Multi-scale Modeling and design of chemical Reactions and Reactors

Guy B. Marin

http://www.lct.ugent.be/methusalem
12 h 00: Posters intro 2 minutes each
12 h 30: Lunch/Poster session
14 h 00: **Summary** of the final report of the **first term** of the programme by Guy B. Marin
14 h 30: Presentation of the **proposal** for the **second term** by Maarten Sabbe and Paul Van Steenberge
15 h 00: Discussion
15 h 45: **Deliberation of IAB** based on received report and presentations
16 h 30: **Feedback by IAB** to MC members
17 h 00: End of meeting
M2dcR2 ⇒ Application Domains

- Biomass to liquids
- Renewables to chemicals
- Functional Polymers
- Environmental

M2dcR2

Methusalem proposal presentation, 11 September 2008

Laboratory for Chemical Technology, Ghent University

http://www.lct.UGent.be

Methusalem Programme: Advisory Board Meeting, June 16 2015
COILSIM1D: en route to a spin-off

COILSIM1D

The advanced simulation and optimization software for the ethylene industry
**COILSIM1D: Current status**

- Over 25 license agreements
- Production, R&D and Consulting clients in 4 different continents
- Strongly client driven
- Commercial strategies
  - Standalone vs. Partnership
• LES method can be used as a reliable and robust tool for the cold flow evaluation and optimization of novel reactor designs

• The tremendous amount of information captured allows improvements to existing RANS models (e.g. turbulent Prandtl/Schmidt numbers, Reynolds stress algebraic/transport models, wall functions, ...)

• Currently in the process of filing a joint patent application with BASF SE for a novel tubular reactor

• Improved heat transfer characteristics for equal pressure losses compared to currently commercialized designs
10 bullets with achievements

Axis 1 Platform for design of polymers

1. Experimental determination of termination rate coefficients
2. Bivariate description of copolymer microstructure

Axis 1 Platform for design of catalysts

1. Integrated Stefan-Maxwell, Mean Field Approximation and Single-Event MicroKinetic (SEMK) models
2. Design of cooperative acid-base catalysts for aldol condensation
3. Validation and application of ab initio based microkinetic model for bio-ethanol dehydration to ethene
10 bullets with achievements

**Axis 2 Reactor design for process intensification**

1. 3D reactor technology for intensified heat transfer
2. Vortex reactor technology for biomass pyrolysis

**Axis 3 Transition from fossil to renewable feedstocks**

1. Thermal conversion of oxygenates to light olefins
2. GCxGC analysis of bio-oils
3. Synthetic pathways for sophorolipid based salts with antimicrobial activity
10 bullets with achievements

Axis 1 Platform for design of polymers


1. Experimental determination of termination rate coefficients
2. Bivariate description of copolymer microstructure
Determination of termination rate coefficients


\[
R_i + R_j \xrightleftharpoons[k_{\text{diff}}(i,j,x,T)]{k_{\text{chem}}(T)} R_i R_j \xrightarrow{k_{\text{chem}}(T)} P_{i+j} \rightleftharpoons R_i + R_j \xrightarrow{k_{\text{app}}(i,j,x,T)} P_{i+j}
\]

\[
\frac{1}{k_{\text{app}}} = \frac{1}{k_{\text{diff}}} + \frac{1}{k_{\text{chem}}}
\]

\(k_{\text{diff}}(i,j,x,T)\): many parameters involved

\(k_{\text{chem}}\): Arrhenius equation

\[
k_{\text{chem}} = A \exp(-\frac{E_a}{RT})
\]

Breakthrough: direct “measurement” of 

\(k_{t,\text{app}}(i,j,x,T)\)

via RAFT-CLD-T technique
Bivariate description of copolymer microstructure

Development of a **novel** and **faster** algorithm to simulate copolymerization processes accounting for two variates: chain length $i$ and cumulative comonomer amount $A F_{A,C}$

