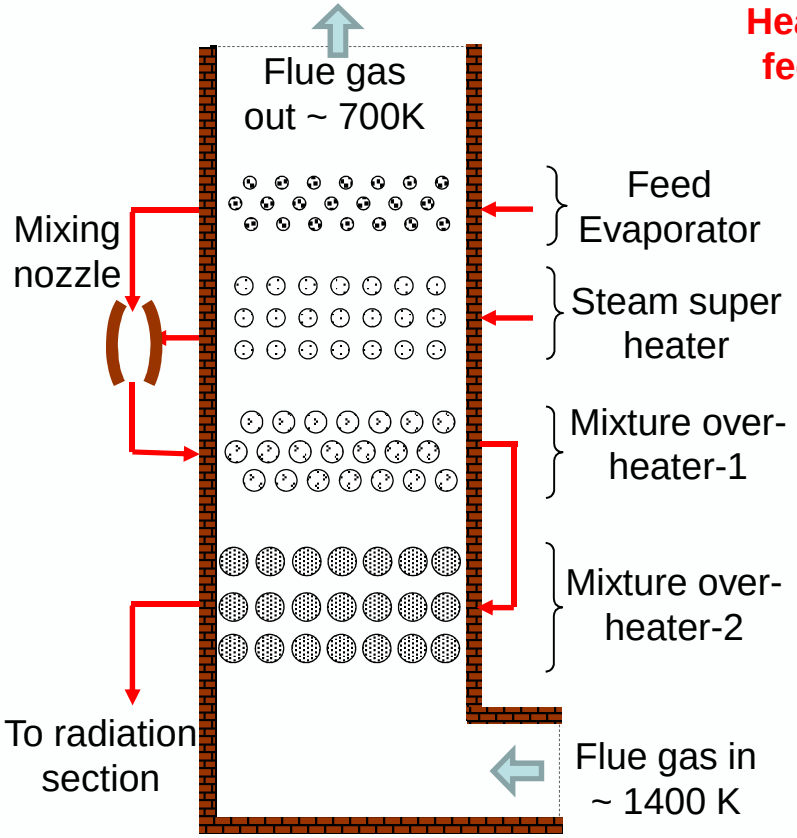
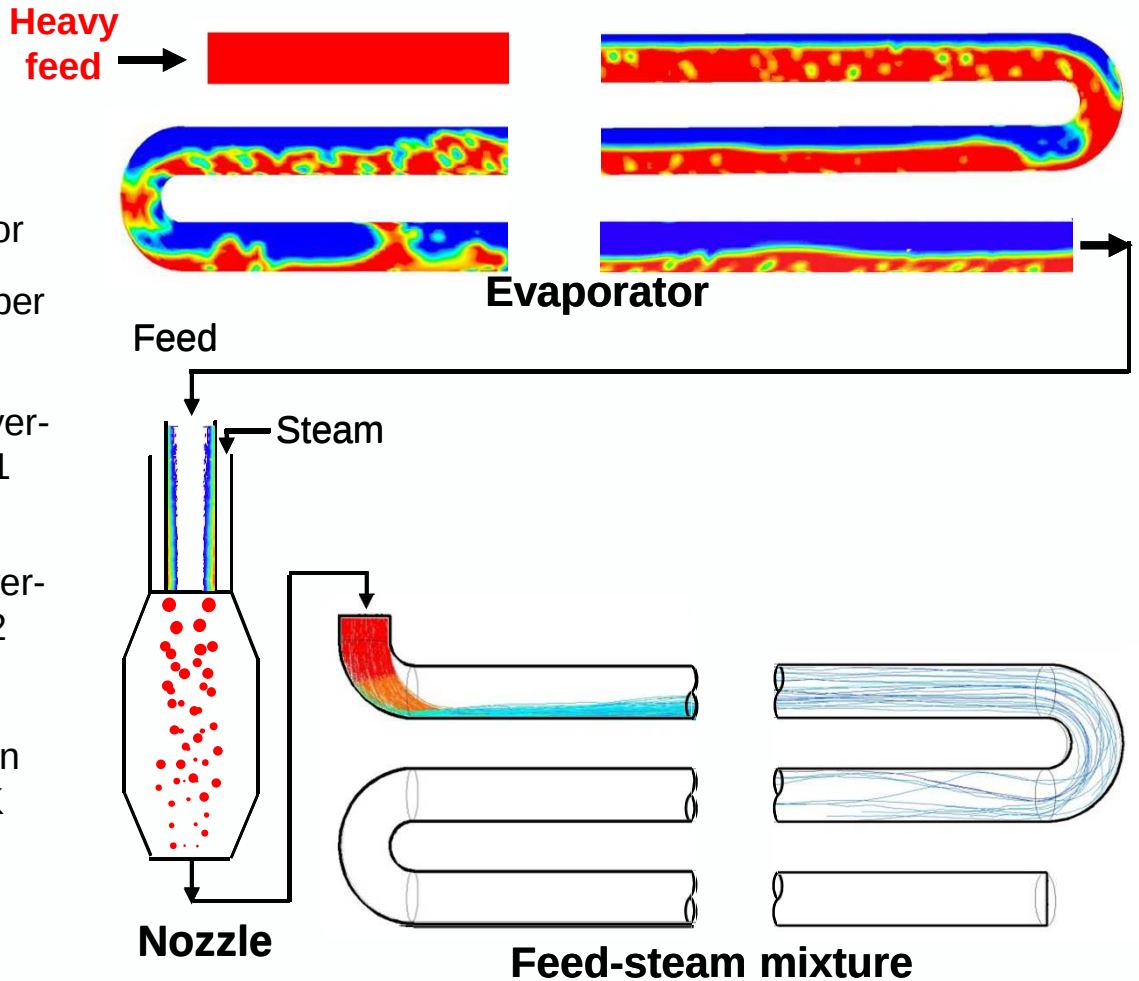
- Reactor
- Process: convection section
- Conclusions

