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FACULTY OF ENGINEERING AND ARCHITECTURE

Oxygen-Containing Contaminants and Steam Cracking: Understanding their Impact Using COILSIM1D

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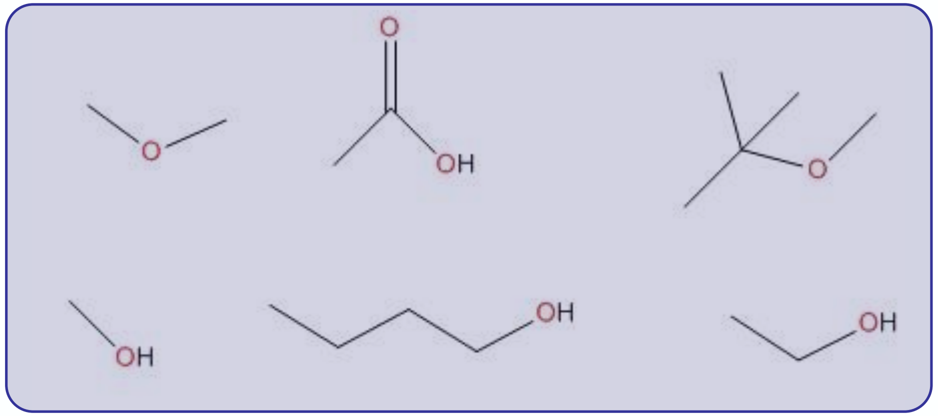
2017 AIChE Spring Meeting – 29th Ethylene Producers' Conference
San Antonio - TX, USA, March 27th, 2017

Steam Cracking

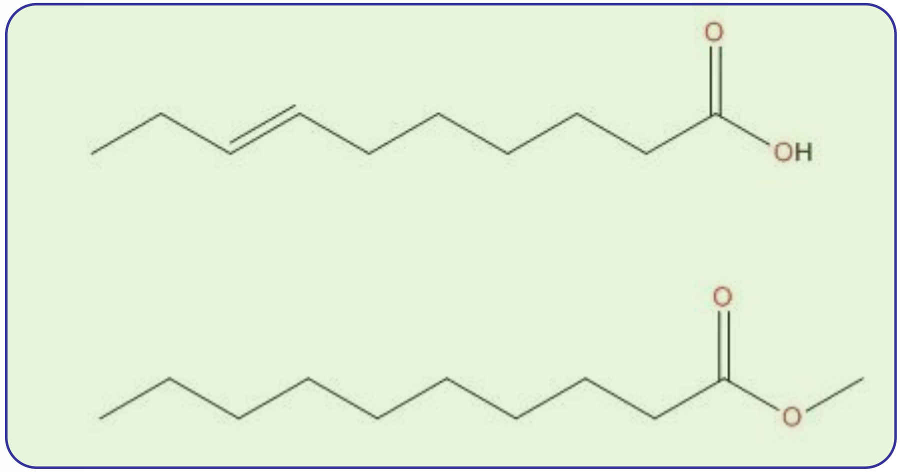
Steam Cracker

Oxygen containing compounds

Typical contaminants in the feed



Bio based species



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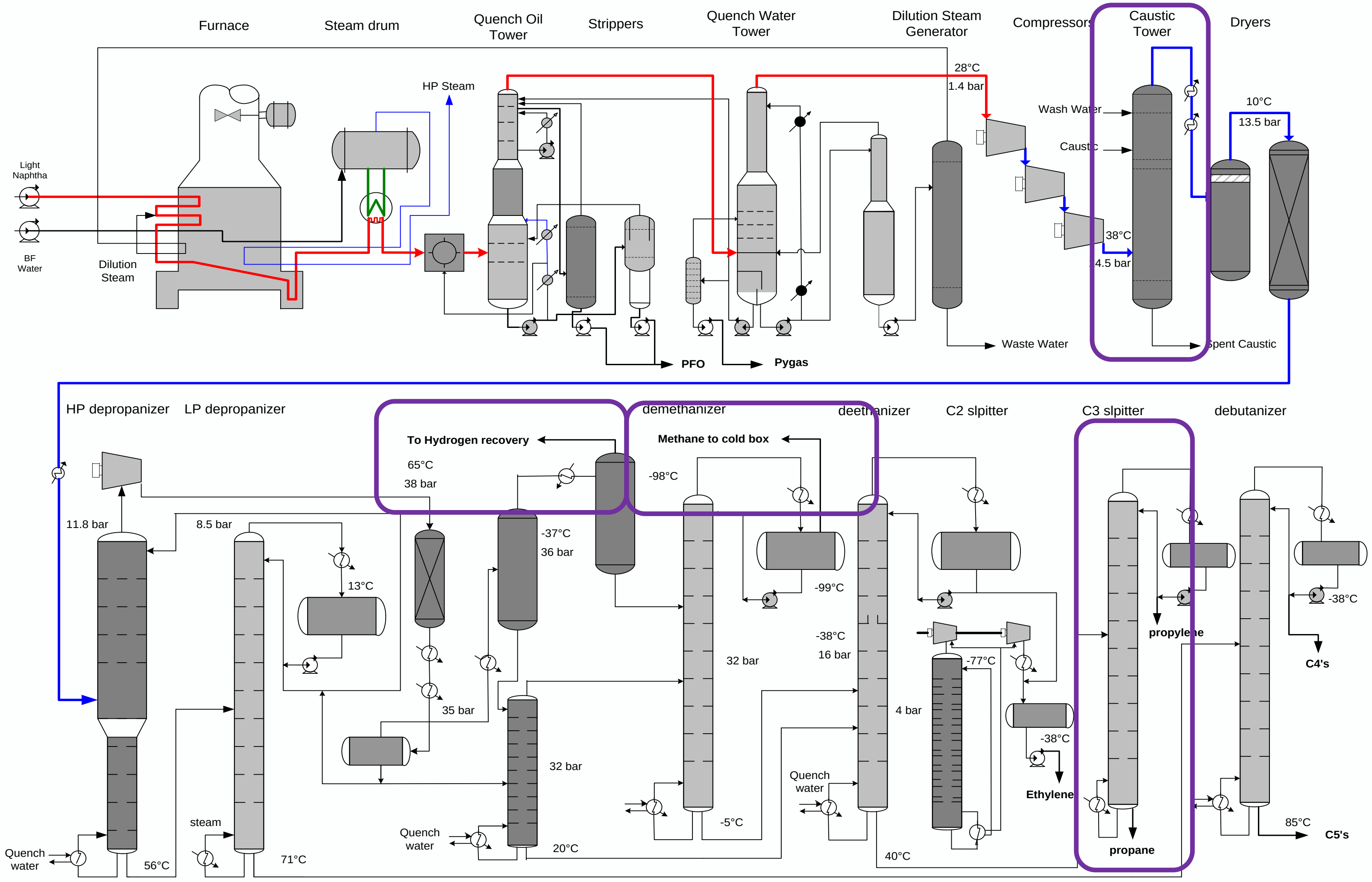
Steam Cracking

