GUANGZHOU INSTITUTE OF ENERGY CONVERSION APRIL 26, 2024

Electricity is in the Catalyst: A Reaction Engineering Approach to Gas Treatment and Valorization

Joris W. Thybaut

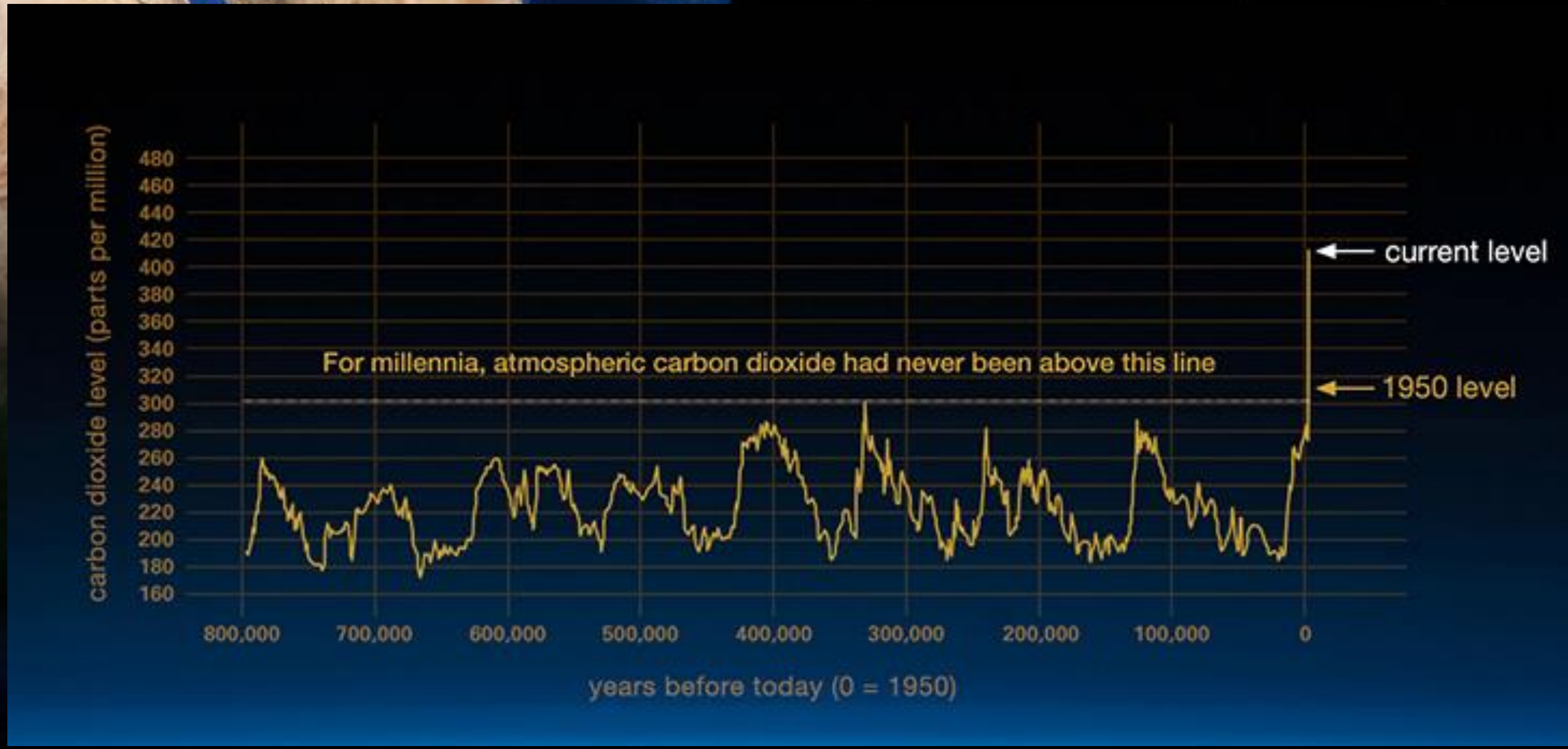
Laboratory for Chemical Technology (LCT), Ghent University, Technologiepark 125, 9052, Ghent , Belgium

GHENT UNIVERSITY

LCT
DRIVING CHEMICAL TECHNOLOGY

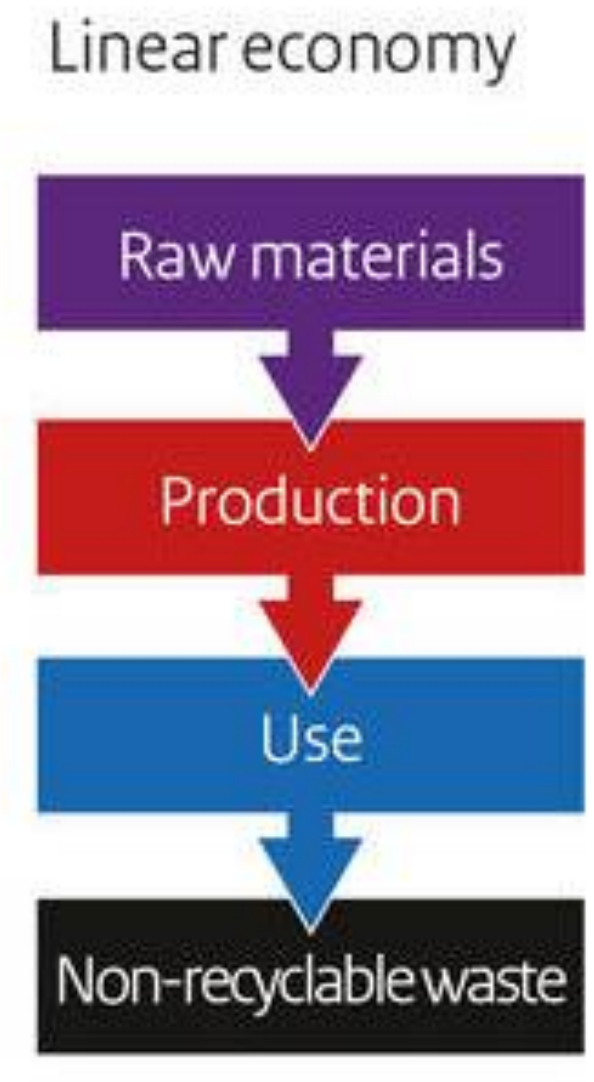
C123
VALORISING METHANE RESOURCES

e-CODUCT



carbon dioxide level (parts per million)
480
460
440
420
400
380
360
340
320
300
280
260
240
220
200
180
160
current level
For millennia, atmospheric carbon dioxide had never been above this line
1950 level
800,000
700,000
600,000
500,000
400,000
300,000
200,000
100,000
0
years before today (0 = 1950)

from a linear to a circular economy



Linear economy

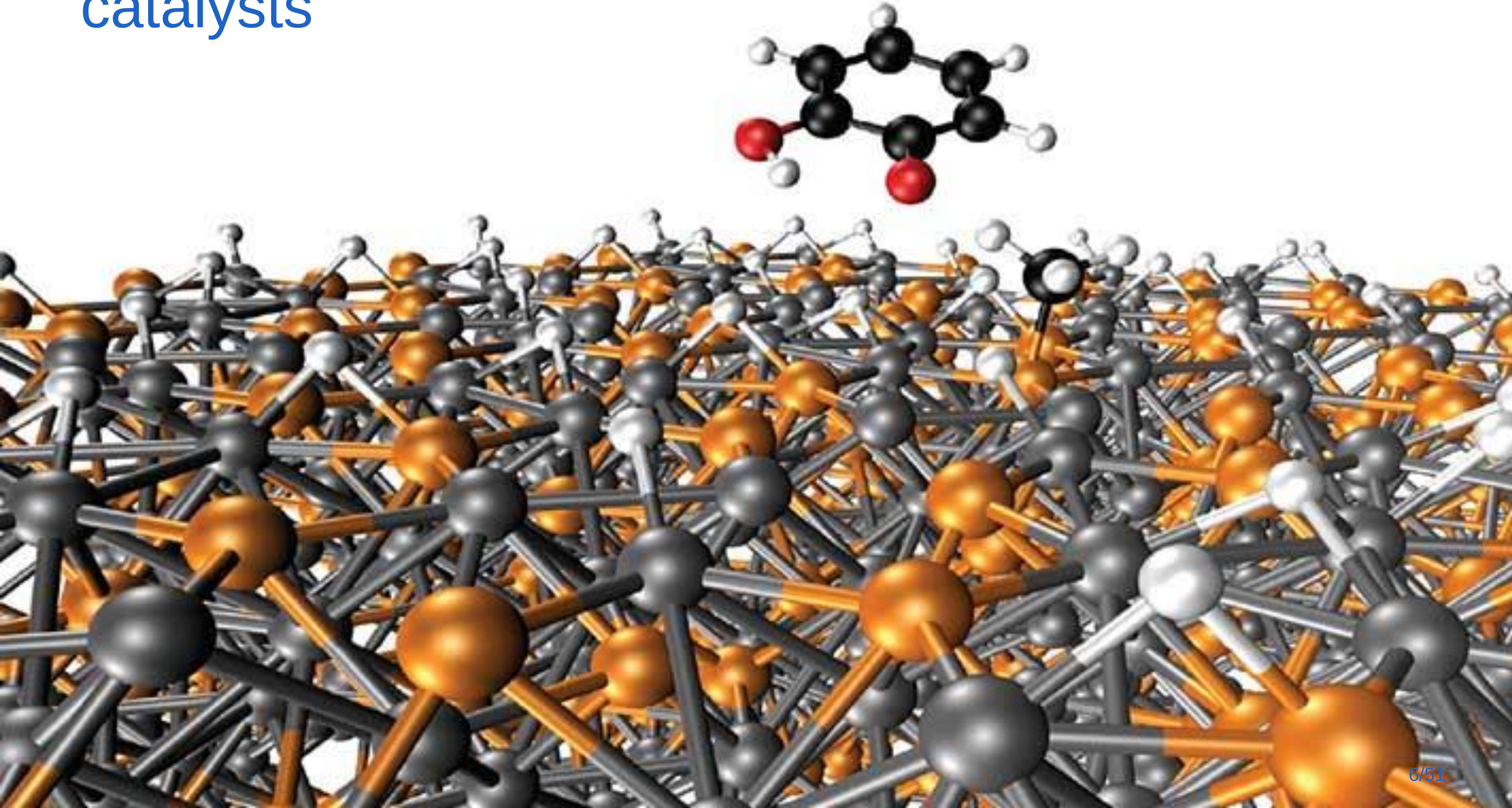
Raw materials

Production

Use

Non-recyclable waste

catalysts

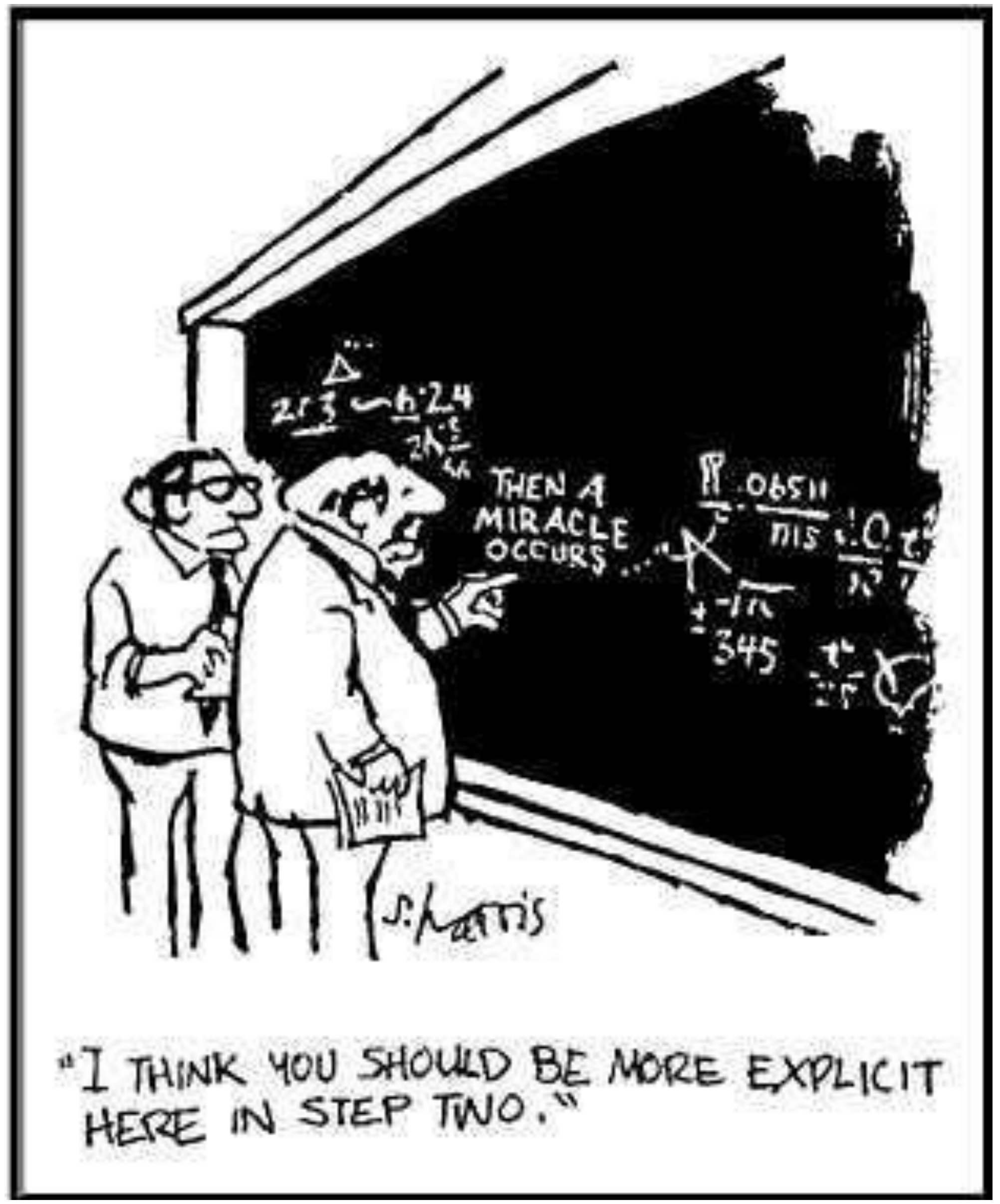


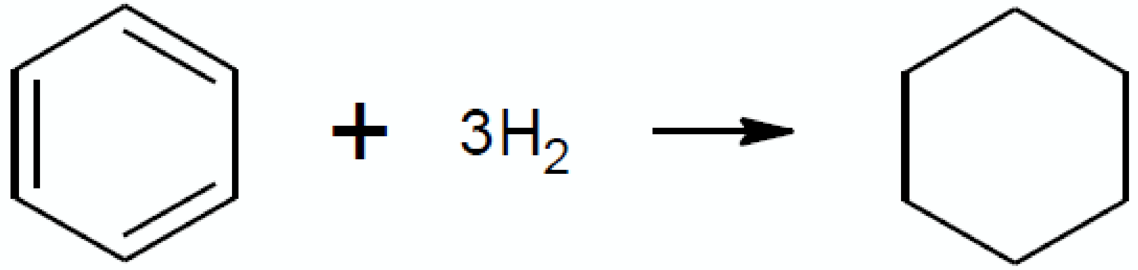
reactors

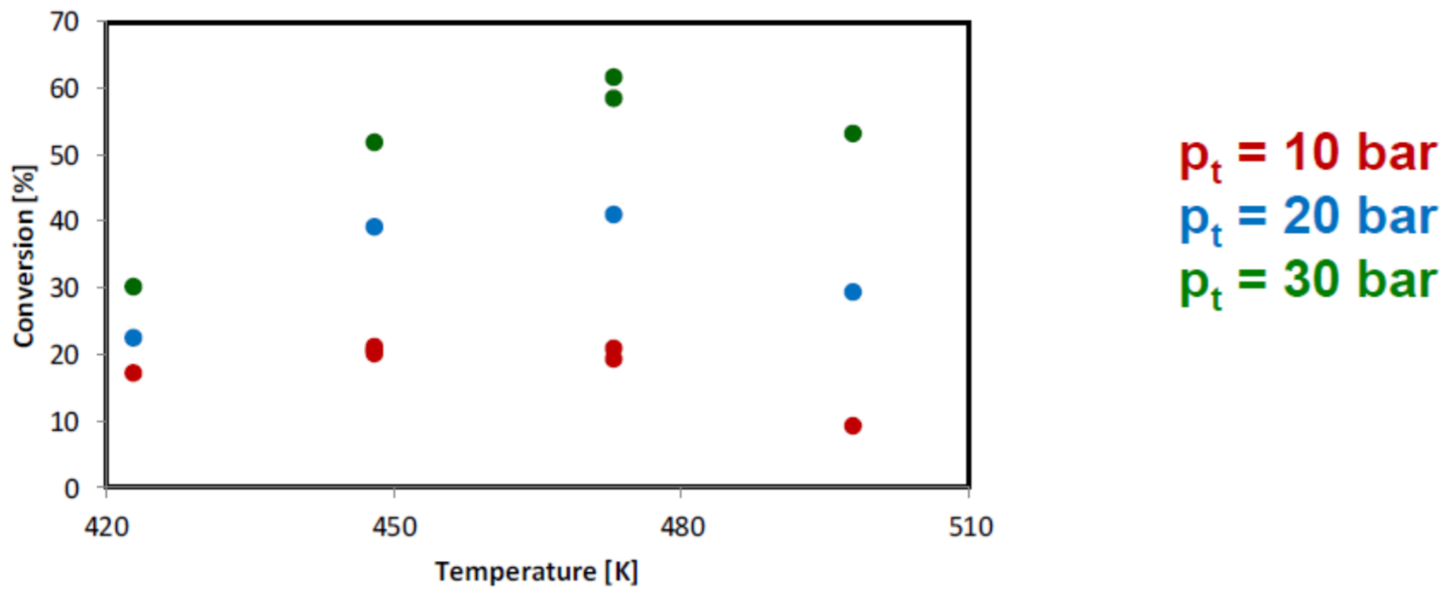
processes

unraveling the miracle

chemical/catalytic kinetics







catalyst

$r_{hydrogenation}$ = ?