Reduction from $10^6$ to 10 operations per step

Direct link with **experimental characterization** and **on-line process control**.
Developed algorithm is also a major step toward the **simulation of individual monomer sequences**.
10 bullets with achievements

Axis 1 Platform for design of catalysts


1. Integrated Stefan-Maxwell, Mean Field Approximation and Single-Event MicroKinetic (SEMK) models


Integrated Single-Event MicroKinetic (SEMK) models

1 dm
reactor scale:
convection

1 μm
crystallite scale:
simultaneous diffusion and reaction

1 nm
unit cell:
diffusion coefficients

effect crystallite geometry on:

a) pore occupancy $n$-C$_6$
and MeC$_5$

b) $n$-C$_6$ hydroconversion
and MeC$_5$ yield ratio


Design of cooperative acid-base catalysts for aldol condensation


Kinetic model accounts for:
- Promoting silanols
- Inhibiting species
- Steric hindrance
- Base strength
- Surface arrangement

Methusalem International Advisory Board Meeting, LCT, Ghent, 16/06/2015
Bio-ethanol dehydration: dominant reaction paths

Bioethanol dehydration: experimental validation

\[ W_{\text{cat}}/F_{\text{EtOH},0} = 6.5 \text{ kg s/mol} \]

\[ P_{\text{EtOH},0} = 24 \text{ kPa} \]
Bio-ethanol dehydration: multibed adiabatic operation

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**Diagram Description:**

- **X_{EtOH,eq}**
- **EtOH conversion**
- **C_{2}H_{4} yield**

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**Graph:**

- **Conversion / Yield (%)**
- **Temperature (K)**

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**Axes:**

- **Conversion / Yield (%)**
- **Temperature (K)**
- **Catalyst mass (ton)**

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**Legend:**

- **Bed I**
- **Bed II**

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**Key Points:**

- The graph illustrates the conversion and yield of ethanol and ethylene as a function of catalyst mass and temperature.
- The multibed adiabatic operation is likely used to optimize the dehydration process.

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**Notes:**

- This diagram is from the M2dcR2 Methusaleum Programme: Advisory Board Meeting, June 16, 2015.
10 bullets with achievements

Axis 2 Reactor design for process intensification


1. 3D reactor technology for intensified heat transfer (patentable)

3D reactor technology for intensified heat transfer

MERT

\[ T \ [K] \]

1200 1160 1120

\[ \sqrt{u_x^2 + u_y^2}/u_b \]

0.03 0.02 0.01

0 0.01 0.02 0.03

1200 1160 1120

Finned

SFT

\[ T \ [K] \]

[Van Cauwenberge, 2015]
Vortex reactor technology for biomass pyrolysis

**Biomass**

**Char**

**Total solids**  
(biomass, char, sand)
Vortex reactor technology for biomass pyrolysis

0.065 char

0.030 biomass

0.55 sand
Vortex reactor technology for biomass pyrolysis

Typical range\(^1,2\) static fluidized beds and risers/CFBs: ~100 – 200 W/(m\(^2\) K)

Axis 3 Transition from fossil to renewable feedstocks


3. Synthetic pathways for sophorolipid based salts with antimicrobial activity (patentable?)
Conversion of oxygenates to light olefins

Poultry Fat & Yellow Grease

\[ \text{Hydrocracking} \rightarrow \text{Green Naphtha} \]  
\[ \text{Hydrotreatment} \rightarrow \text{HDO - FAT} \]

Pine Wood

\[ \text{Kraft Pulping} \rightarrow \text{HDO - TOFA} \]

Pilot Plant
Steam Cracking

- High olefin yields
- High run-length
- Lower heat requirement
GC×GC analysis of bio-oils