Methanol
Acids
Formaldehyde
CO/CO_2
Gum formation



K. M. Van Geem, G. B. Marin, N. Hedebouin, J. Grootjans, Energy efficiency of the cold train of anethylene cracker, Oil Gas-European Magazine 34 (2008) 95-99

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Outline

- Introduction
- Reactor and kinetic model
- Simulations and Results
- Conclusions

Modeling

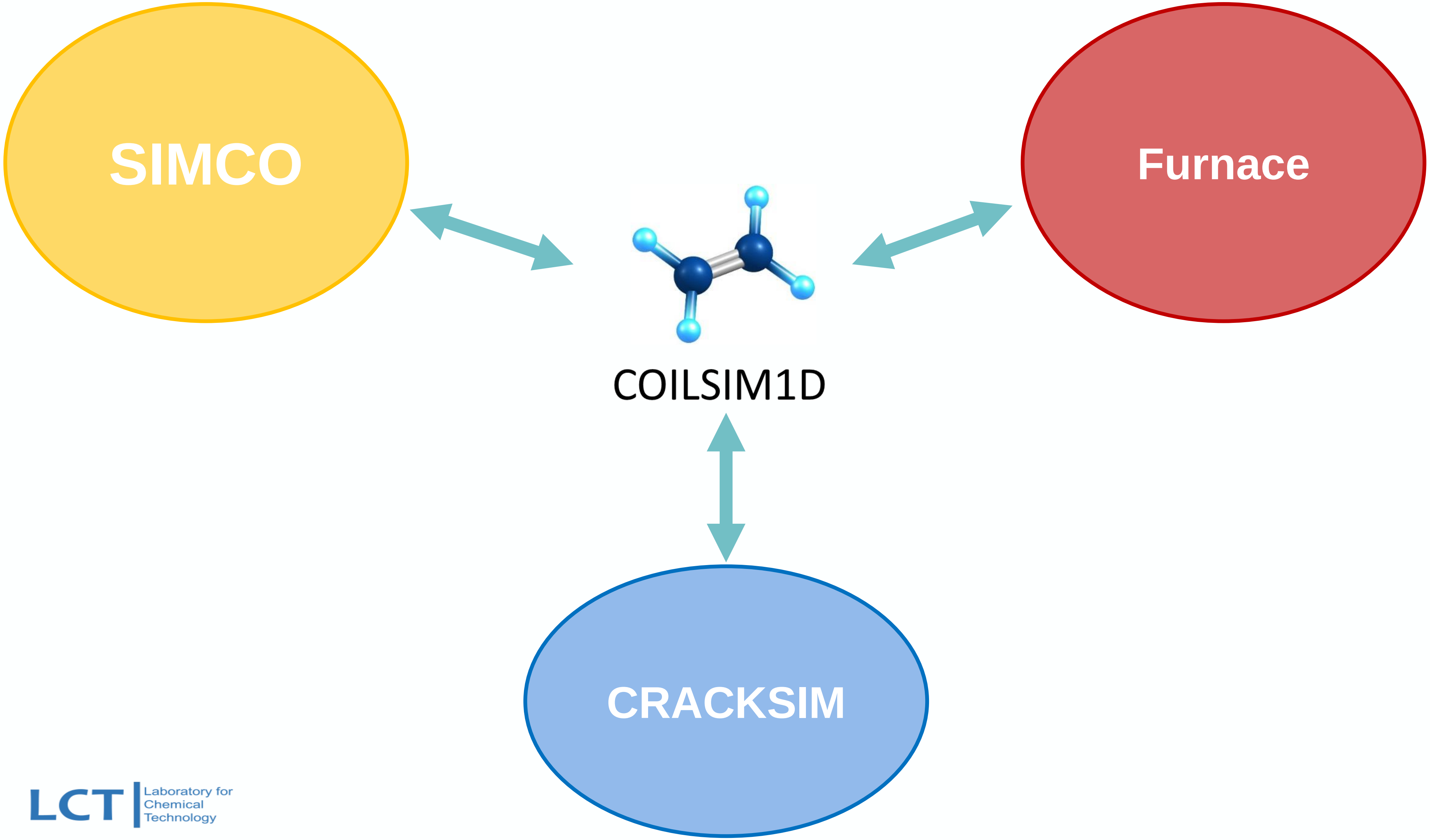
The challenge:

- Complex chemistry
  - Large number of species
  - Large number of reactions
- Reactor model
- Unknown mixture

The solution:

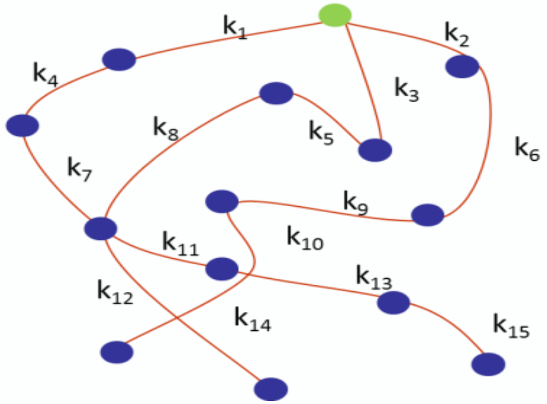
- COILSIM1D
  - Detailed Chemistry
  - 1D reactor model
  - Feed reconstruction
  - Reasonable computational times

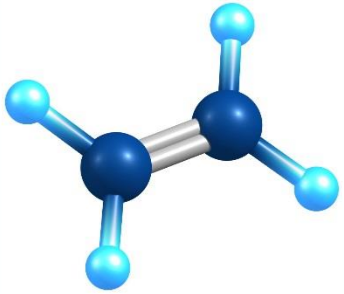
Key elements of COILSIM1D



COILSIM1D

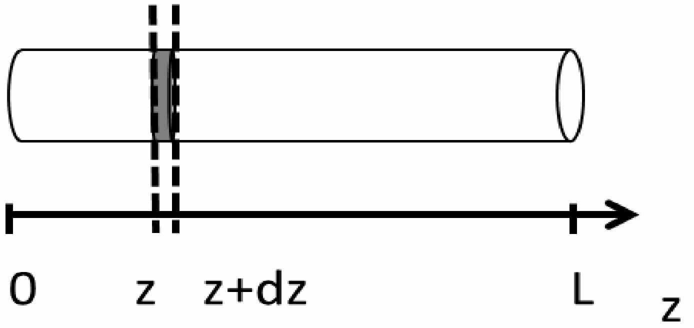
Kinetic model





COILSIM1D

1D reactor model



- Broadest kinetic model for steam cracking
  - 720+ molecules
  - 43 radicals
  - 300,000+ reactions

- Based on high level Ab initio data, and validated (pilot and industrial)

Free radical mechanism

3 main reaction families:

1. C–C and C–H scission of molecules and reverse radical–radical recombination

$$R_1 - R_2 \leftrightarrow R_1^{\bullet} + R_2^{\bullet}$$

2. H abstraction reactions (intra- and intermolecular)

$$R_1 - H + R_2^{\bullet} \leftrightarrow R_1^{\bullet} + R_2 - H$$

3. Radical addition to olefins and reverse β-scission of radicals, both intra- and intermolecular

$$R_1^{\bullet} + R_2 - R_3 \leftrightarrow R_1 - R_2 - R_3^{\bullet}$$

Assumption for accurate network of manageable size

- μ-hypothesis: bimolecular reactions can be neglected for certain radicals (C_6^+)
- PSSA for large radical species

Kinetic model consists of two parts:

- **β-network**: network with elementary reactions of C_5^- radicals
- **μ-network**: describes the thermal decomposition of large molecules