$p_{benzene}$

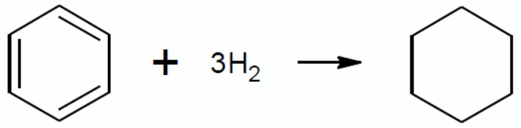
T

k

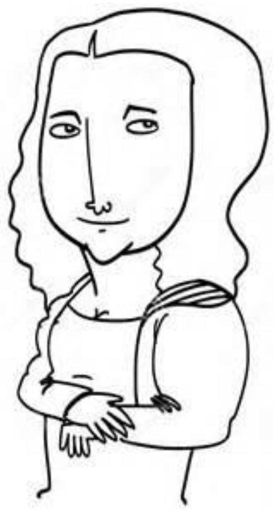
$p_{hydrogen}$

model detail: kinetics

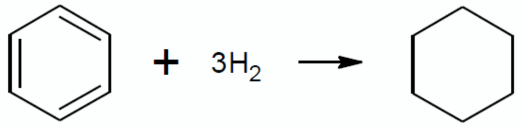
power law



$$r = kp_B^n p_{H_2}^m$$



Langmuir-Hinshelwood



$$r = C_t k_i \left(\prod_{j=1}^{i-1} K_j\right) K_B K_{H_2}^{i/2} p_B p_{H_2}^{i/2} \theta_{*_{free}}^2$$

$$1 = \theta_{*_{free}} + \theta_{H_2^*} + \theta_{B^*}$$

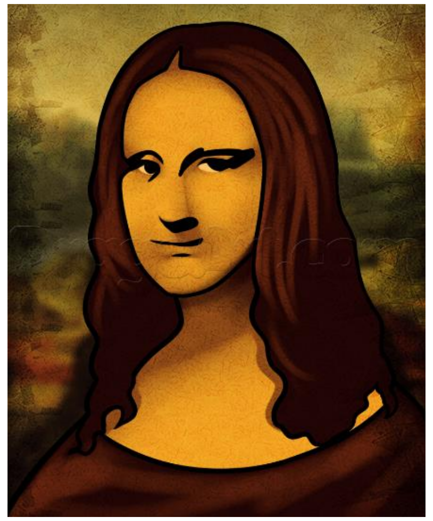
$$1 = \theta_{*_{free}} + \sqrt{K_{H_2} p_{H_2}}\,\theta_{*_{free}} + K_B p_B \theta_{*_{free}}$$

$$1 = \theta_{*_{free}} \left(1 + \sqrt{K_{H_2} p_{H_2}} + K_B p_B\right)$$

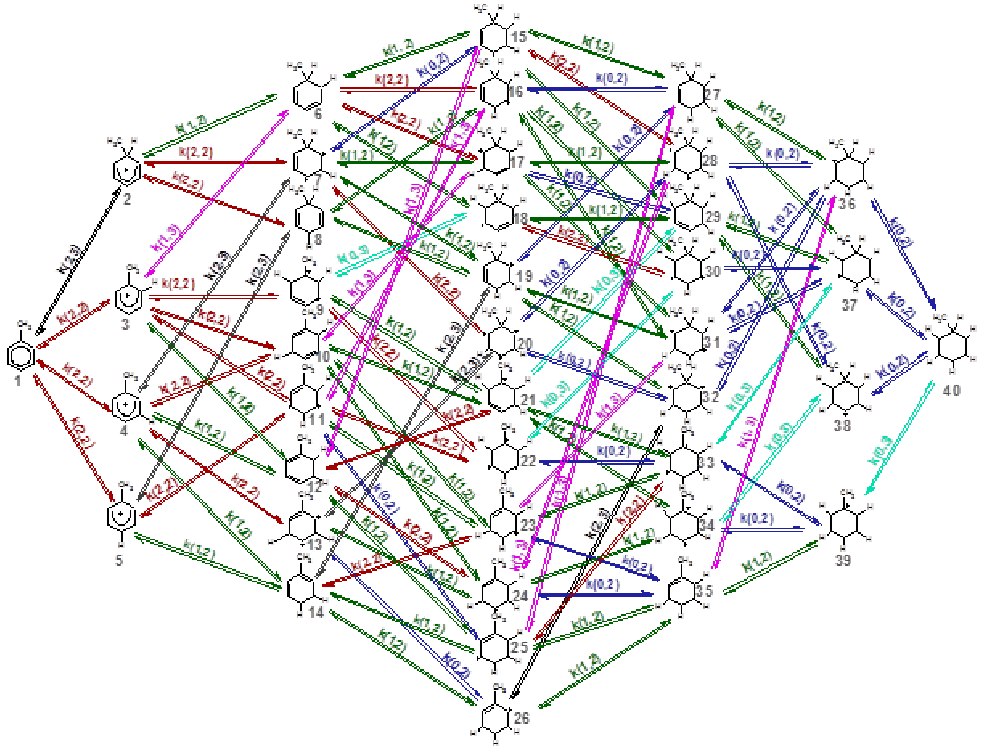
$$\theta_{*_{free}} = \frac{1}{\left(1 + \sqrt{K_{H_2} p_{H_2}} + K_B p_B\right)}$$

$B + * \Leftrightarrow B^*$	K_B
$H_2 + 2* \Leftrightarrow 2H^*$	K_{H_2}
$B^* + H^* \leftrightarrow BH^* + *$	K_1
$BH^* + H^* \leftrightarrow BH_2^* + *$	K_2
$BH_2^* + H^* \leftrightarrow BH_3^* + *$	K_3
$BH_3^* + H^* \leftrightarrow BH_4^* + *$	K_4
$BH_4^* + H^* \leftrightarrow BH_5^* + *$	K_5
$BH_5^* + H^* \leftrightarrow BH_6 + *$	K_6

$$r = \frac{C_t k_i \left(\prod_{j=1}^{i-1} K_j\right) K_B K_{H_2}^{i/2} p_B p_{H_2}^{i/2}}{\left(1 + \sqrt{K_{H_2} p_{H_2}} + K_B p_B\right)^2}$$



microkinetics

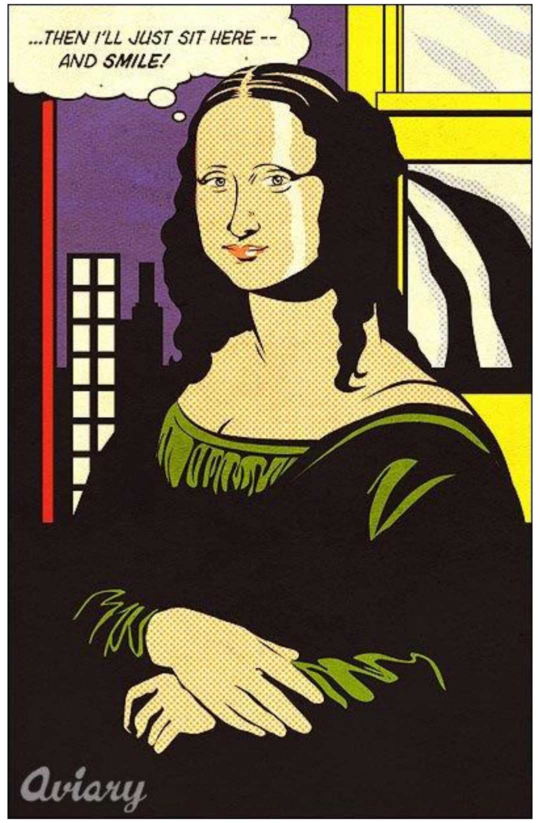


no unique style (or single truth!)

cubism

Da Vinci

simpson



pop art

‘de gustibus et coloribus,

non disputandum est’

‘taste and color are

not to be discussed’

outline

- introduction
- methane valorization – C123
- electrification
- e-CODUCT
- OBIWAN
- conclusions

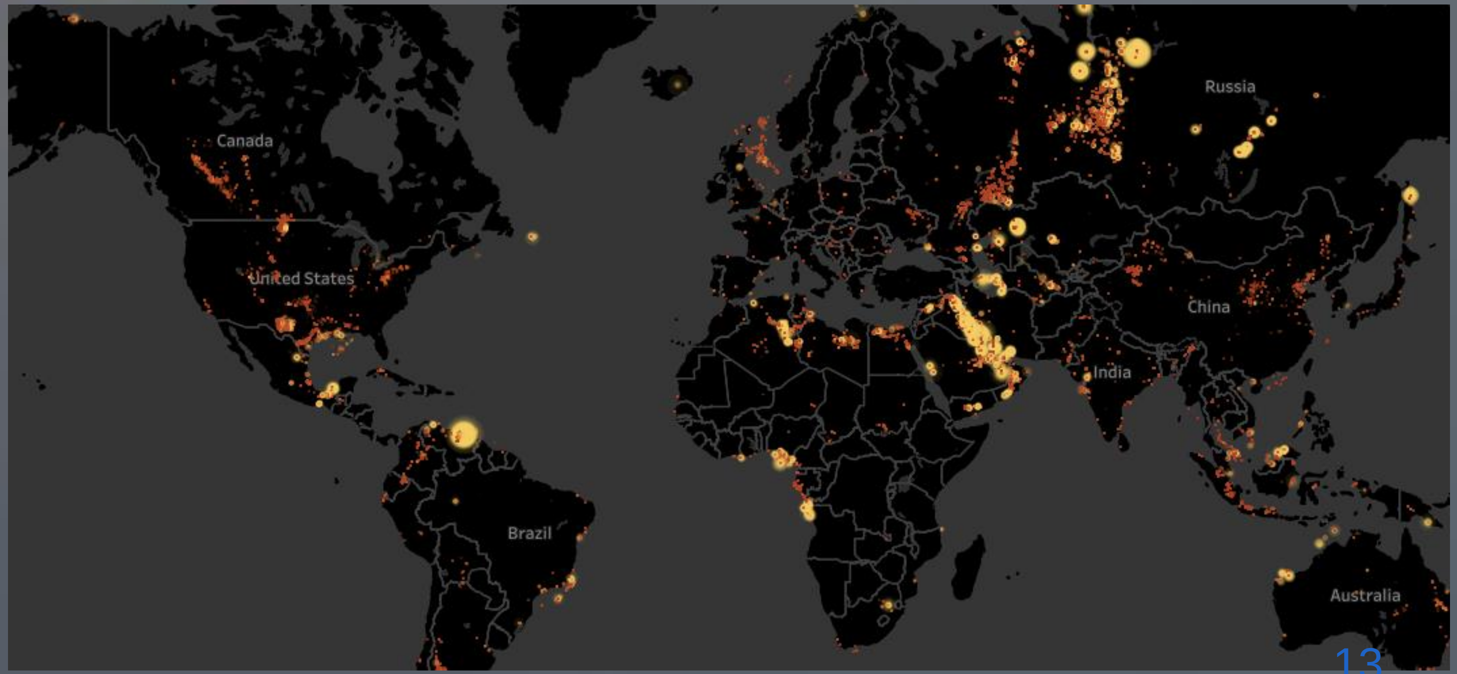
C123
VALORISING METHANE RESOURCES

e-CODUCT

GHENT UNIVERSITY

LCT
DRIVING CHEMICAL TECHNOLOGY

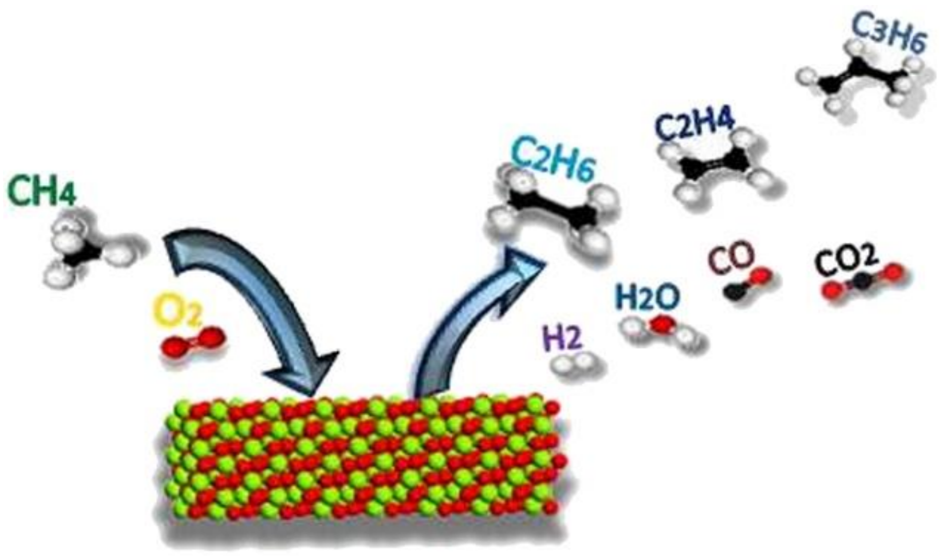
today’s reality



requires immediate solutions

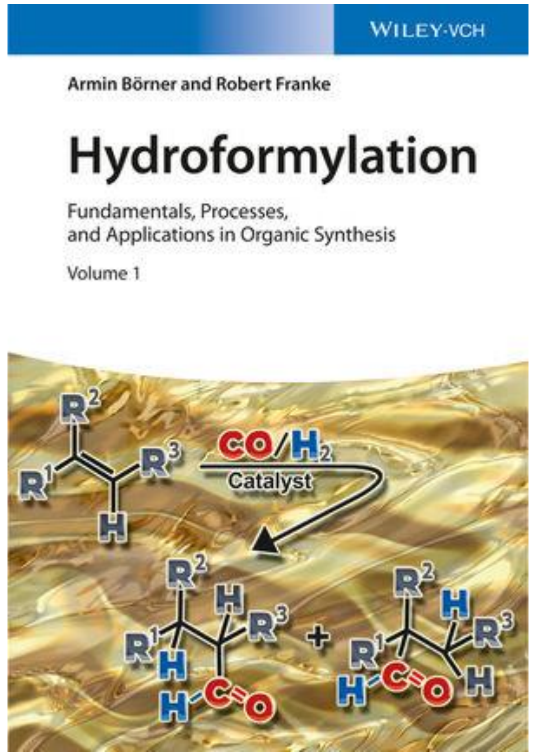
C123

VALORISING METHANE RESOURCES



Noon et al. J. Nat. Gas Sci. Eng. 18 (2014) 406

methane oxidative conversion (OCoM) into ethylene, CO and H_2 followed by **hydroformylation to propanal**


WILEY-VCH

Armin Börner and Robert Franke

Hydroformylation

Fundamentals, Processes,
and Applications in Organic Synthesis

Volume 1

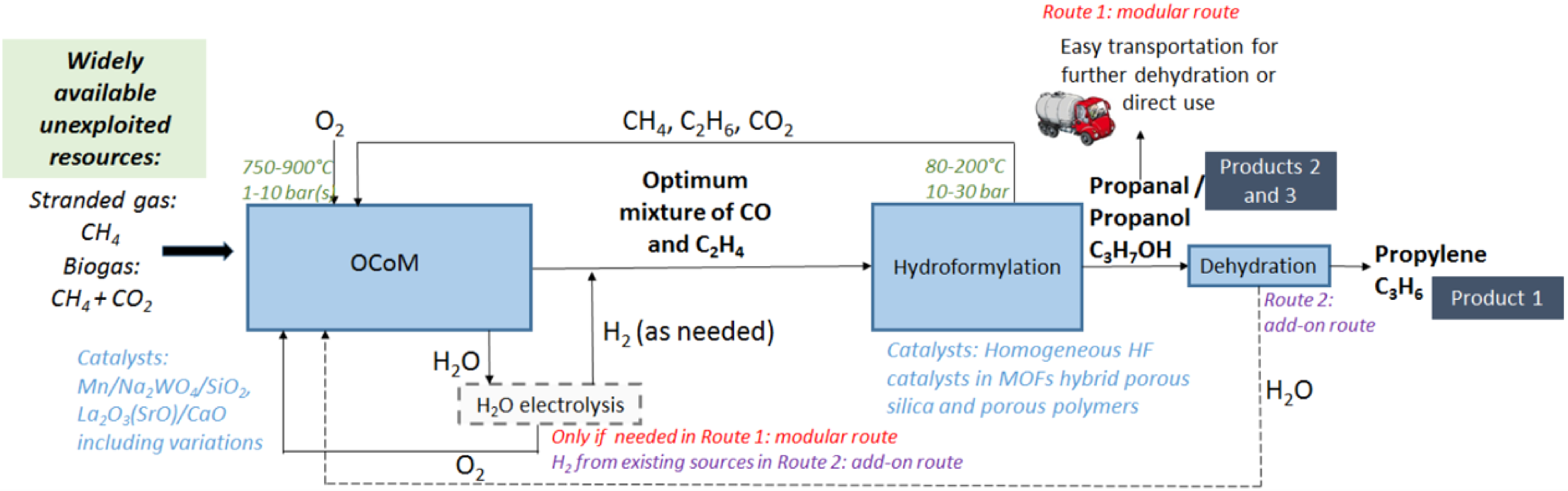
Börner and Franke, Wiley, 2016

GHENT UNIVERSITY

LCT
DRIVING CHEMICAL TECHNOLOGY

https://www.sintef.no/projectweb/c123/

C123 methane oxidative conversion and hydroformylation to propylene



Route 1: modular route

Easy transportation for further dehydration or direct use

Widely available unexploited resources:

Stranded gas:
CH_4
Biogas:
$CH_4 + CO_2$

O_2

CH_4, C_2H_6, CO_2

750-900°C
1-10 bar(s)

OCoM

Optimum mixture of CO and C_2H_4

80-200°C
10-30 bar

Hydroformylation

Propanal / Propanol C_3H_7OH

Products 2 and 3

Dehydration

Propylene C_3H_6

Product 1

Route 2: add-on route

H_2 (as needed)

H_2O

H_2O electrolysis

H_2O

O_2

Catalysts: $Mn/Na_2WO_4/SiO_2$, $La_2O_3(SrO)/CaO$ including variations

Catalysts: Homogeneous HF catalysts in MOFs hybrid porous silica and porous polymers

Only if needed in Route 1: modular route

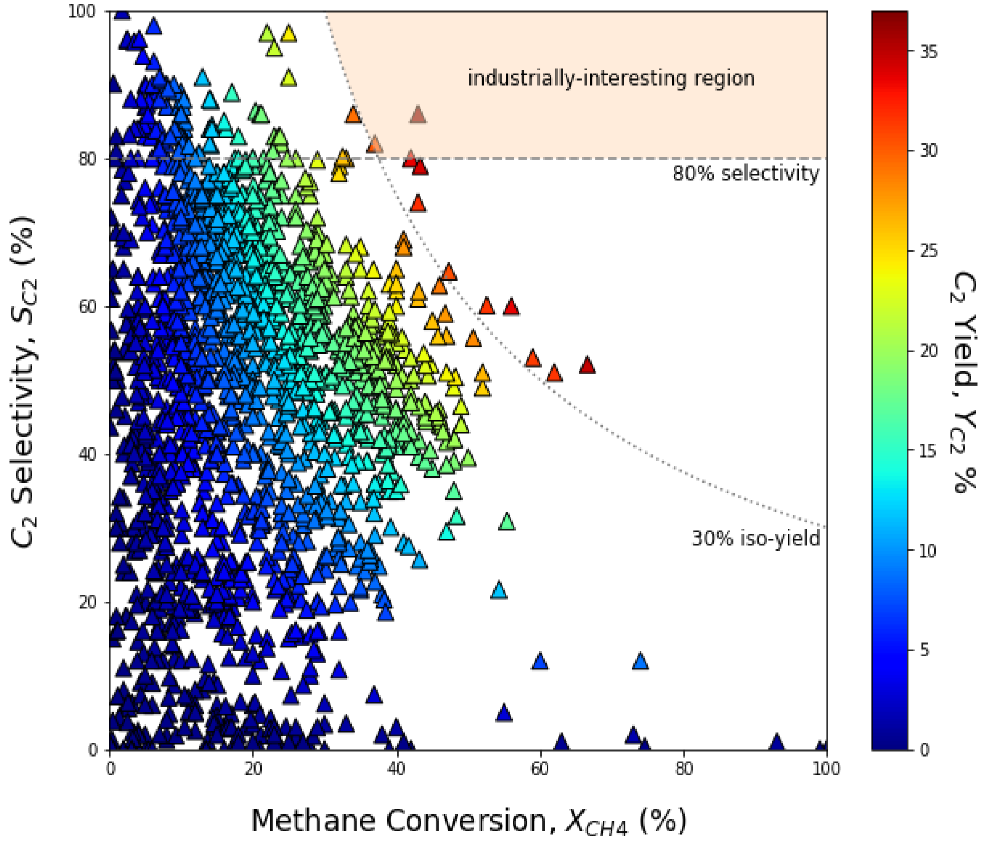
H_2 from existing sources in Route 2: add-on route

- feedstock: natural gas/associated gas/biogas (methane and CO_2)
- targeted product: easily transportable/high-value chemical (propanal, propanol, propylene)
- add-on vs modular route

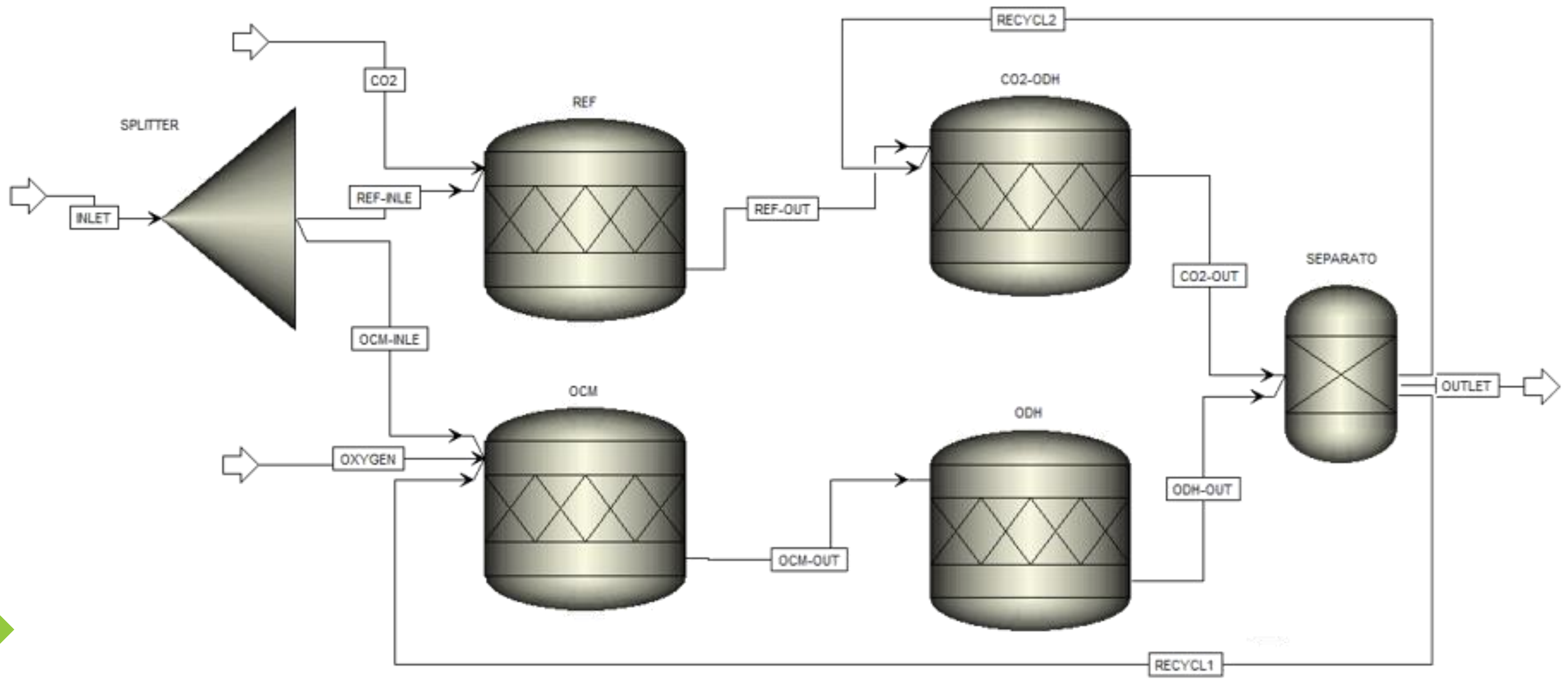
Oxidative Conversion of Methane (OCoM)

Oxidative Coupling of Methane (OCM)

- decades of research
- entire periodic table as potential catalyst
- awaiting successful commercialization



Pirro et al. Reac. Chem. Eng. 5 (2020) 584

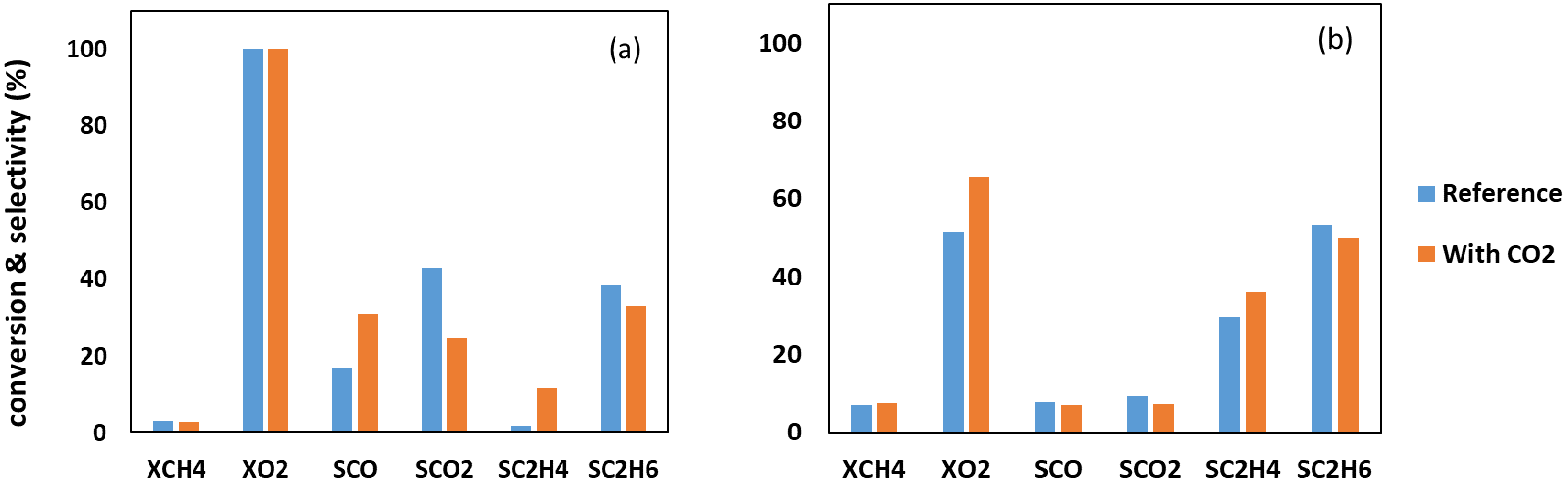


hydroformylation feedstock production

- save on separation
- enhance atom efficiency
- incorporate CO_2
- easily liquefiable product

Romero-Limones et al. Chem. Eng. Proc. (2024) revision submitted

CO_2 impact at O_2-lean conditions



(Conditions: T = 800 °C, P = 1 bar, O_2/CO_2 = 0.5%/9.5% for La-Sr/CaO, O_2/CO_2 = 1.0%/9.0% for NaMnW/SiO_2)

- Selectivity of C_2H_4 is increased at the expense of C_2H_6 selectivity
- CO_2 selectivity is decreased

Seemingly CO_2-ODH has occurred at these conditions

Cheng et al. Int. J. Chem. Kinet. (2024) revision submitted

CO_2 assisted dehydrogenation of ethane (CO_2-ODH)

$$C_2H_6 + CO_2 \rightarrow C_2H_4 + CO + H_2O$$

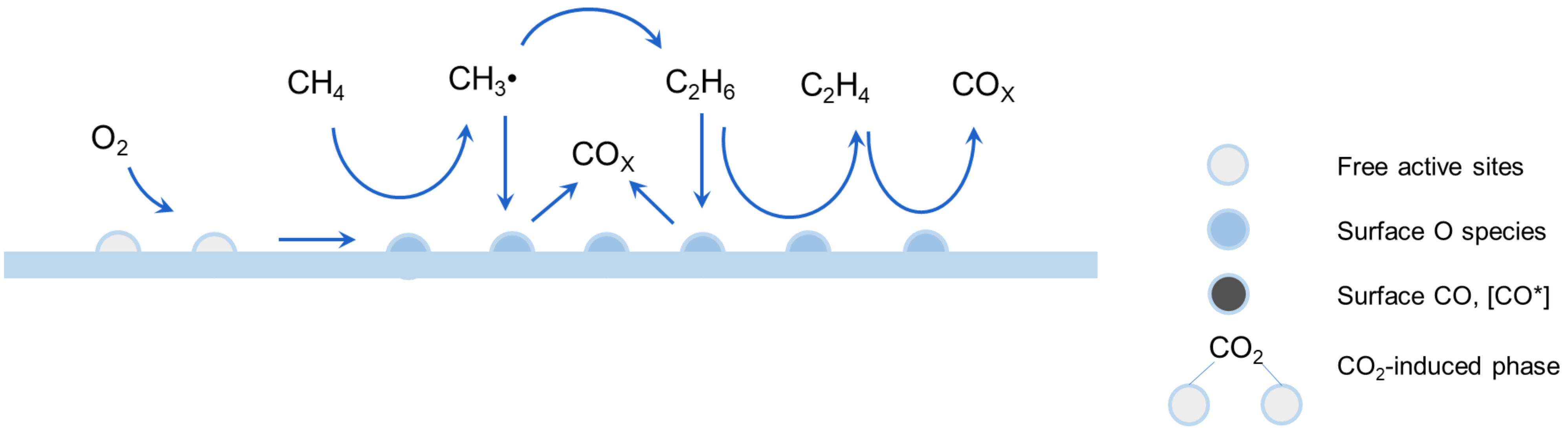
	X_{C2H6}	X_{CO2}	S_{C2H4}	S_{CO}
Blank 1	29.7%	1.9%	99.7%	0.3%
La-Sr/CaO	36.7%	10.6%	99.5%	0.5%
Blank 2	24.3%	1.3%	99.4%	0.6%
NaMnW/SiO_2	27.3%	4.6%	99.2%	0.8%

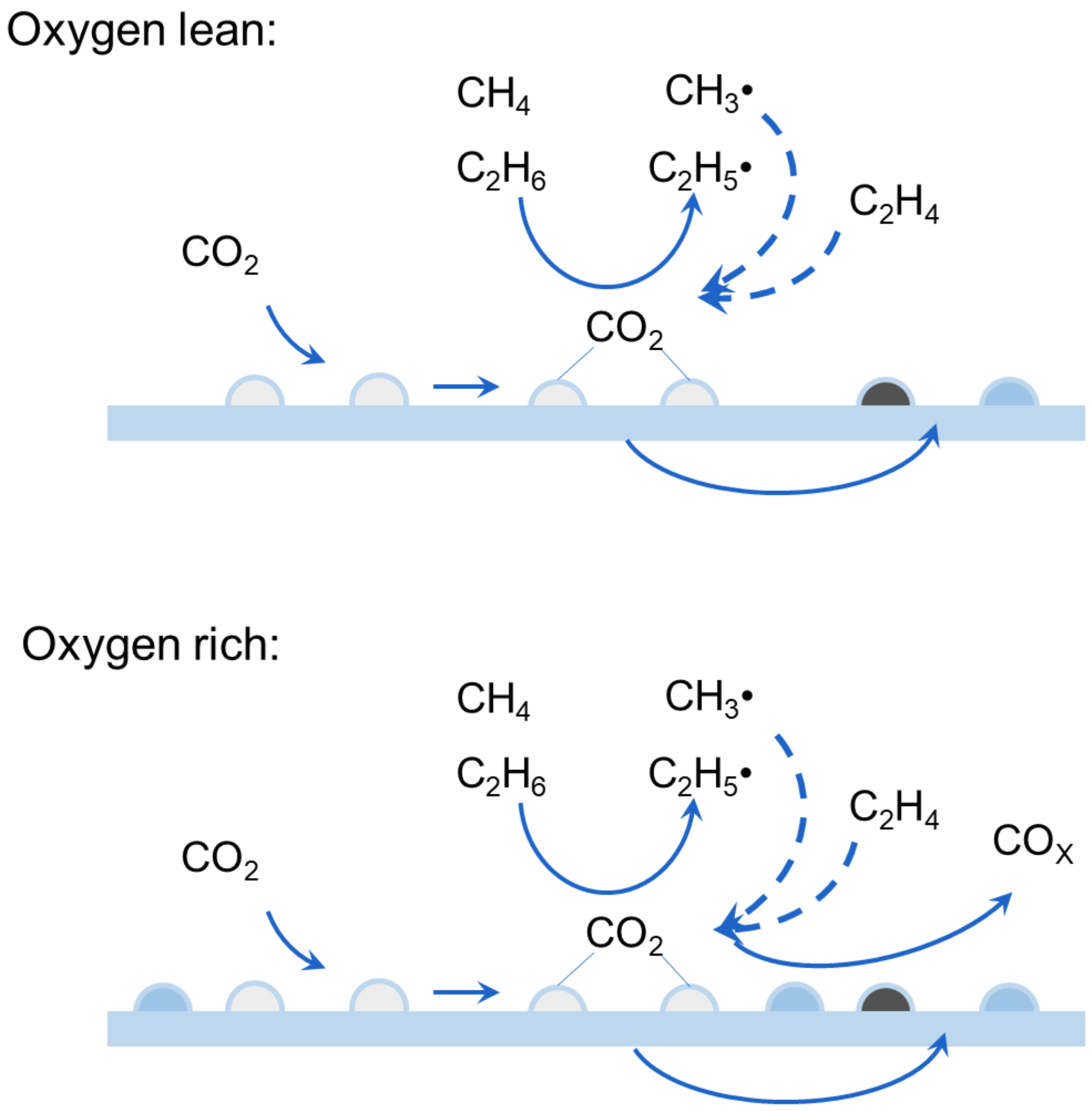
(Conditions: T = 800 °C, P = 1 bar, C_2H_6/CO_2 = 8%/8%, F_v = 142 ml/min for La-Sr/CaO, 160 ml/min for NaMnW/SiO_2)