Fast Pyrolysis

500 – 800°C
0.5 – 2s

Gas & Char

GC×GC-FID chromatogram

Aldehydes, Furans, Ketones & Alcohols

- Carboxylic Acids
- Phenols & Phenones
- Guaicols, Syringols & Catechols

Anhydrosugars
Hydroxy Acids
GC×GC analysis of bio-oils

Group Type

- Acids & Esters
- Aldehydes & Ketones
- Sugars
- Aromatics
- Benzenediols
- Phenols
GC×GC analysis of bio-oils

Detailed composition
Antimicrobial sophorolipid based salts

Chemical modification of microbial product:
Chemical modification of microbial product:

- Synthesis of aldehyde intermediate
- Modification to amine oxides and ammonium salts

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## TOP-10 Publications


Kinetics of Chemical Reactions
Decoding Complexity
Monograph “ADAMICE”

Advanced Data Analysis and Modeling in Chemical Engineering (Elsevier)

Exhaustive presentation of leading-edge techniques involving mathematics in chemical engineering.

Based on 15 years of collaboration of G.S. Yablonsky, D. Constales, G.B. Marin et al.

To be completed by September 1, 2015.
Coincidences and ordering: patterns

- $A \xrightarrow{k_1} B \xrightarrow{k_2} C$: one point parameter plane $(k_1, k_2)$

$$
(t_B, \text{max}, C_B, \text{max}) \\
(t_{A=B}, C_{A=B}) \\
(t_{B=C}, C_{B=C}) \\
(t_{A=C}, C_{A=C})
$$

$t_{A=B} < t_{A=C} < t_{B,\text{max}} < t_{B=C}$

$C_{A=C} < C_{A=B} < C_{B=C} < C_{B,\text{max}}$
**Coincidence maps: parametric subdomains**

Intersection times of A and B when feeding:
A: t₁
B: t₂

\[ A \leftrightarrow B \rightarrow C \]

Parameter space: \( k_1^+, k_1^-, k_2^+ \)
Coincidence maps: parametric subdomains

Combining all intersections in time and value an intricate map is obtained...

where each different patch is a qualitatively separate subdomain: similar to abstract compositions.

Felix De Boeck (1898-1995)

Denis Constales
MaCKiE conferences and seminars

Acronym of *Mathematics in (bio)Chemical Kinetics and Engineering*. Aim to bring together (bio)chemical engineers and mathematicians to explore collaboration on leading-edge modeling questions.

International conferences: 2002 (Ghent), 2007 (Houston, with NASCRE), 2009 (Ghent), 2011 (Heidelberg), 2013 (Chennai), 2015 (Ghent). Special Issues of Chemical Engineering Science.

Annual Seminars every other year from 2002-now.
MaCKiE-2015 (Ghent)

July 2-3, 2015; held back to back with ICCK-2015.

First conference in the series to include “bio” in the title, and to have parallel sessions.

Special Bykov-Gorban-Yablonsky seminar on 135 man-years of kinetics research.

Mackie Award for lifetime achievement in (bio)Chemical Engineering.
The 9th International Conference on Chemical Kinetics

June 28th – July 2nd, 2015, Ghent, Belgium

Plenary speakers: Donald Truhlar (U. Minn.), Enrique Iglesia (Berkeley), Michelle Coote (Austr. NU), Markus Kraft (Cambridge), Paul Seakins (Leeds)

Special issue of International Journal of Chemical Kinetics dedicated to ICCK 9
Cumulative budget breakdown

<table>
<thead>
<tr>
<th>Year</th>
<th>Methusalem2</th>
<th>Total Planned</th>
<th>Engagements</th>
<th>New Initiatives</th>
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M2dcR2 Methusalem Programme: Advisory Board Meeting, June 16 2015
Post 2015: evaluation of budget

1. Oorspronkelijk gestelde doelstellingen
2. Maximum 10 bullets with achievements
3. Explanation of achievements (6-10 pages)
4. 10 publications with brief explanation
5. 5 pages with plans
6. Composition of Management Committee
7. Composition International Advisory Board
8. Advice of International Advisory Board