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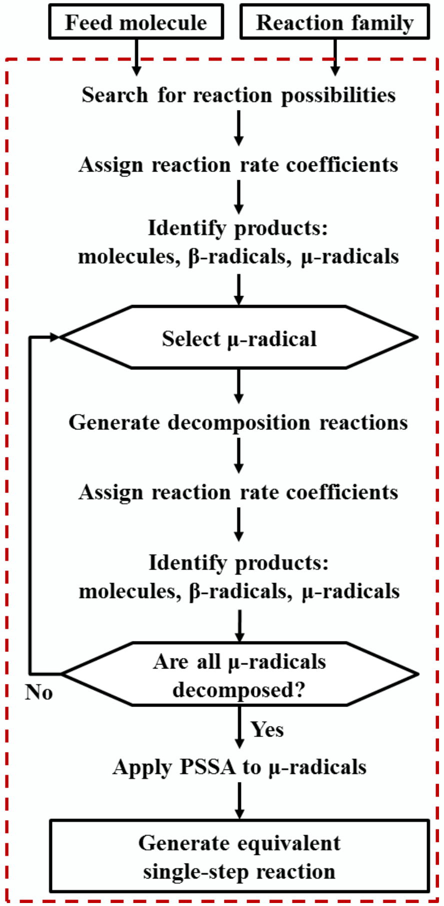
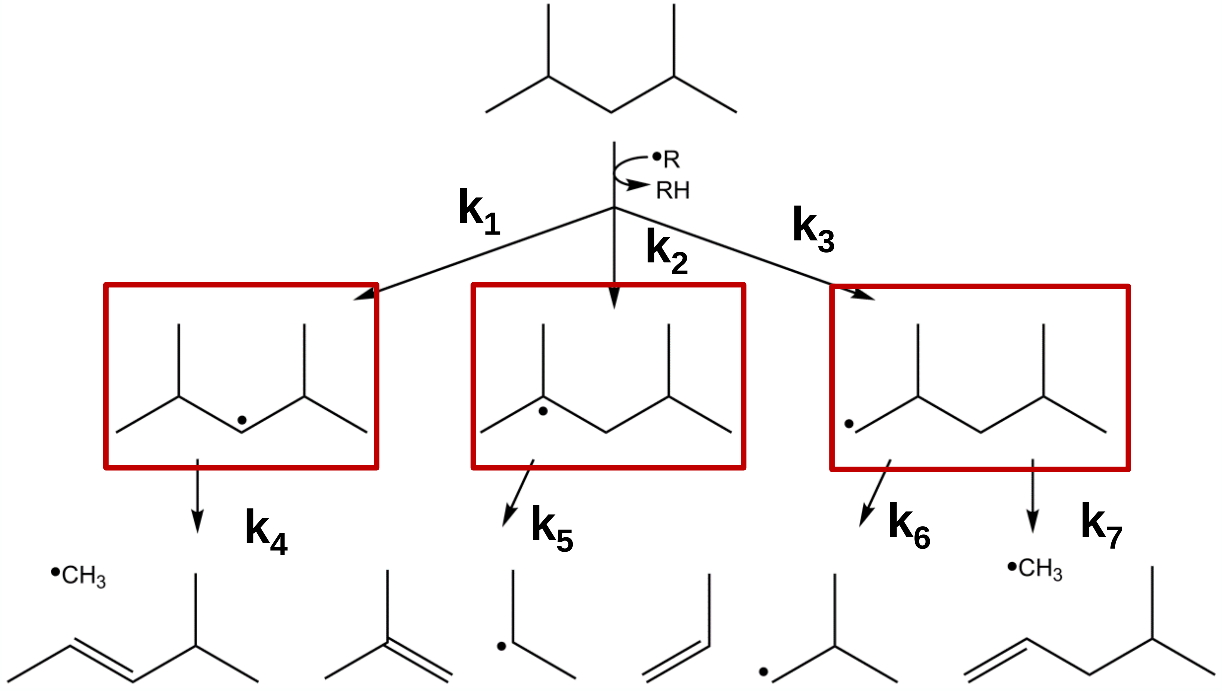
PRIM-O