- OCM catalysts promotes CO_2-ODH
- previous reports also verify NaMnW/SiO_2 and $La_2O_2CO_3$ are active in ODH of alkenes[1, 2]

1. J. Zhu et al. *Catal. Today*. **148,** 310–315 (2009)
2. Y. Bi et al. *Catal. Today*. **61,** 369-375 (2000)

proposed mechanism





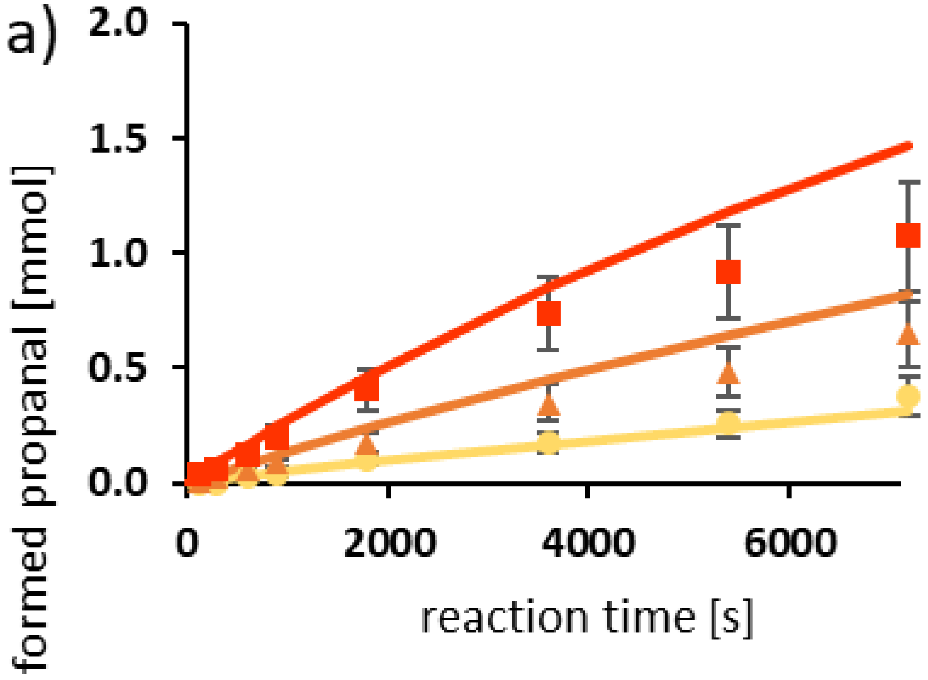
- CO_2 competes with O_2 and forms [O*]’
- [O*]’ is less active but capable of converting C_2H_6 into C_2H_4
  - O_2-rich: C_2H_4 further oxidized into CO_x – no or negative effect
  - O_2-lean: C_2H_4 survives from oxidation – positive effect

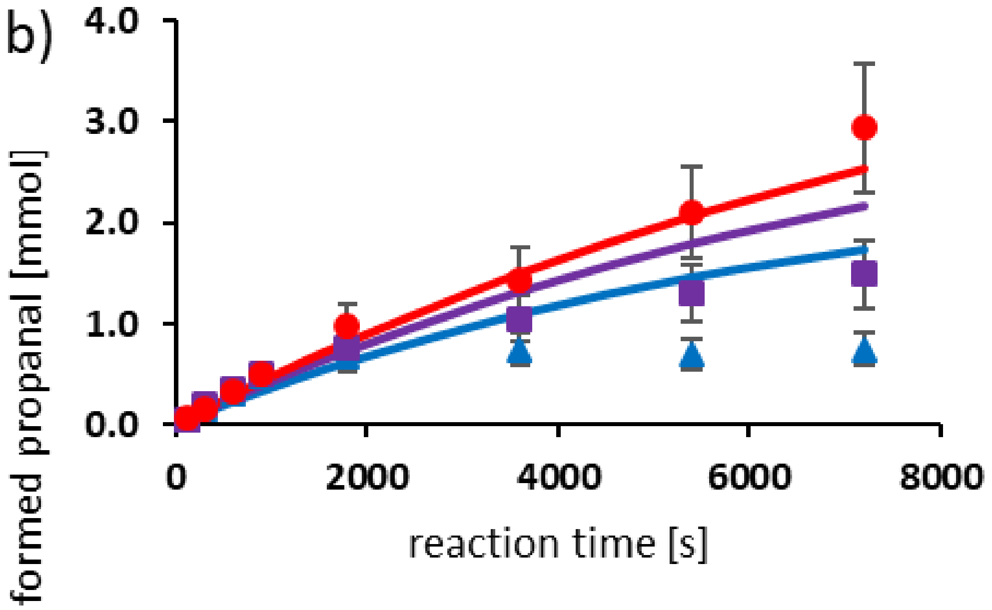
Cheng et al. Int. J. Chem. Kinet. (2024) revision submitted

ethylene hydroformylation

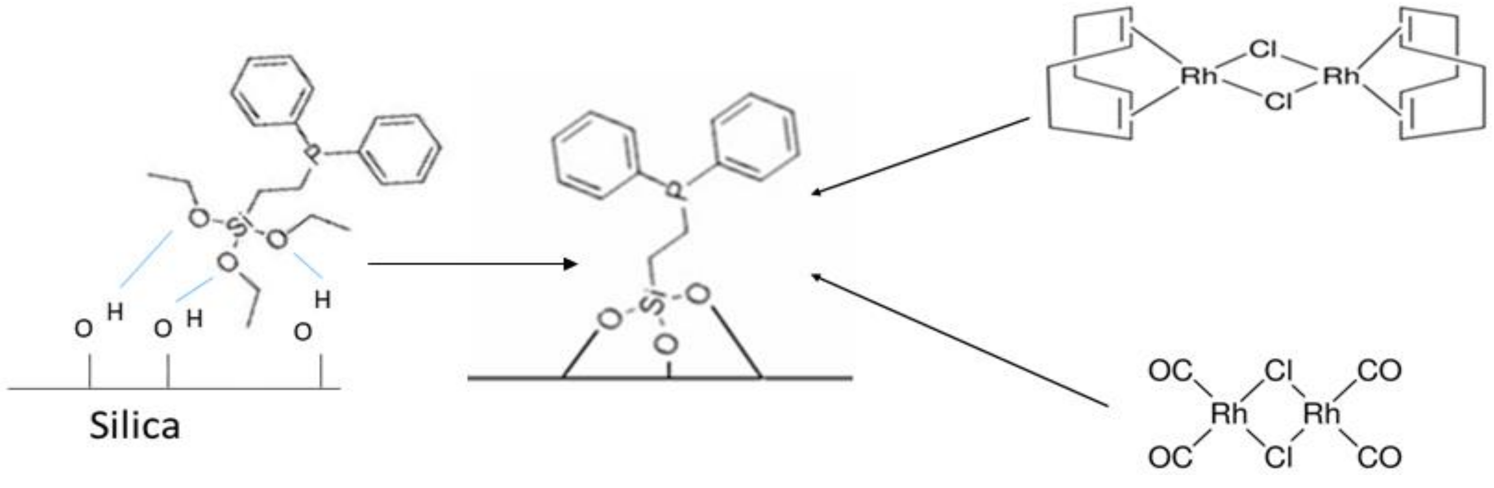
homogeneous catalysis

- Rh or Co complexes
- high pressure
- liquid phase





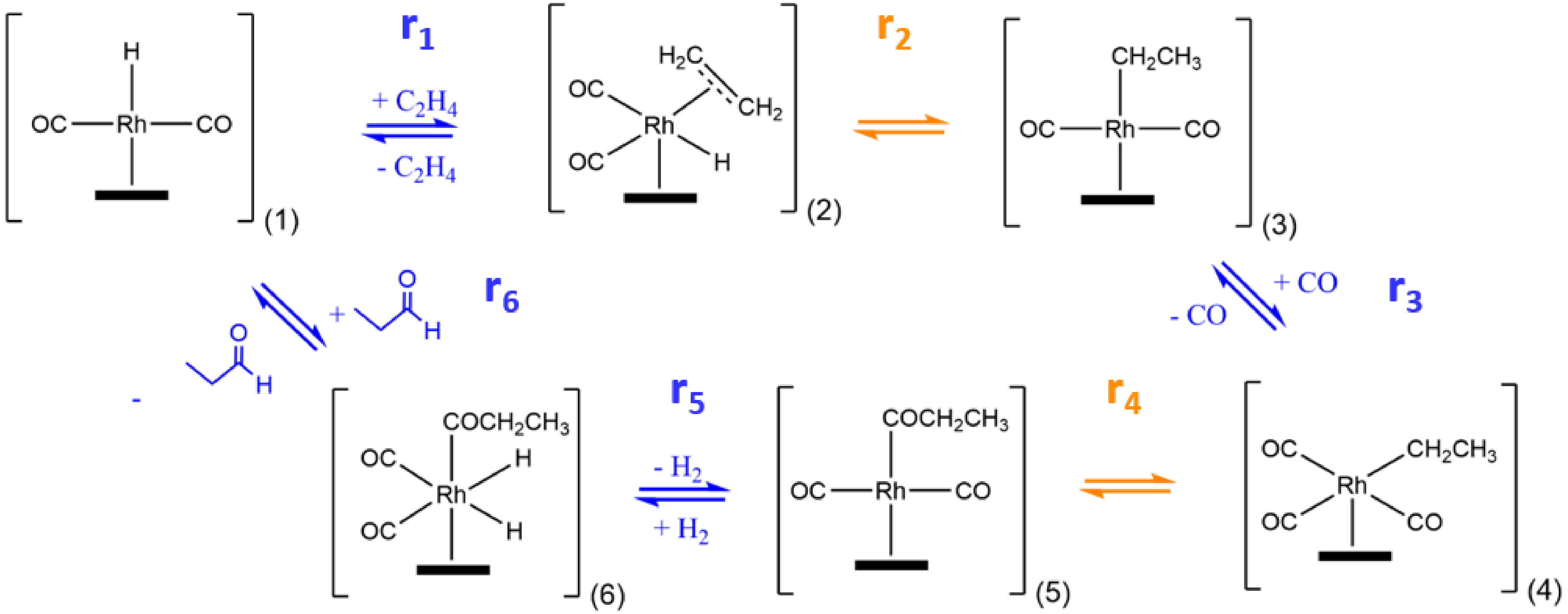
Siradze et al. Ind. Eng. Chem. Res. (2021)



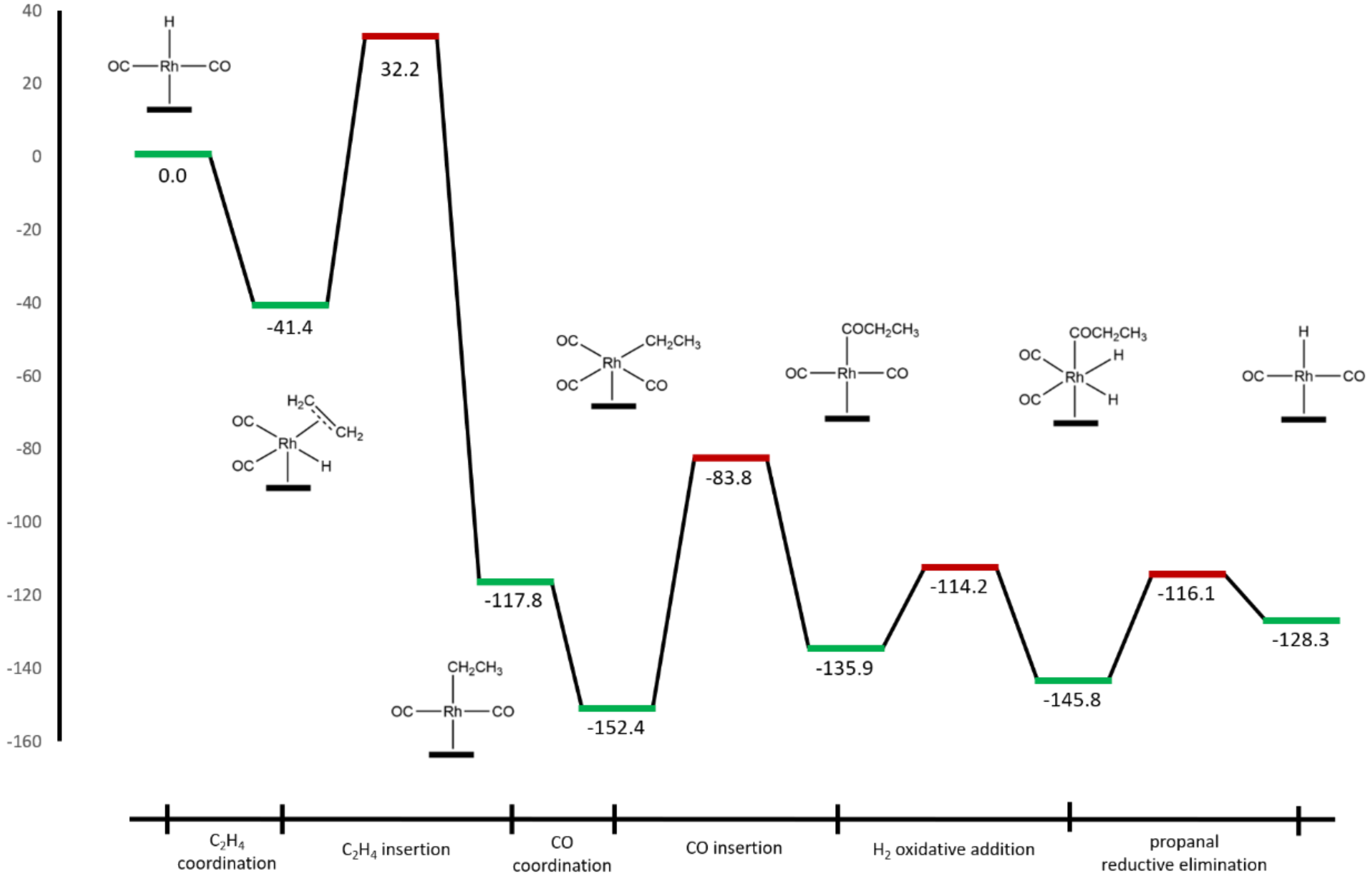
heterogeneous catalysis

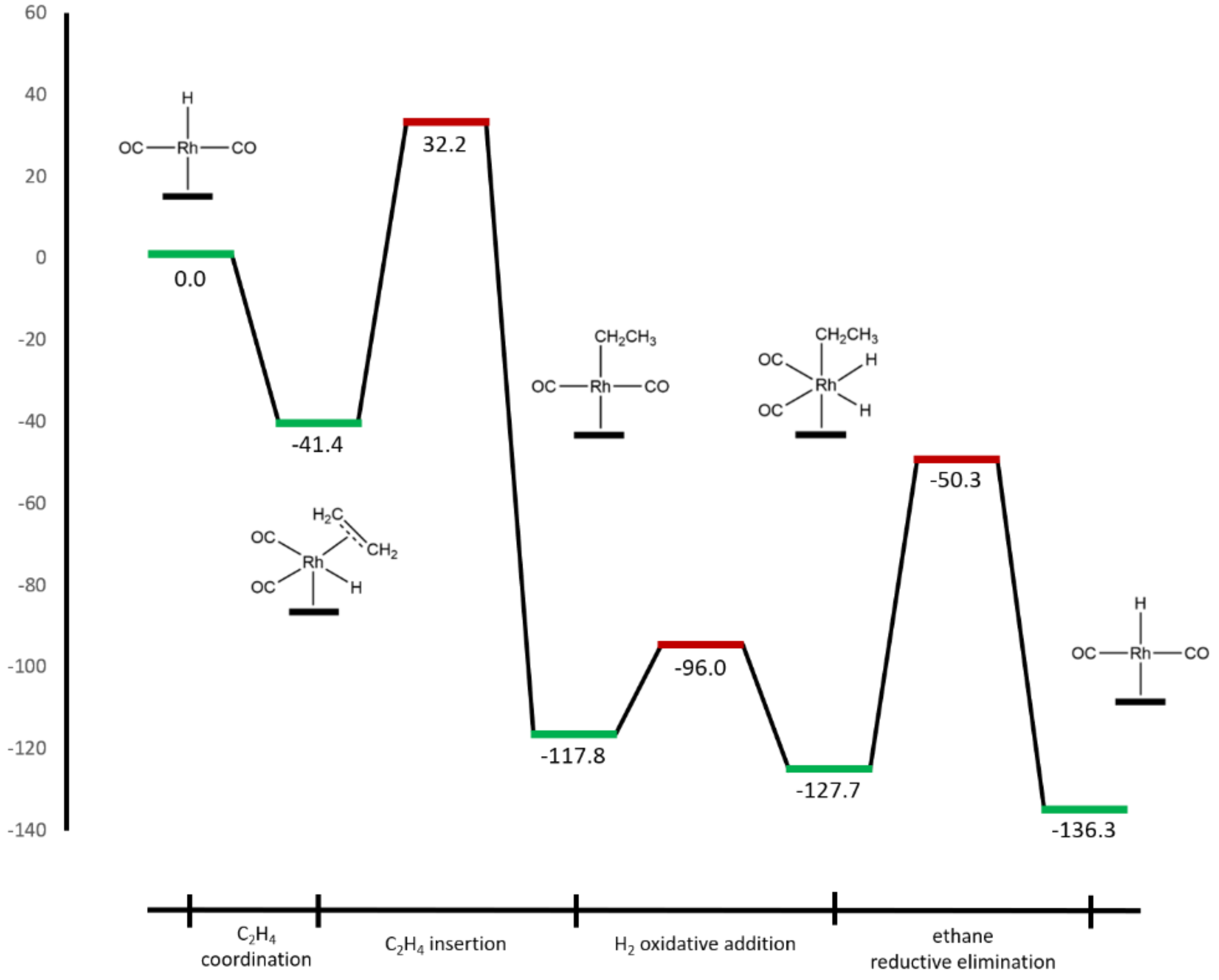
- grafting phosphine ligand on silica support
- rhodium coordination complexes
- tethered hydroformylation catalyst