Steam cracker convection section

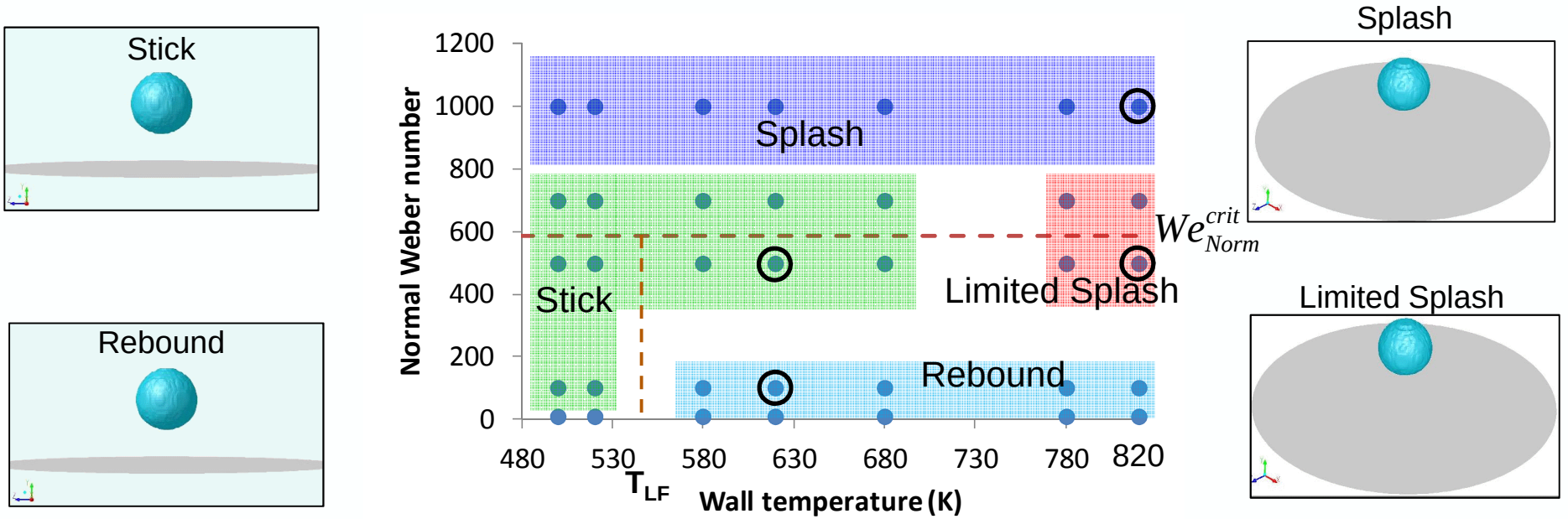


Schematic of convection section



Mahulkar, A.V. et al., Chemical Engineering Science, 110, 31-43, 2014

Gas condensate: multicomponent mixture



- Wider stick regime as compared to that in single component droplet regime map
- For splash and limited splash, the no. of daughter droplets formed is greater than predicted by correlations available in literature