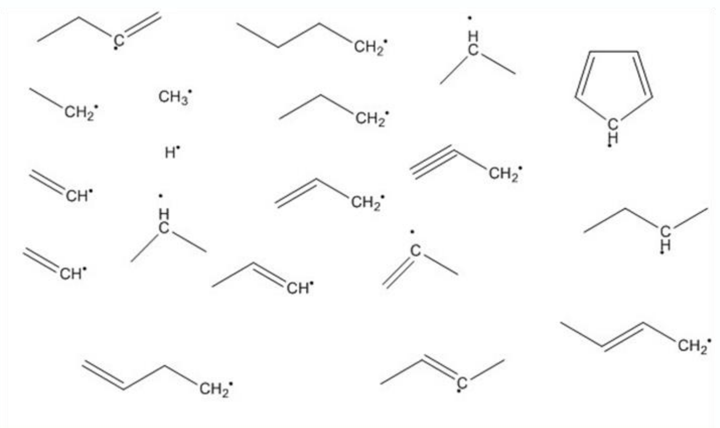


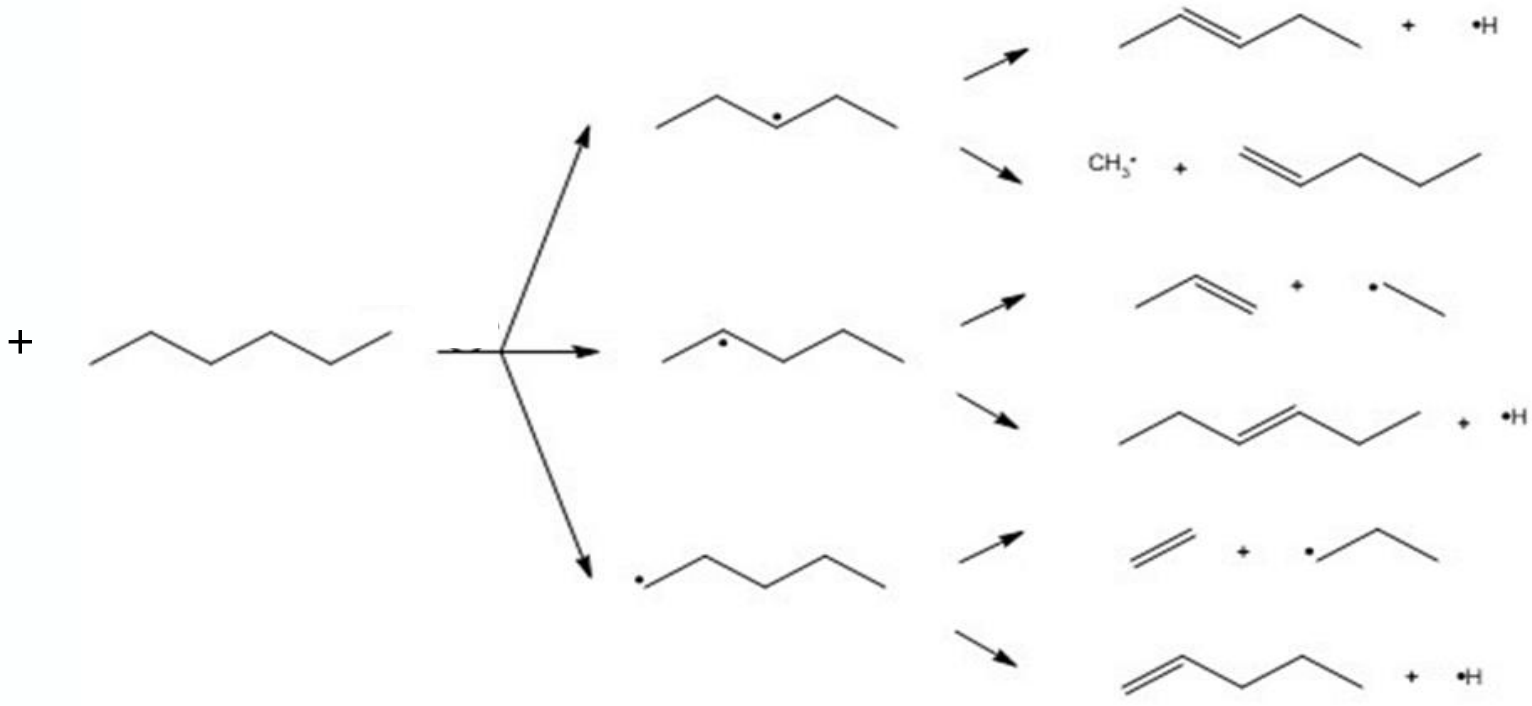


De Bruycker, R. Production of green base chemicals through conventional and emerging pyrolysis processes. Ghent University, 2016.

Inclusion of oxygenates

Introduction of new species and radicals which can interact with hydrocarbon matrix





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Validation

Pilot plant of LCT - UGent

- Fire-heated Furnace
- Reactor: 12.8 m long
- 7 independently heated cells
- Online analytics:
  - Permanent Gas Analyzer
  - Refinery Gas Analyzer
  - Detailed HC Analyzer
  - GCxGC-FID/TOF-MS
  - Light Oxygenates Analyzer
  - CO / CO_2 detector

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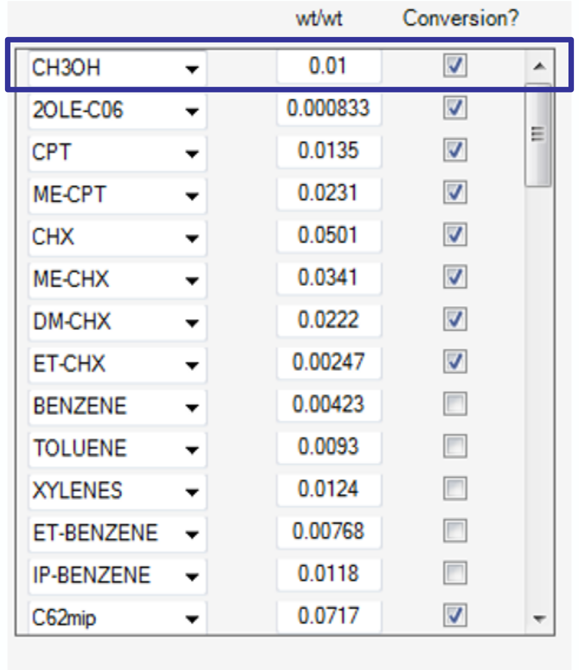
Simulation cases

Two contaminants:

- Methanol
- DME



	wt/wt	Conversion?
CH3OH	0.01	✓
2OLE-C06	0.000833	✓
CPT	0.0135	✓
ME-CPT	0.0231	✓
CHX	0.0501	✓
ME-CHX	0.0341	✓
DM-CHX	0.0222	✓
ET-CHX	0.00247	✓
BENZENE	0.00423	
TOLUENE	0.0093	
XYLENES	0.0124	
ET-BENZENE	0.00768	
IP-BENZENE	0.0118	
C62mip	0.0717	✓