from homogeneous to heterogenized catalysis



hydroformylation vs hydrogenation





Siradze et al. Chem. Eng. J. (2024) submitted

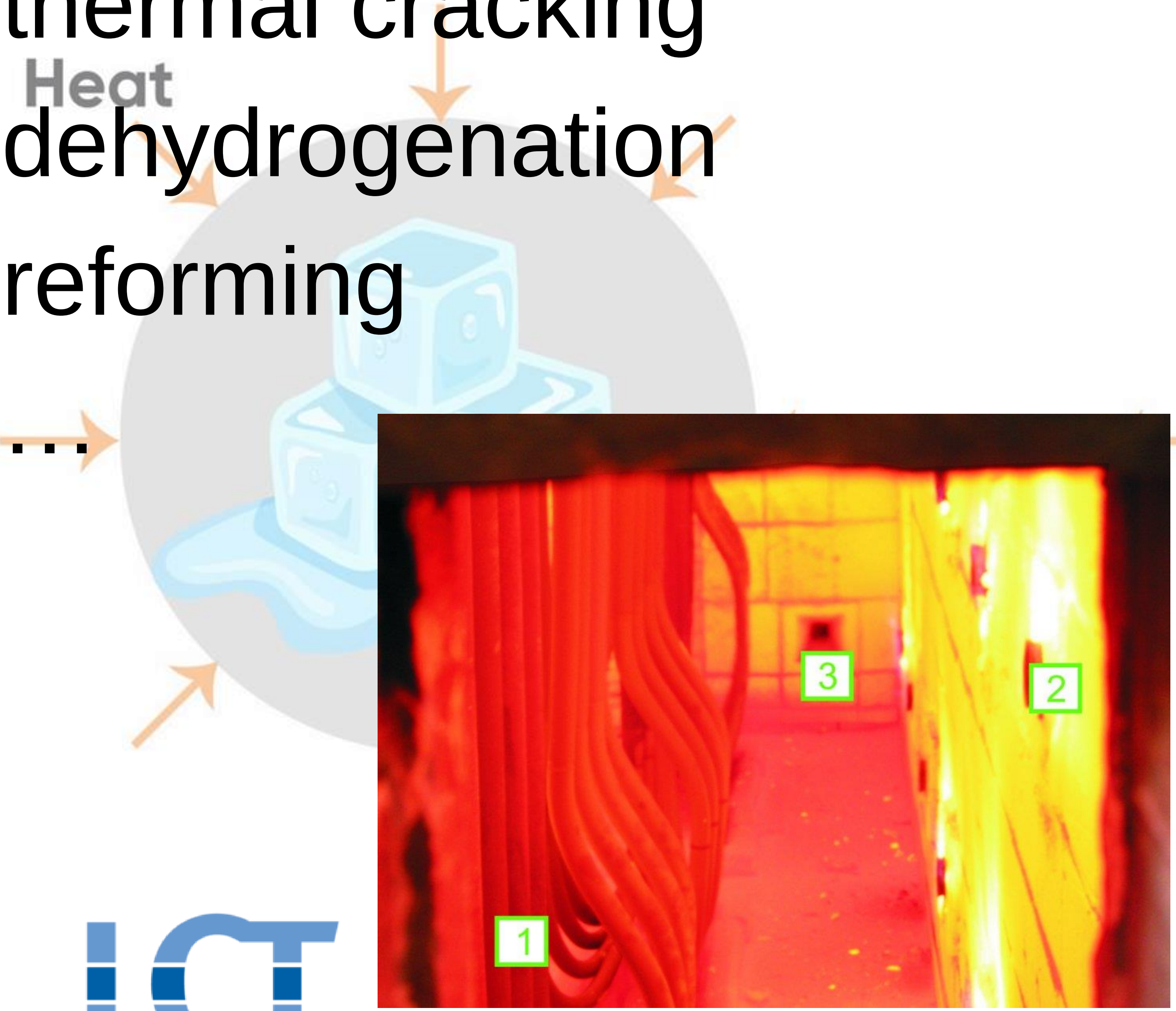
outline

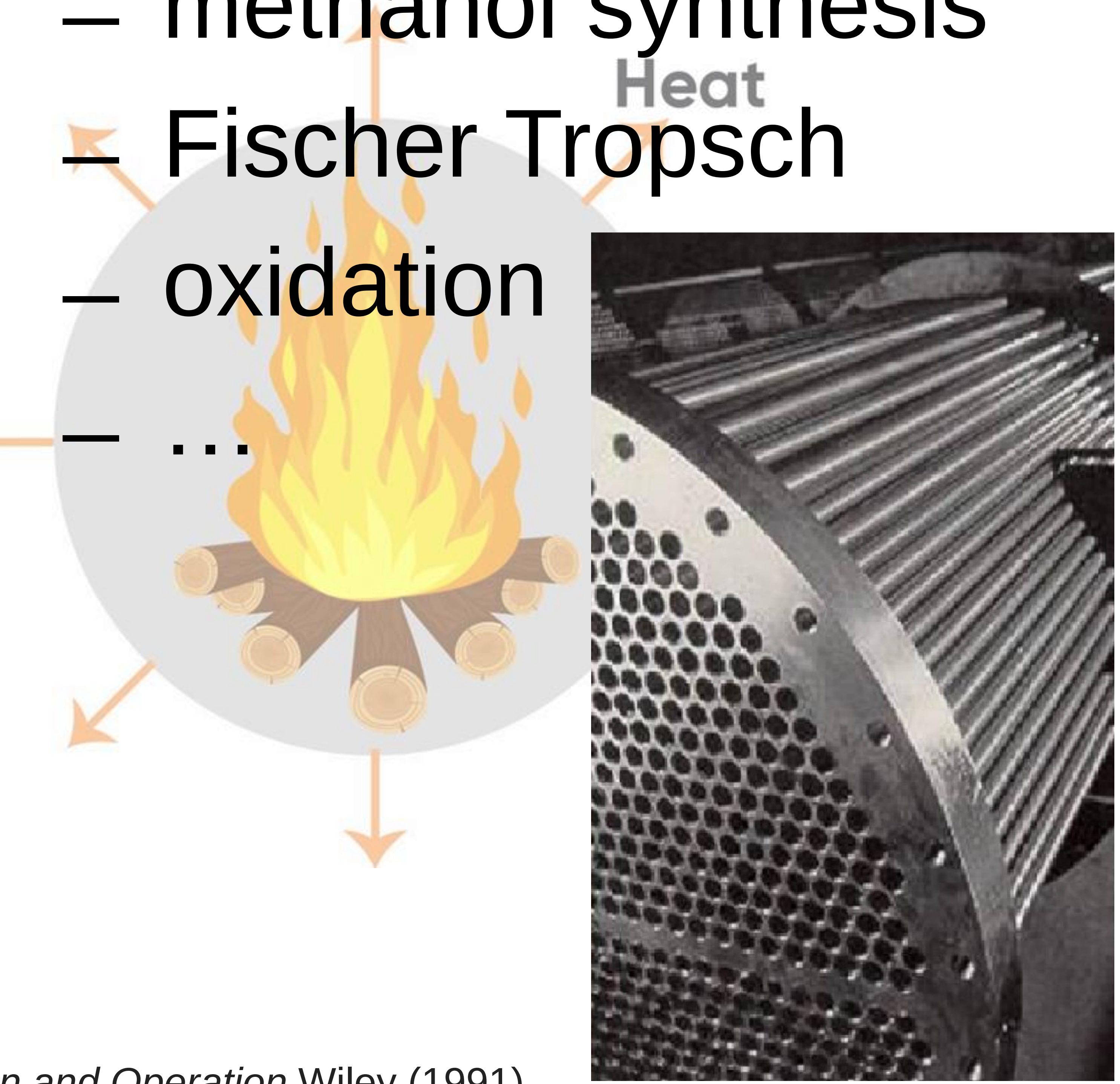
- introduction
- methane valorization – C123
- electrification
- e-CODUCT
- OBIWAN
- conclusions

heat requirements in chemical reactions

- endothermic reactions
  - thermal cracking
  - dehydrogenation
  - reforming
  - …

- exothermic reactions
  - methanol synthesis
  - Fischer Tropsch
  - oxidation
  - …

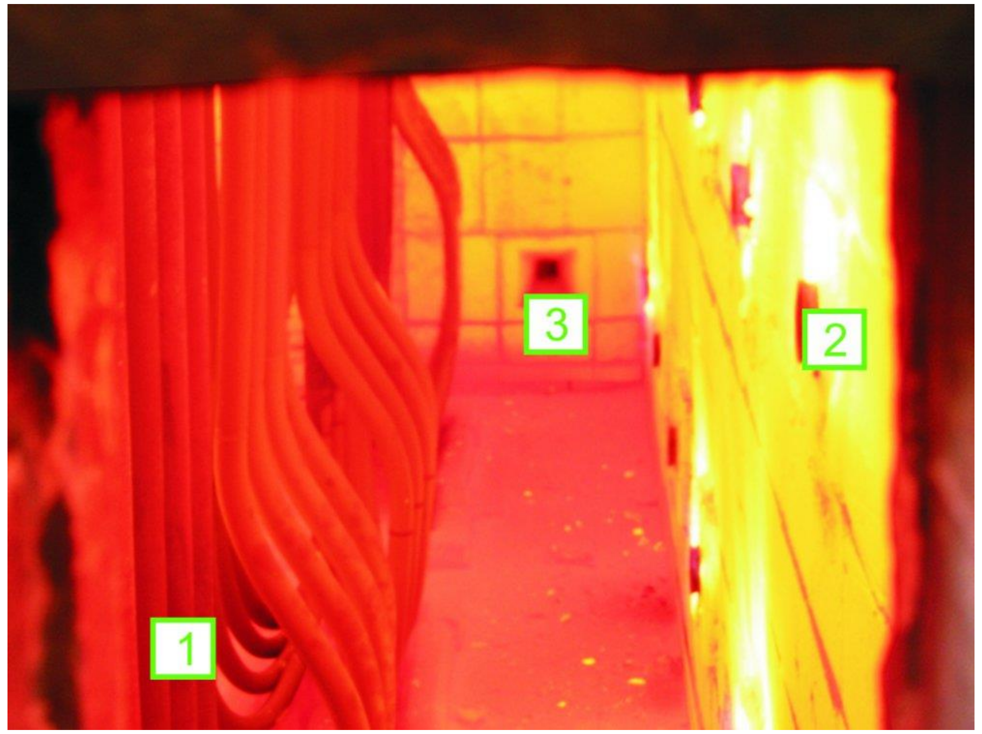


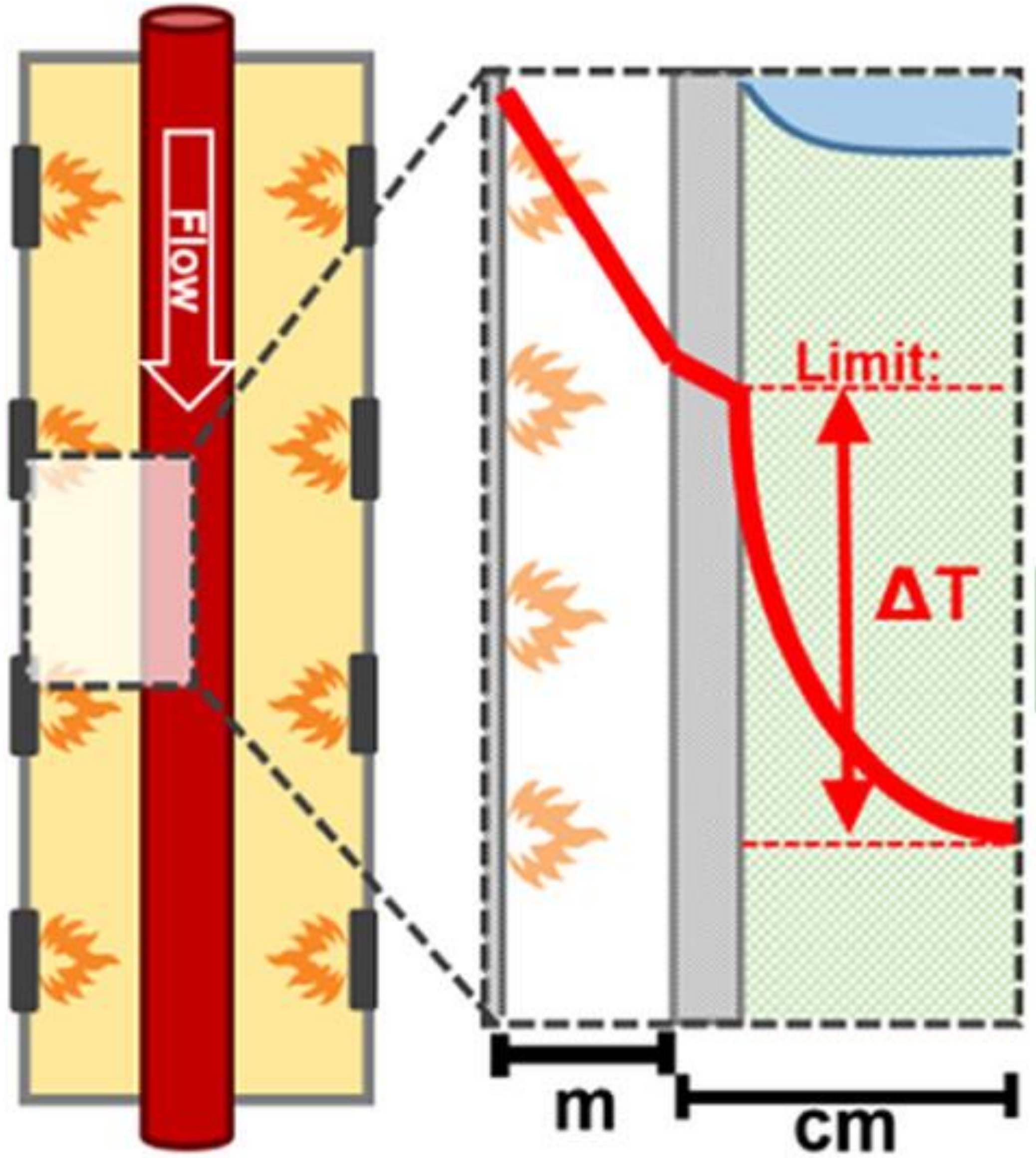


Westerterp, et al. *Chemical Reactor Design and Operation* Wiley (1991)

(strongly) endothermic reactions

- heat transport focused reactor design
  - narrow tubes
  - fired furnace
- pronounced temperature gradients





Wismann, et al. *Ind. Eng. Chem. Res.* 58 (2019) 23380

how can we do better?

chemistry ~ cooking

heat containment

electrification

how can we do even better?

microwave

induction

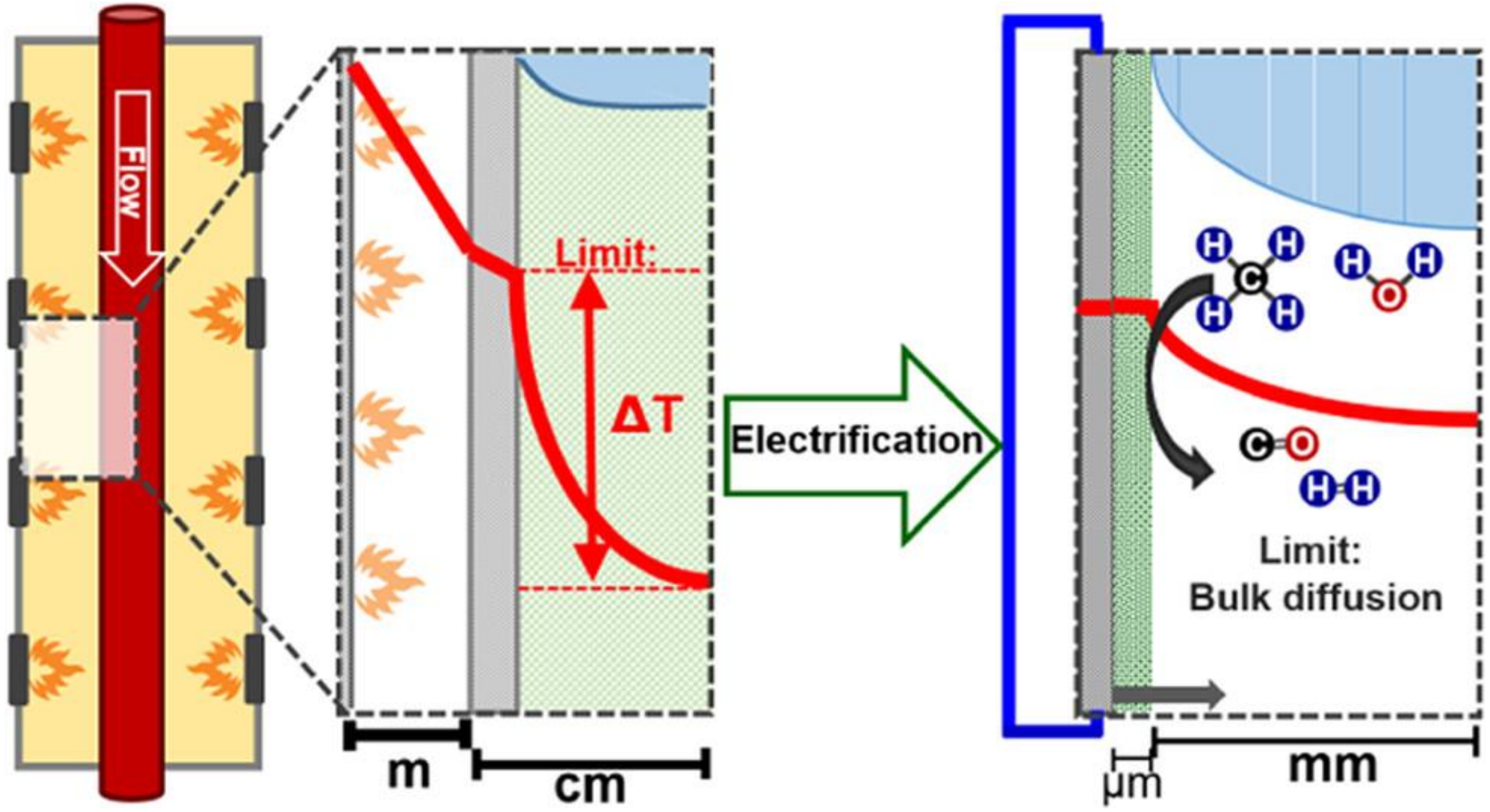
heating from the inside

reactor electrification

electrical heating -> overcoming limitations of combustion

advantageous in terms of:

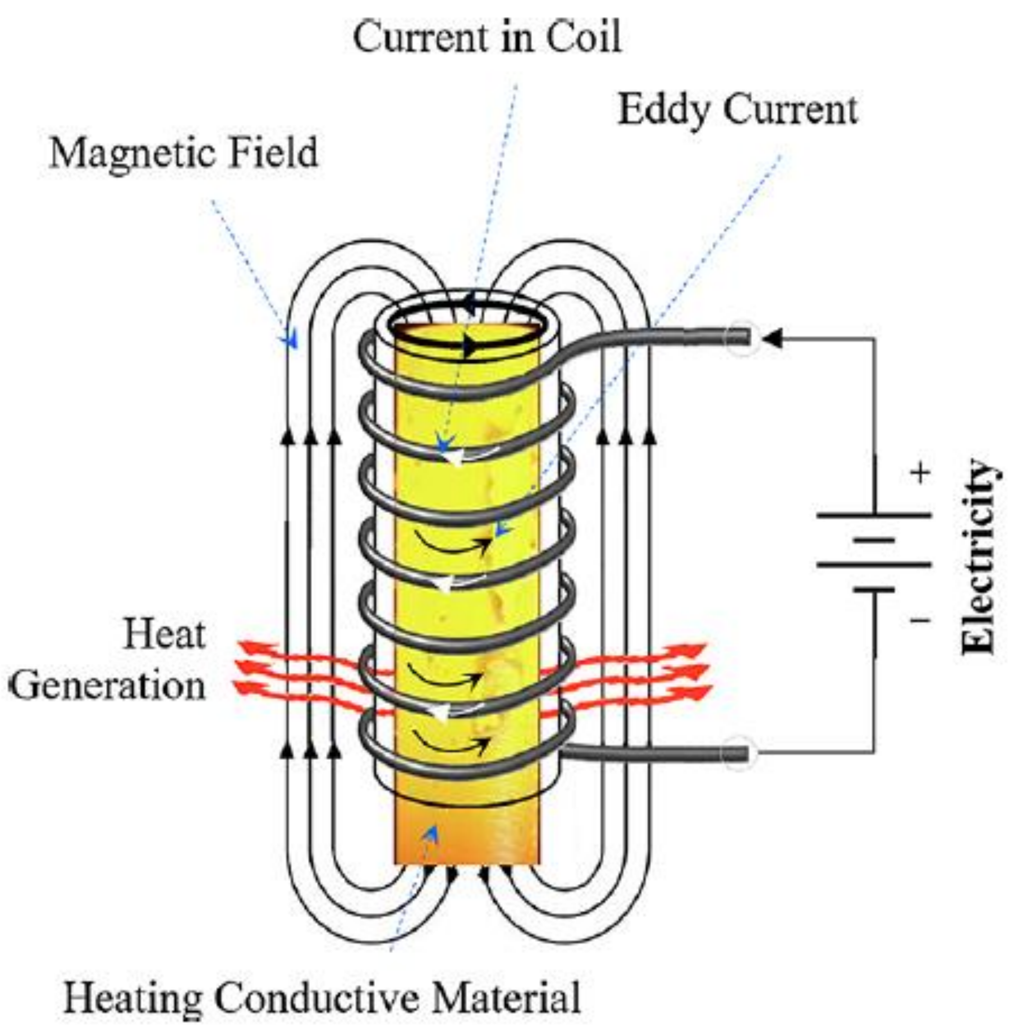
- energy efficiency
- process control
- safety and maintenance
- rapid heating
- …



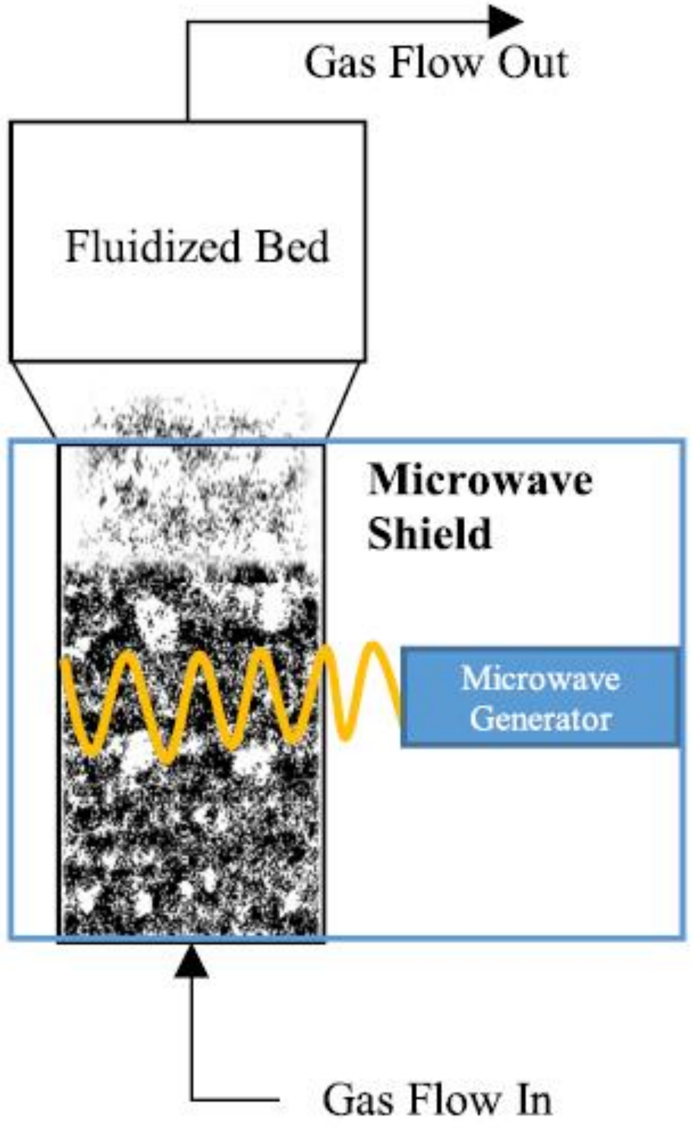
Wismann, et al. *Ind. Eng. Chem. Res.* 58 (2019) 23380