Mahulkar, A.V. et al., Chemical Engineering Science, 130, 275-289, 2015

Outline

- Introduction
- Feedstock
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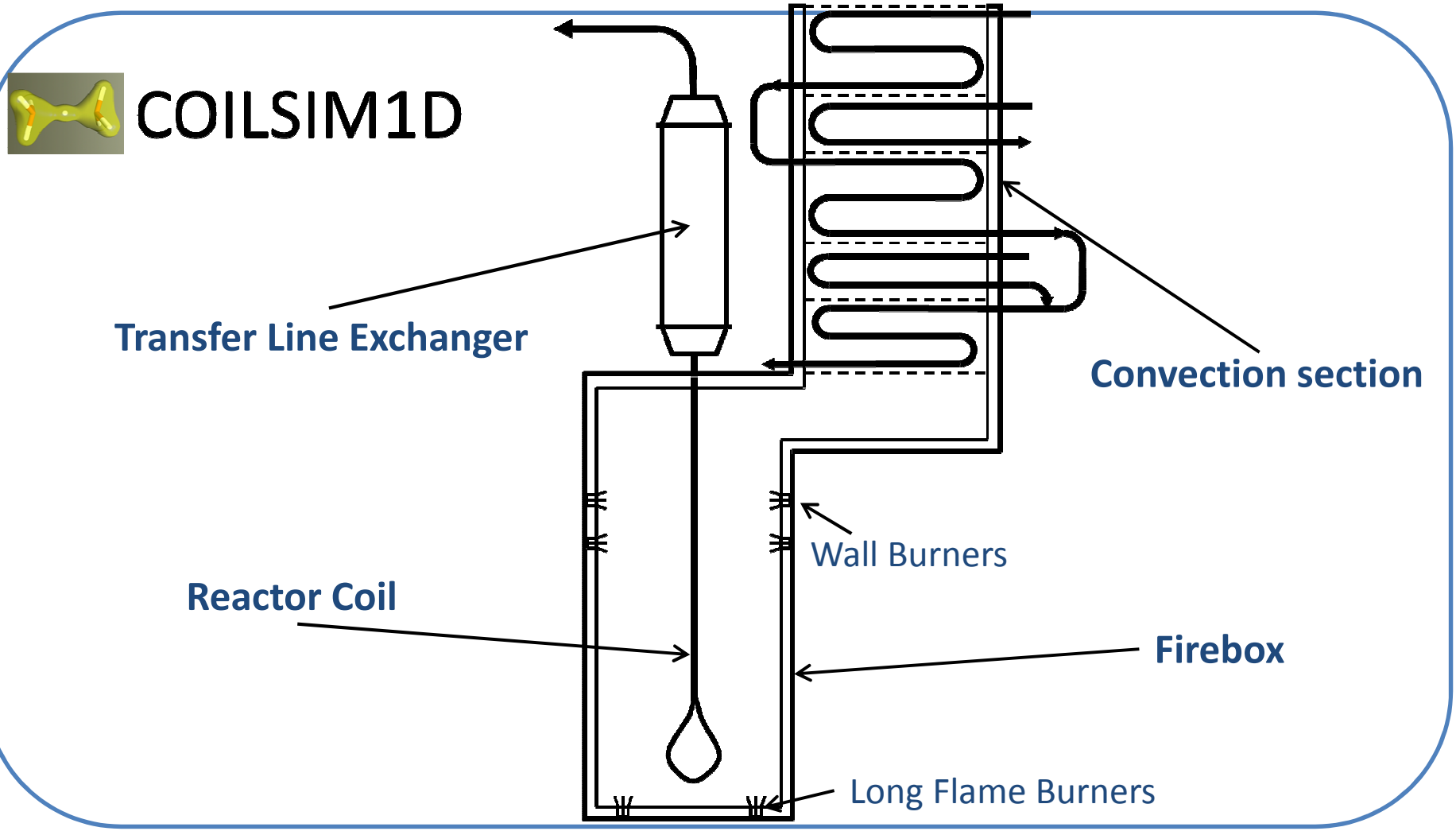
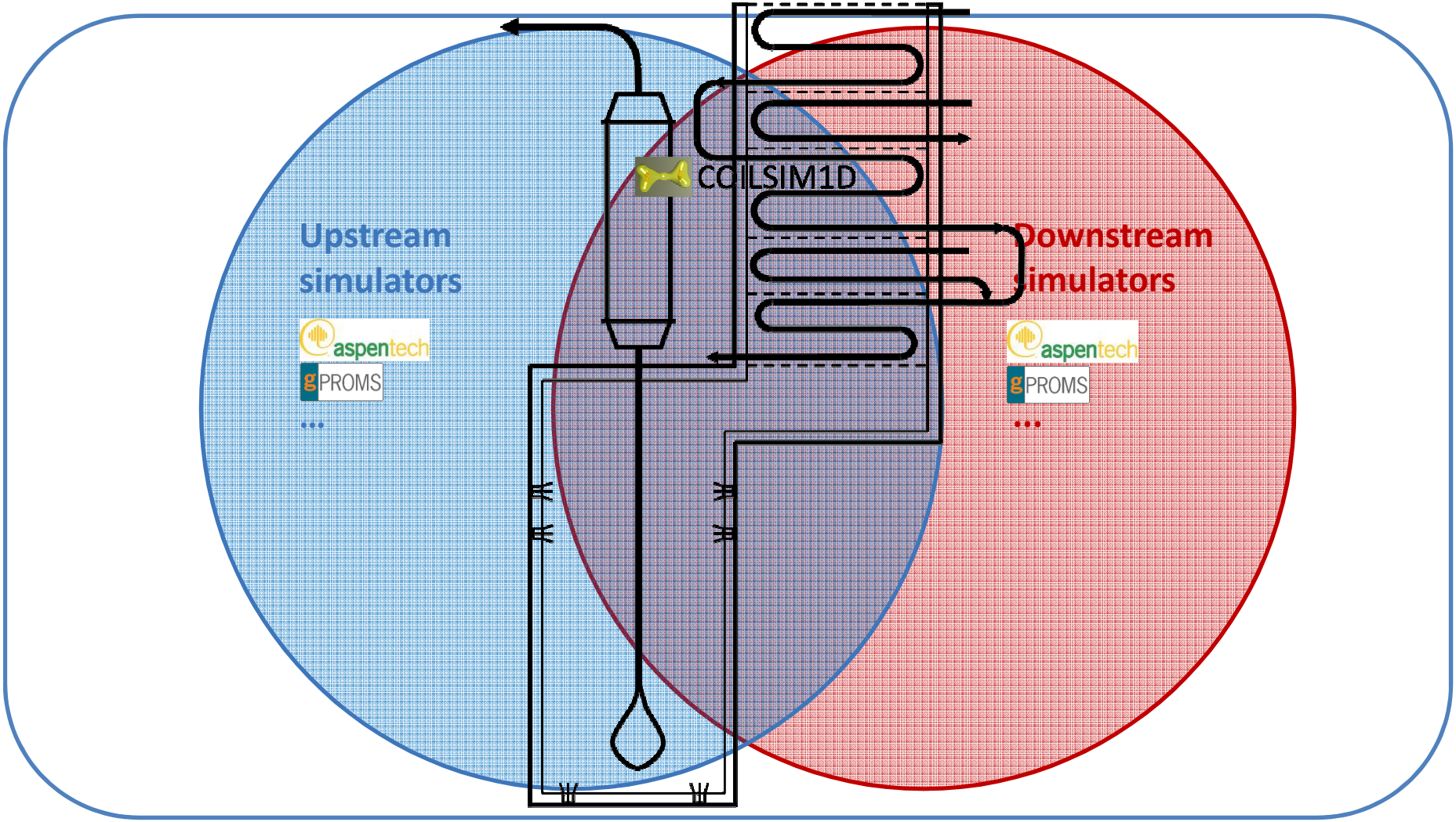
- Reactor
- Process: hot section
- Conclusions

The COILSIM1D package



The COILSIM1D package



Outline

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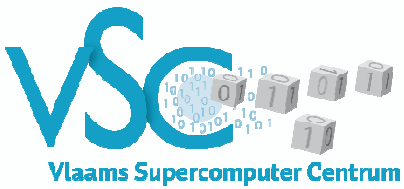
Conclusions

- Shannon Entropy maximization to reconstruct feedstocks in terms required for a microkinetic model
- Consistent data set for thermochemistry and kinetics of hydrocarbon and oxygenates radical chemistry
- Ab initio simulation of steam cracking of $C_2/C_3/C_4$ and oxygenates
- Compatibility of renewable feedstocks with existing plants
- Emergence of 3D reactor technologies based on CFD
- Integration of reactor/convection section/furnace

→ integration of computational chemistry methods with engineering tools at larger time and length scales and experimental validation provides a powerful tool for the optimization and/or design of industrial units

Acknowledgments

The Long Term Structural Methusalem Funding



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People

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.