Two illustrative cases:

Case	Hydrocarbon	Oxygenate	Concentrations [wt%]	COT [°C]	COP [bar]	δ [kg$_{H_2O}$ / kg$_{\text{dry feed}}$]
i	Naphtha	Methanol	[0, 0.025, 0.05, 0.075, 0.1, 0.5, 1.0, 2.0]	840	1.8	0.35
ii	Naphtha	DME	[0, 0.025, 0.05, 0.075, 0.1, 0.5, 1.0, 2.0]	840	1.8	0.35

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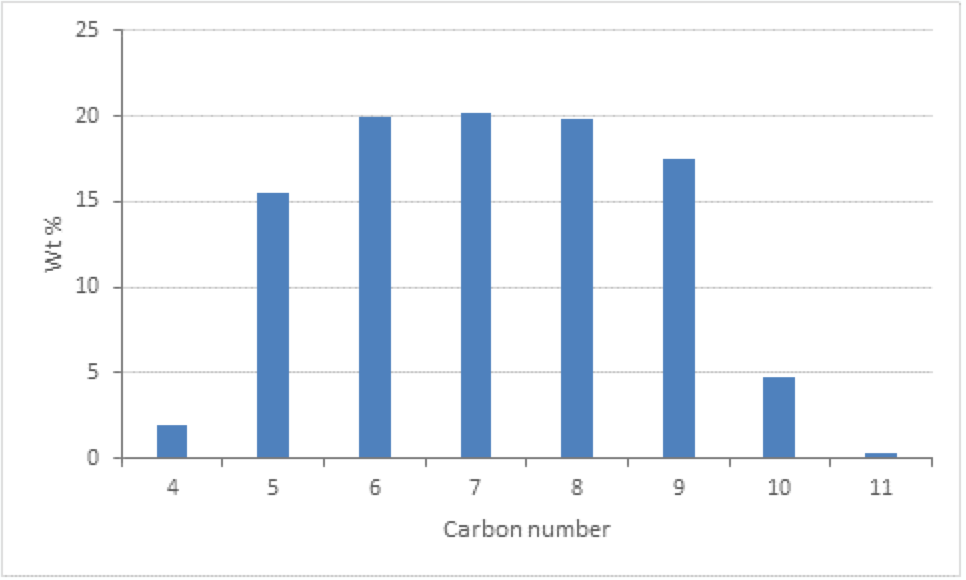
Simulation cases

Naphtha composition

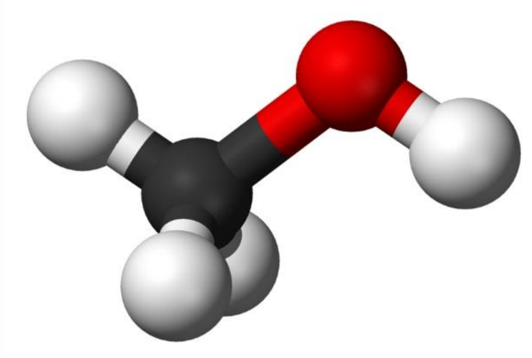
– Reconstructed from commercial indices using SIMCO