electrical heating

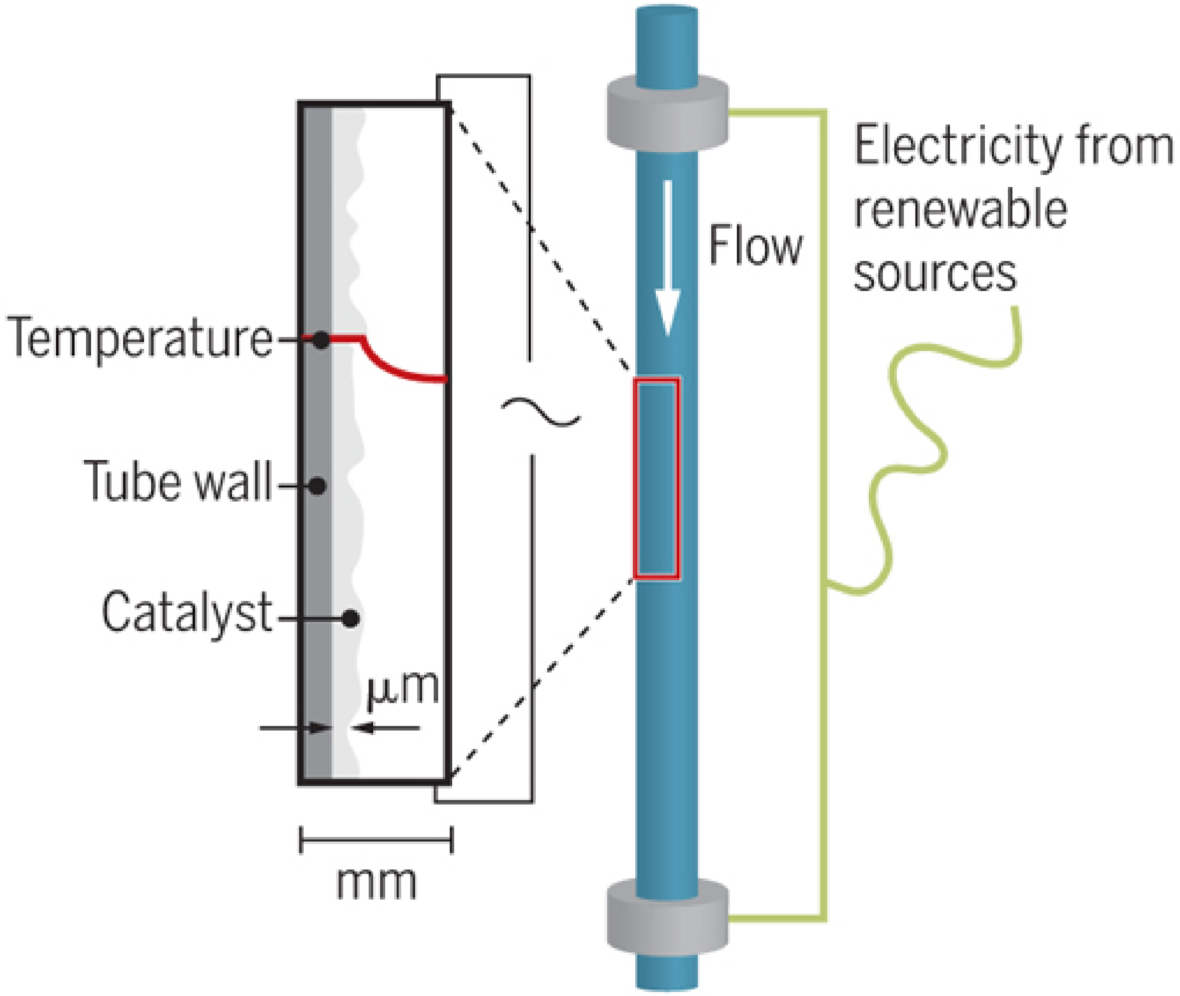
induction



microwave



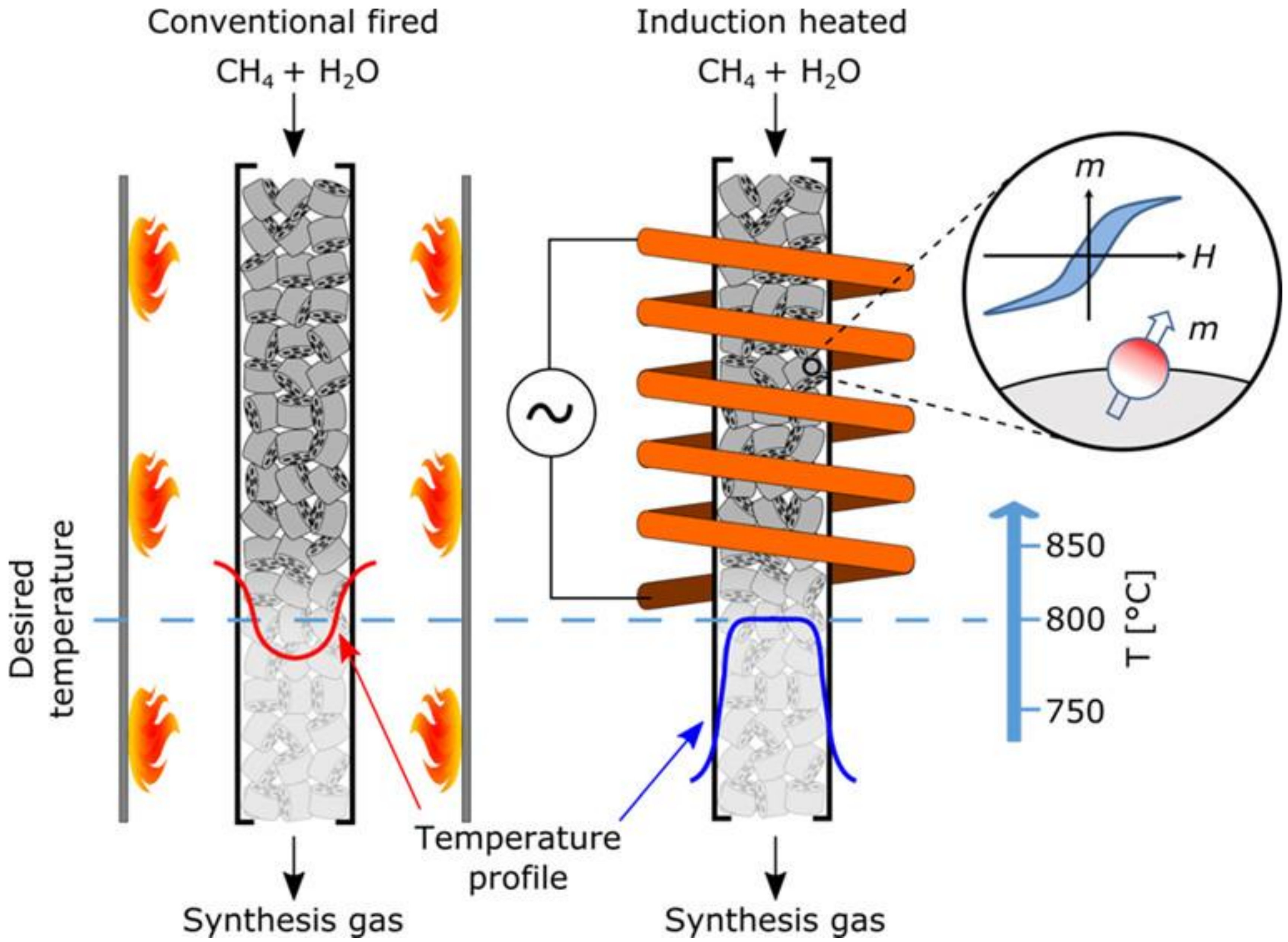
Joule



Imtiaz, et al. *Ind. Eng. Chem. Res.* 63 (2024) 4205

sonication
plasma

induction heating

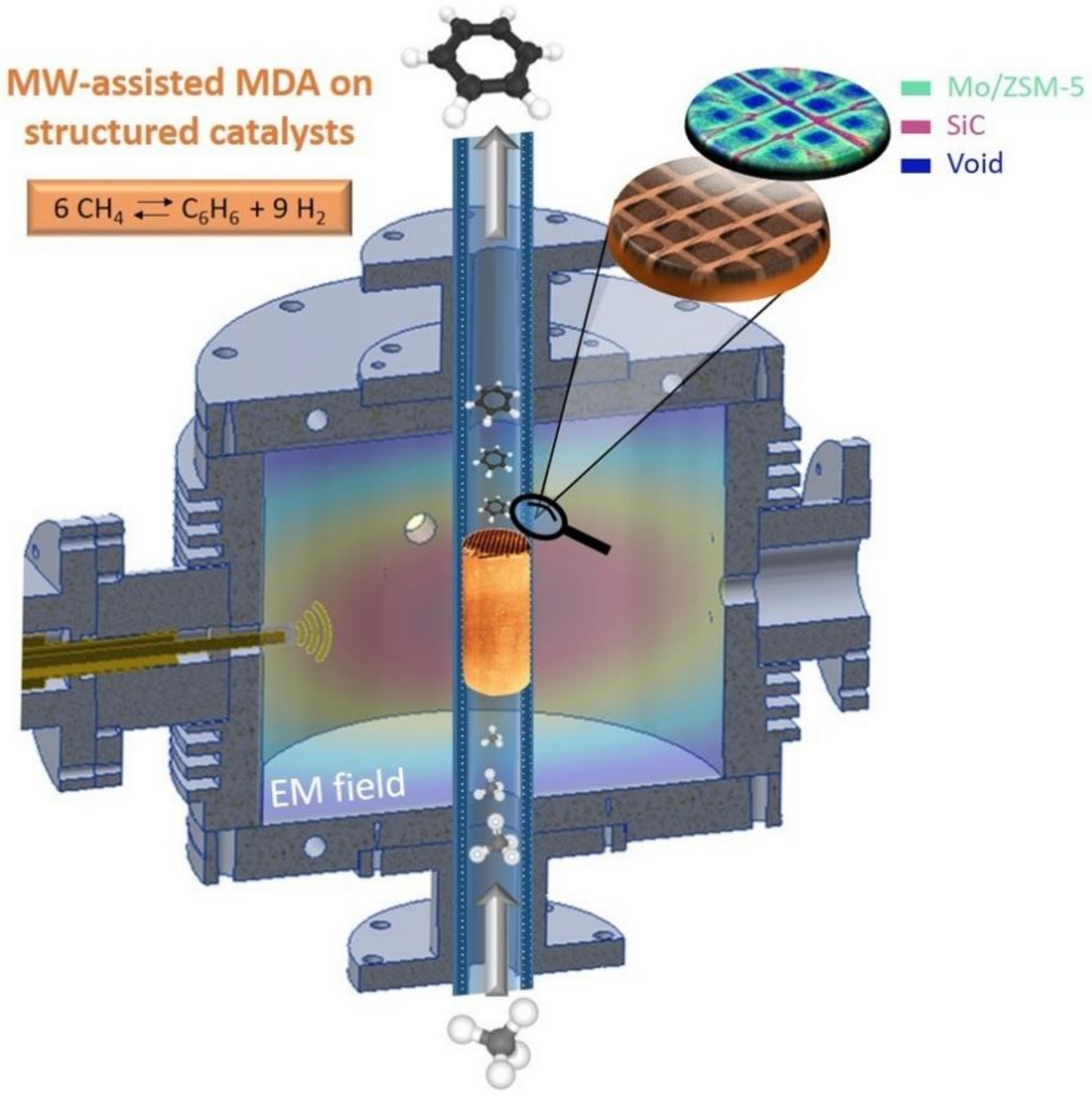


- alternating magnetic field with a high frequency

- heating without physical contact

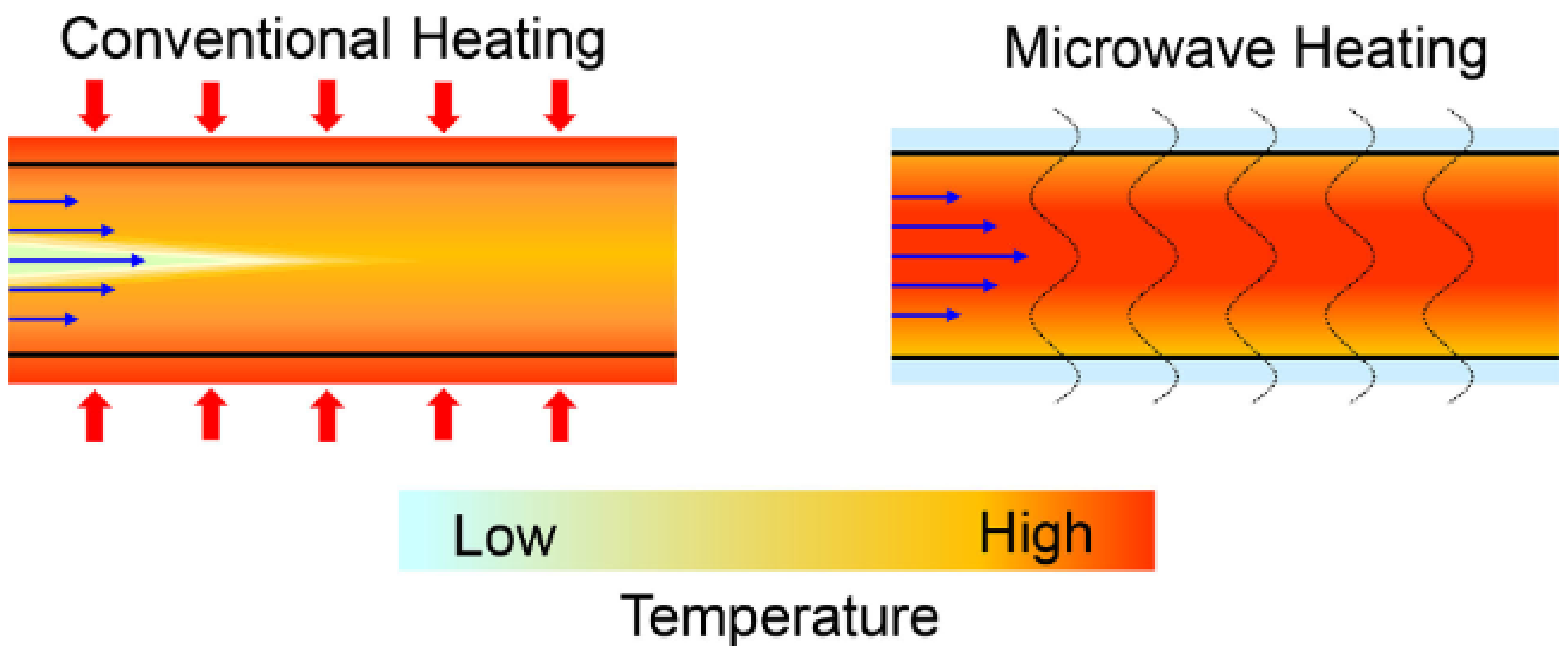
Mortensen, et al. *Ind. Eng. Chem. Res.* 56 (2017) 14006

microwave heating



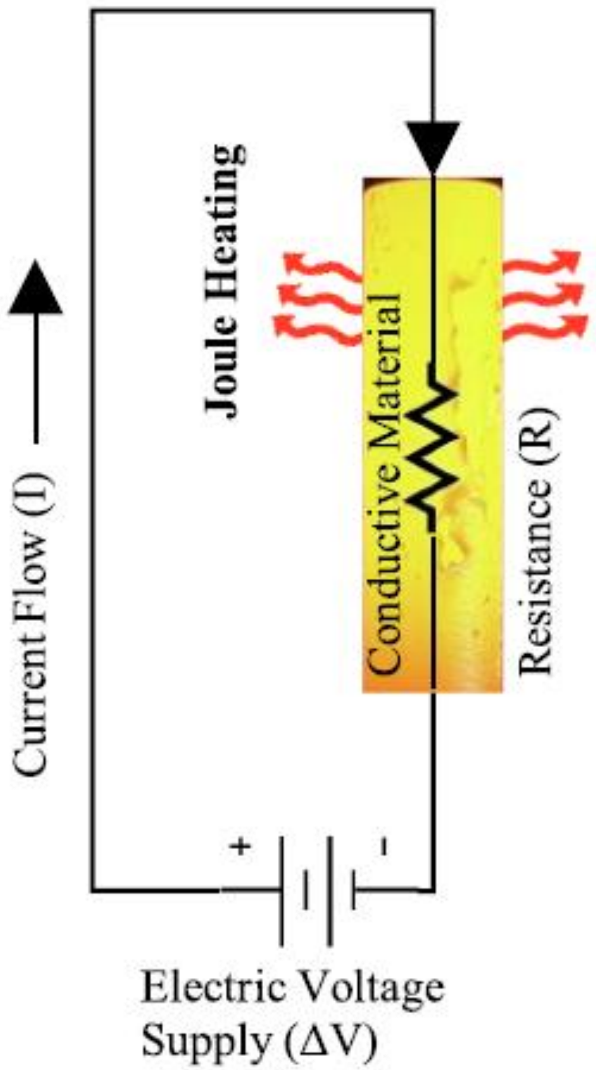
Ignacio, et al. *Catal. Today* 383 (2022) 21

- heating through electromagnetic energy

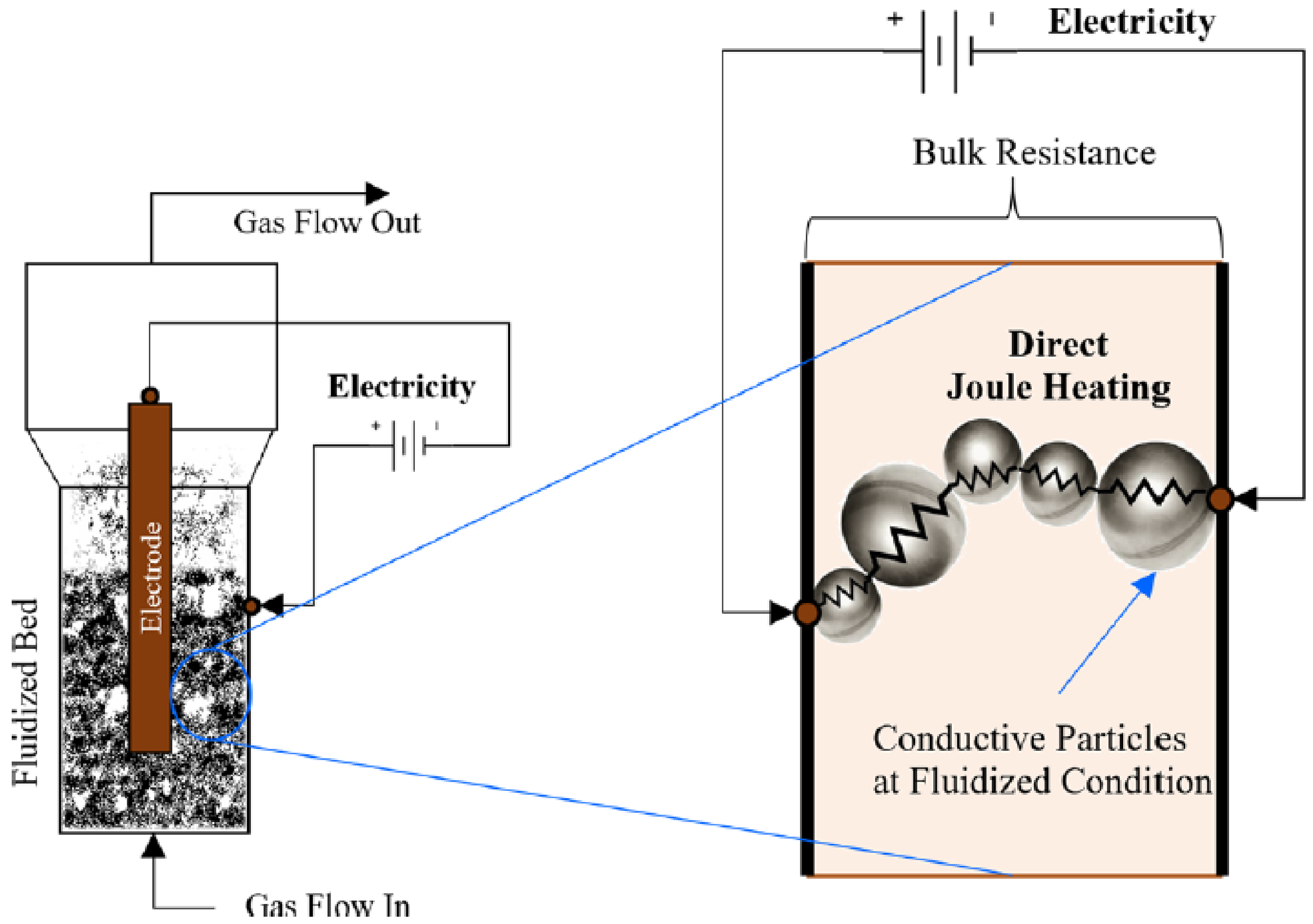


Barham, et al. *Chem. Rec.* 19 (2019) 188

Joule heating



- electrical energy transformation to thermal energy
- current flow between electrodes
- high energy efficiency



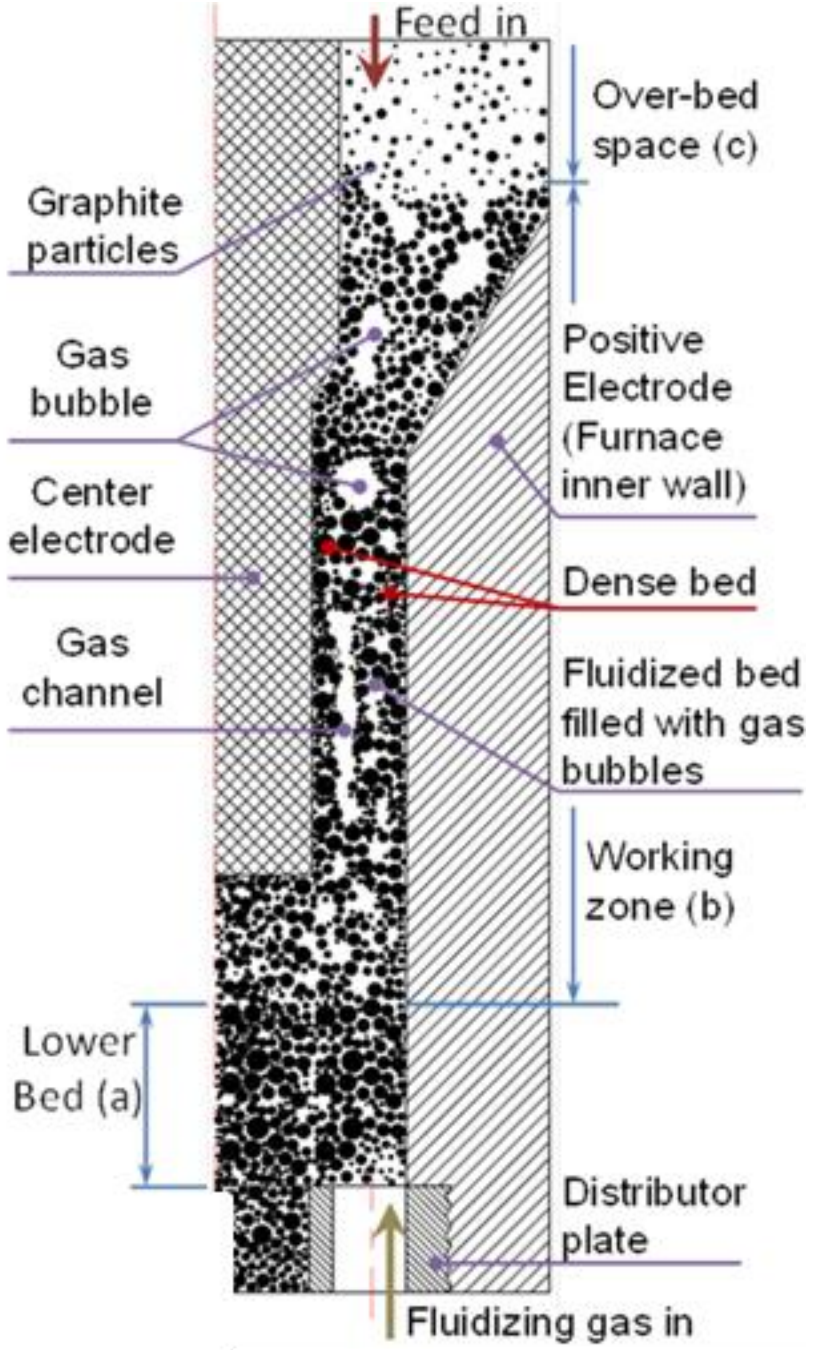
Imtiaz, et al. *Ind. Eng. Chem. Res.* 63 (2024) 4205

GHENT UNIVERSITY

LCT DRIVING CHEMICAL TECHNOLOGY

ElectroThermal Fluidized Bed reactor (ETFB)

- combination:
  - fluidization
  - Joule heating
- compared to conventional fluidized beds
  - better control over bed temperature
  - highly energy efficient
  - rapid and uniform heating