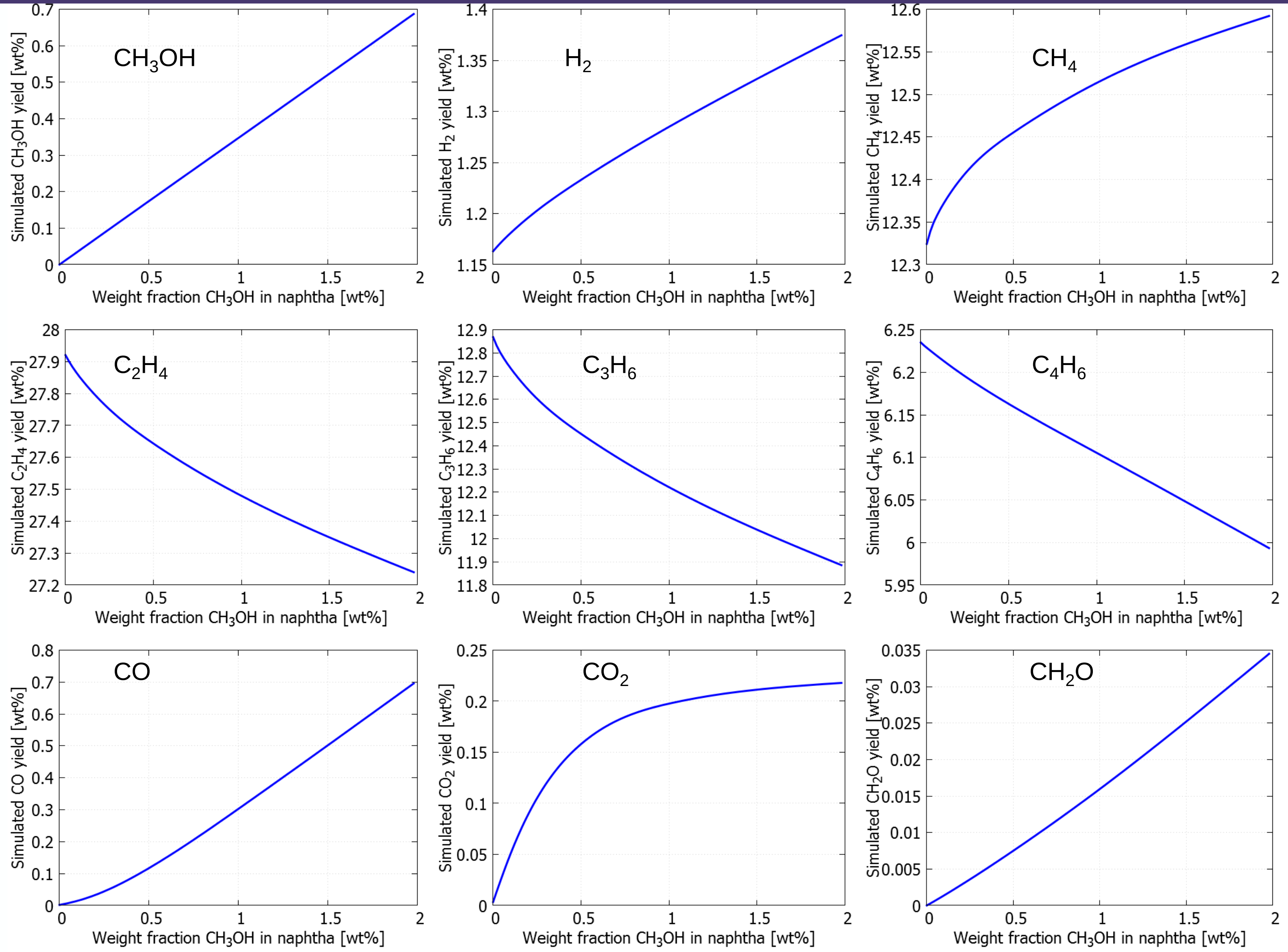
Commercial indices of the naphtha feed	
Specific density [kg/m³]	708.8
ASTM D86 [°C]	
IBP	39
50%	99
FBP	165
PIONA [wt%]	
Paraffins	36.5
Iso-paraffins	32.8
Olefins	0.0
Naphthenes	21.4
Aromatics	9.20

Reconstructed feed

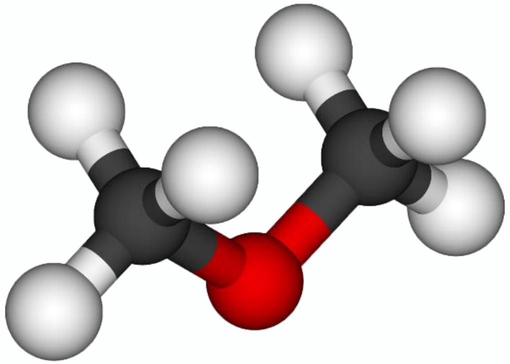


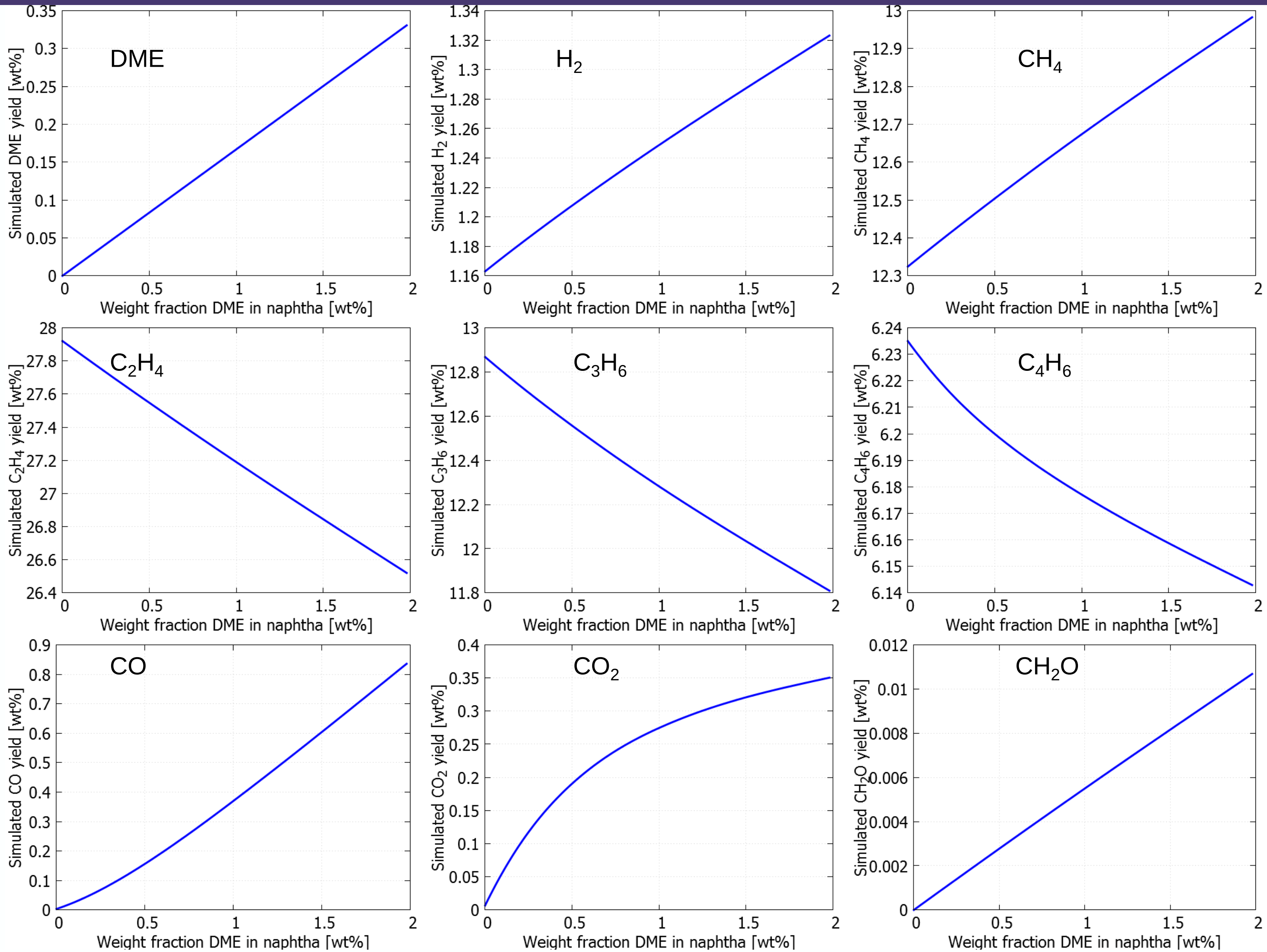
Results: Case I





Results: Case II





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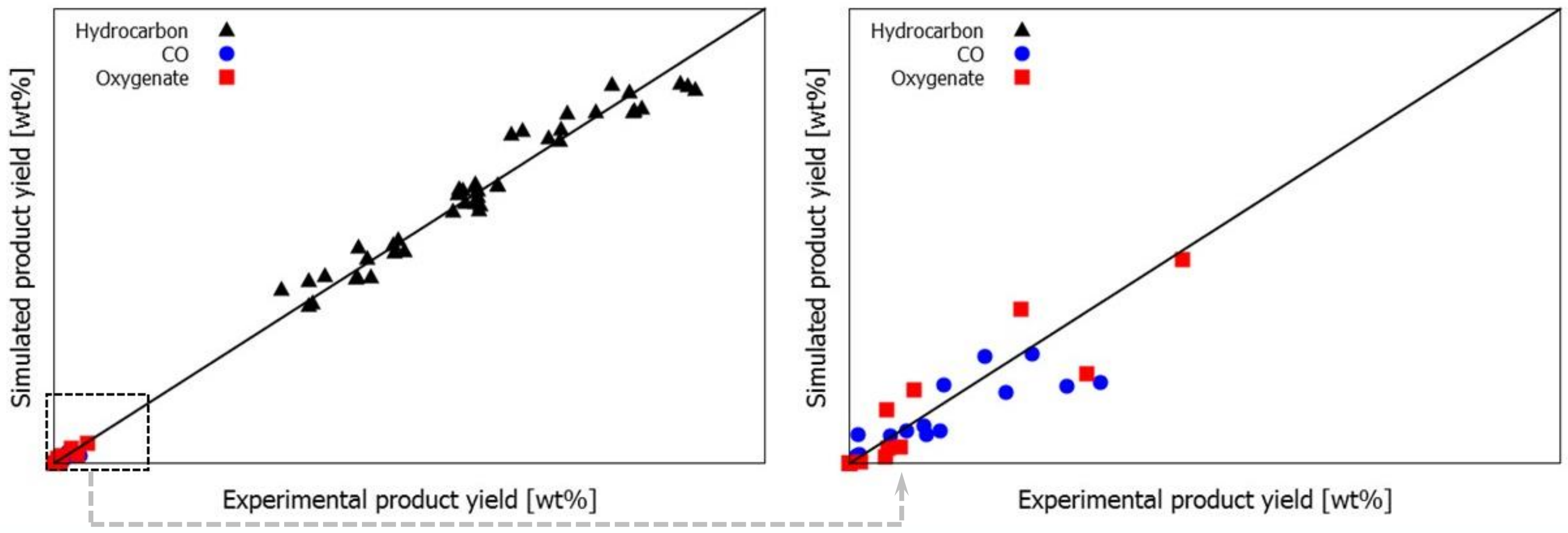
Validation

Simulated vs experimental data

– Temperatures: 800 - 860 °C

– Conc. Oxygenates: 0 – 2 wt%



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Wrapping up

- CRACKSIM has been extended with the thermal decomposition of oxygenates
- COILSIM1D can explicitly account for the effect of oxygenates on reactor outlet yields
- Presence of oxygen compounds in the feed negatively impact the yields of valuable products

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Wrapping up

- The simulated cases (methanol and DME) showed an increased yield of CO, CO_2 and formaldehyde, compared to pure HC feed
- Validation with pilot plant experiments showed good agreement of the model for a broad range of conditions

Acknowledgements

The Long Term Structural Methusalem Funding

Methusalem programma

Long Term Structural Methusalem Funding of the Flemish Government

Questions

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