Fedorov *J. Fluids Eng.* 138 (2016) 044502

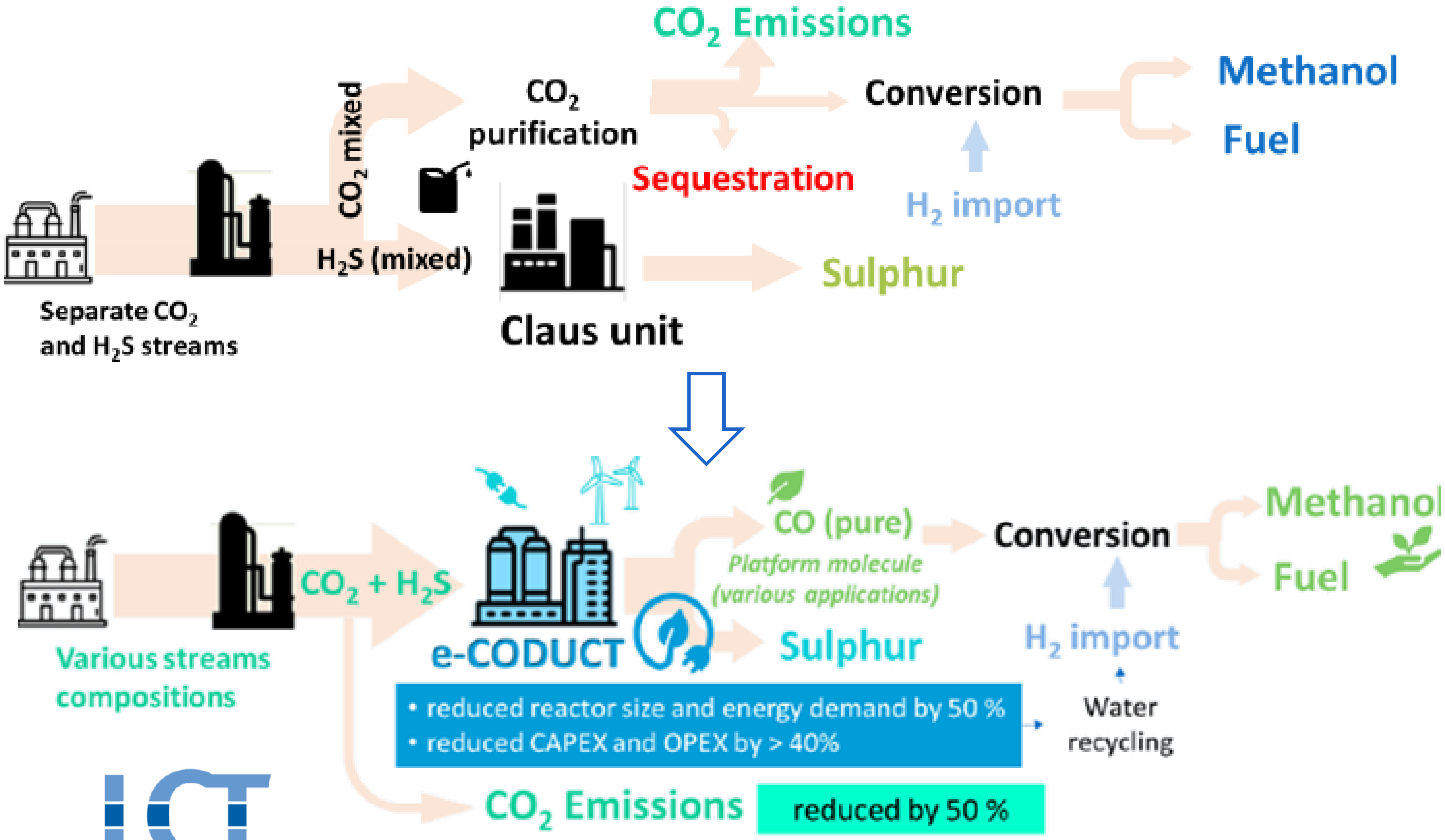
GHENT UNIVERSITY

LCT DRIVING CHEMICAL TECHNOLOGY

outline

- introduction
- methane valorization – C123
- electrification
- e-CODUCT
- OBIWAN
- conclusions

e-CODUCT: context



- reduced reactor size and energy demand by 50 %
- reduced CAPEX and OPEX by > 40%

GHENT UNIVERSITY

LCT DRIVING CHEMICAL TECHNOLOGY

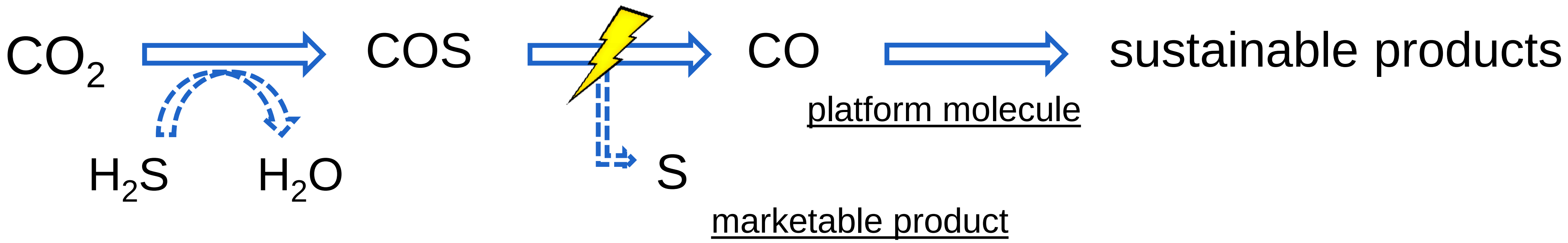
e-CODUCT: rationale

fast-response electrically heated catalytic reactor technology for CO_2 reduction

why?

- current CO_2 reduction technologies require highly pure streams
- no existing technologies for simultaneous CO_2 and H_2S reduction
- making more feedstock sources available

e-CODUCT: process lay-out



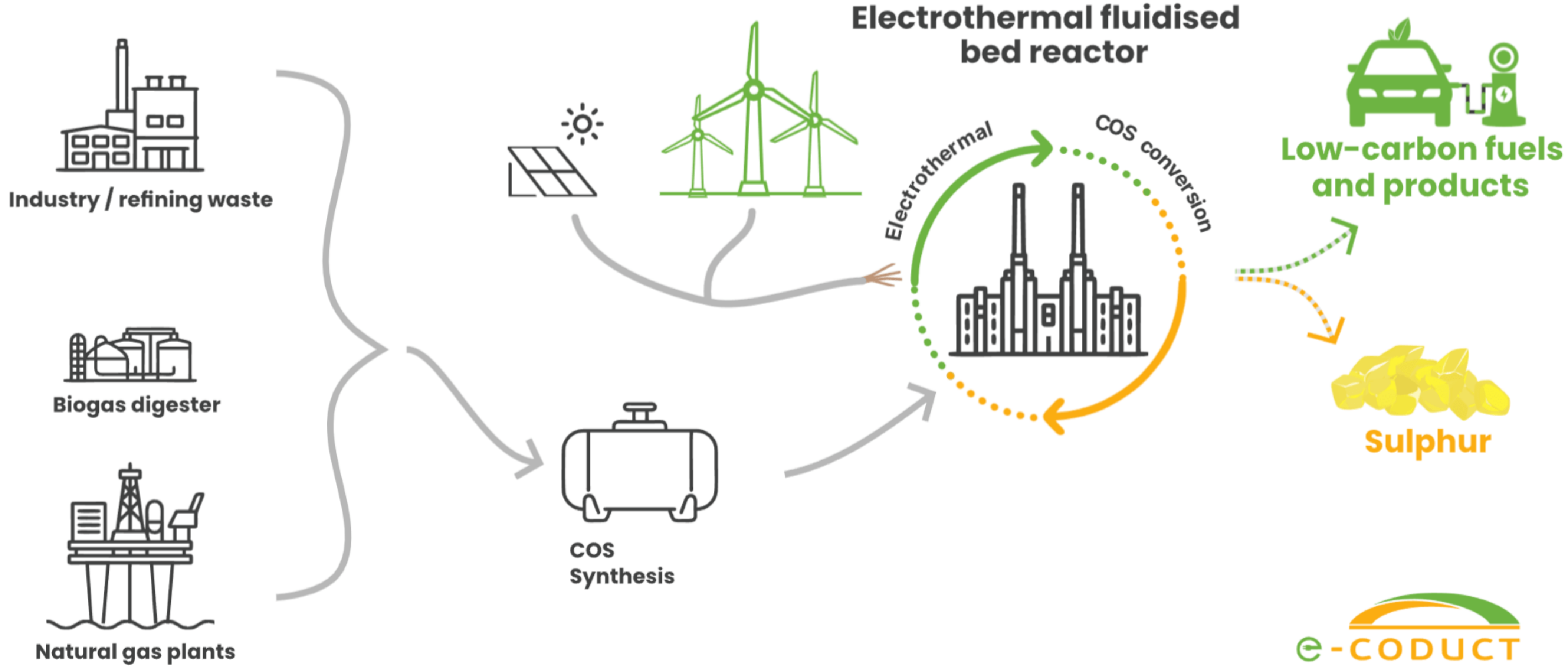
$CO_2 \rightarrow COS \rightarrow CO \rightarrow$ sustainable products

H_2S H_2O

S

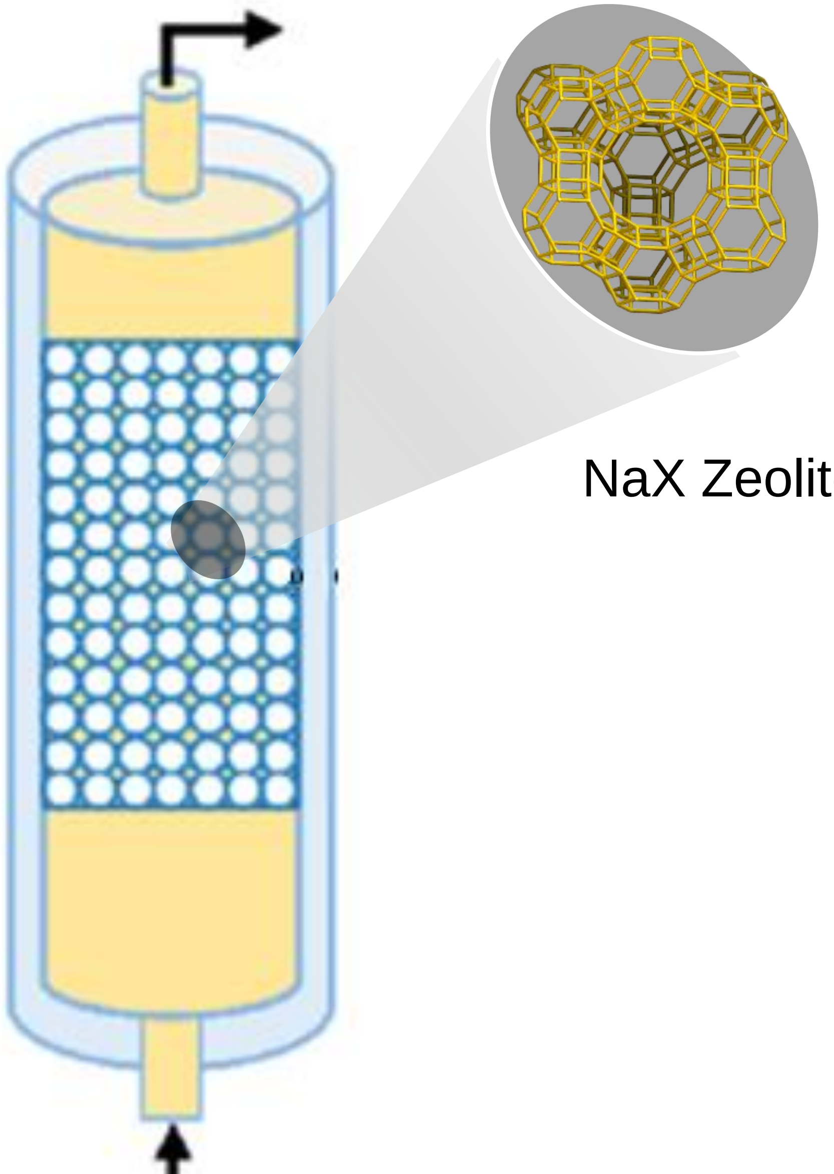
platform molecule

marketable product



http://www.ecoduct.eu 2022-2025 GA 101058100

COS synthesis: experimental

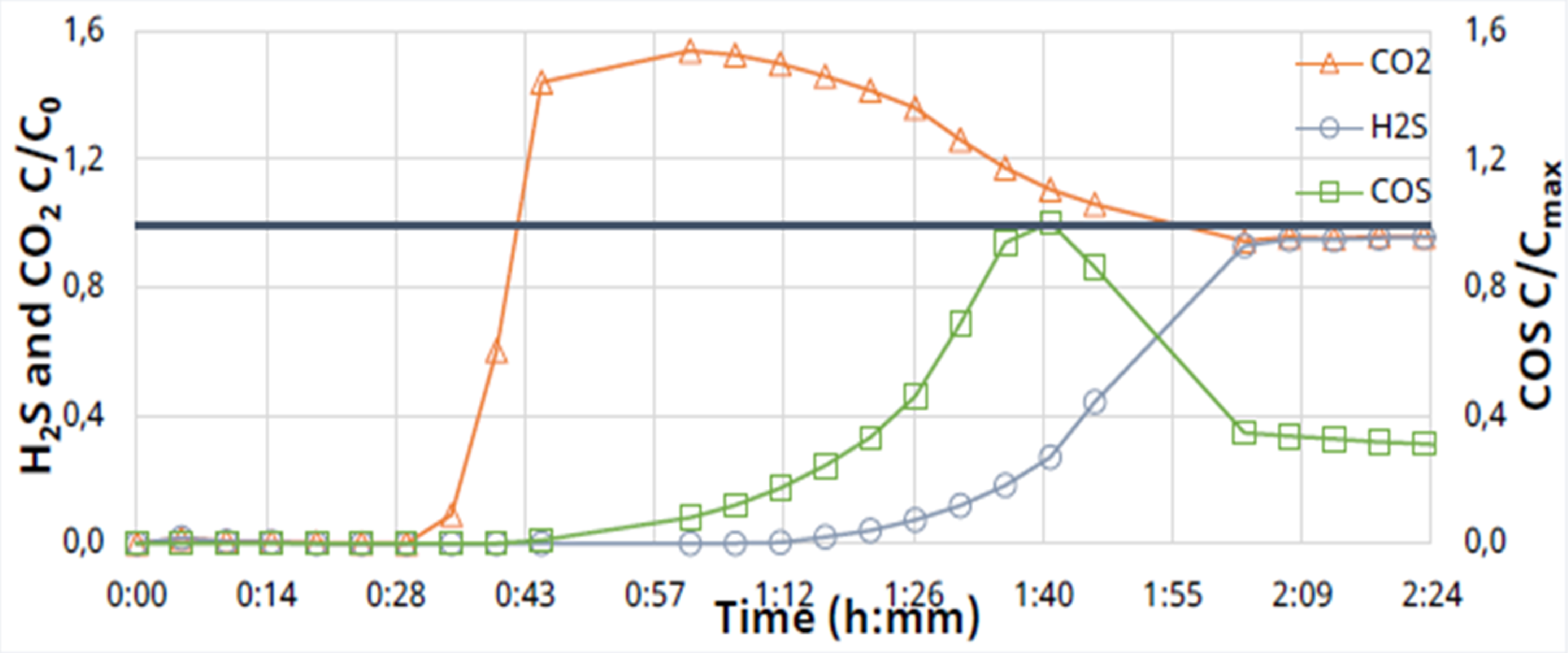


NaX Zeolite

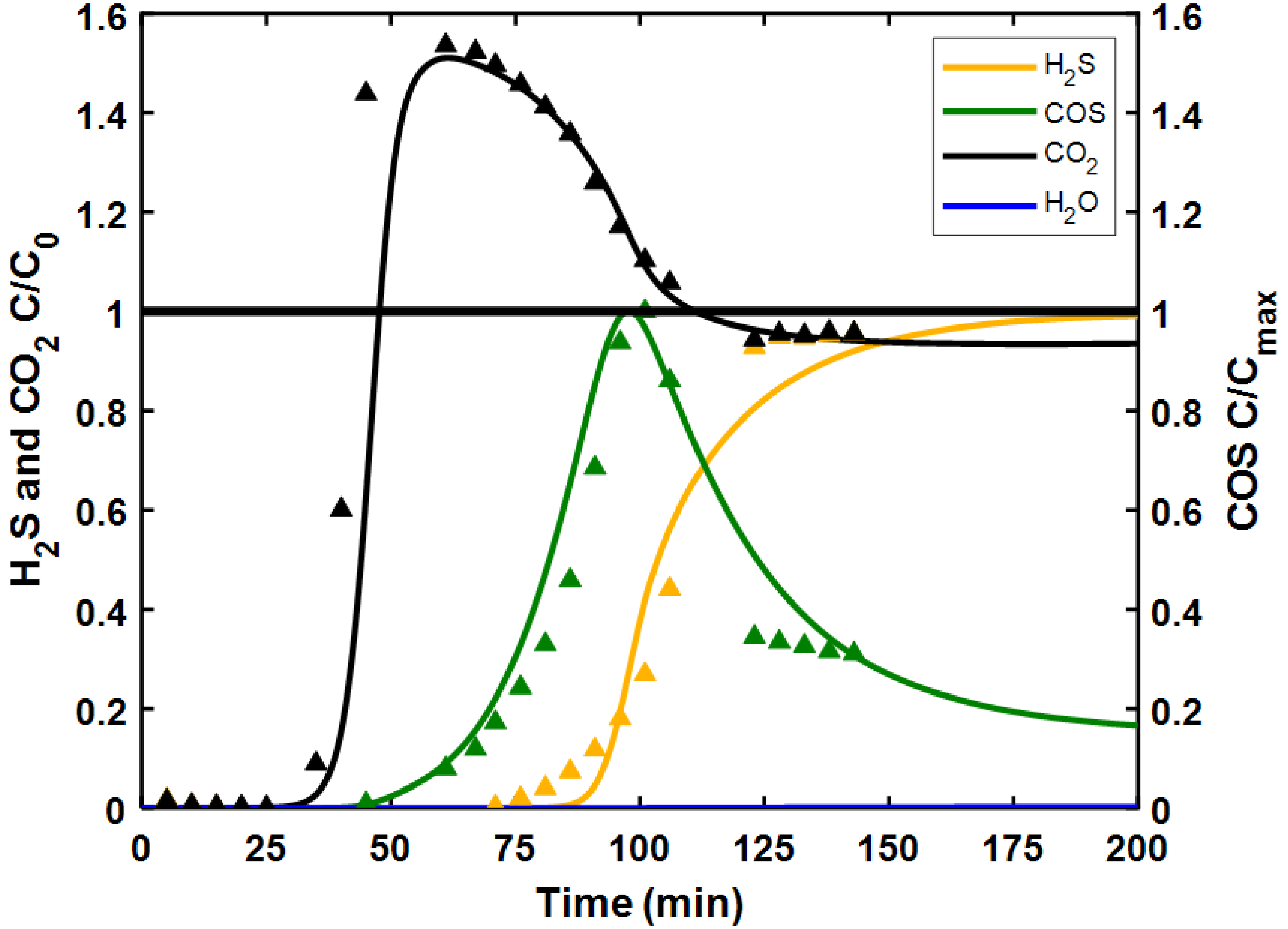
CO_2/H_2S: 1/1

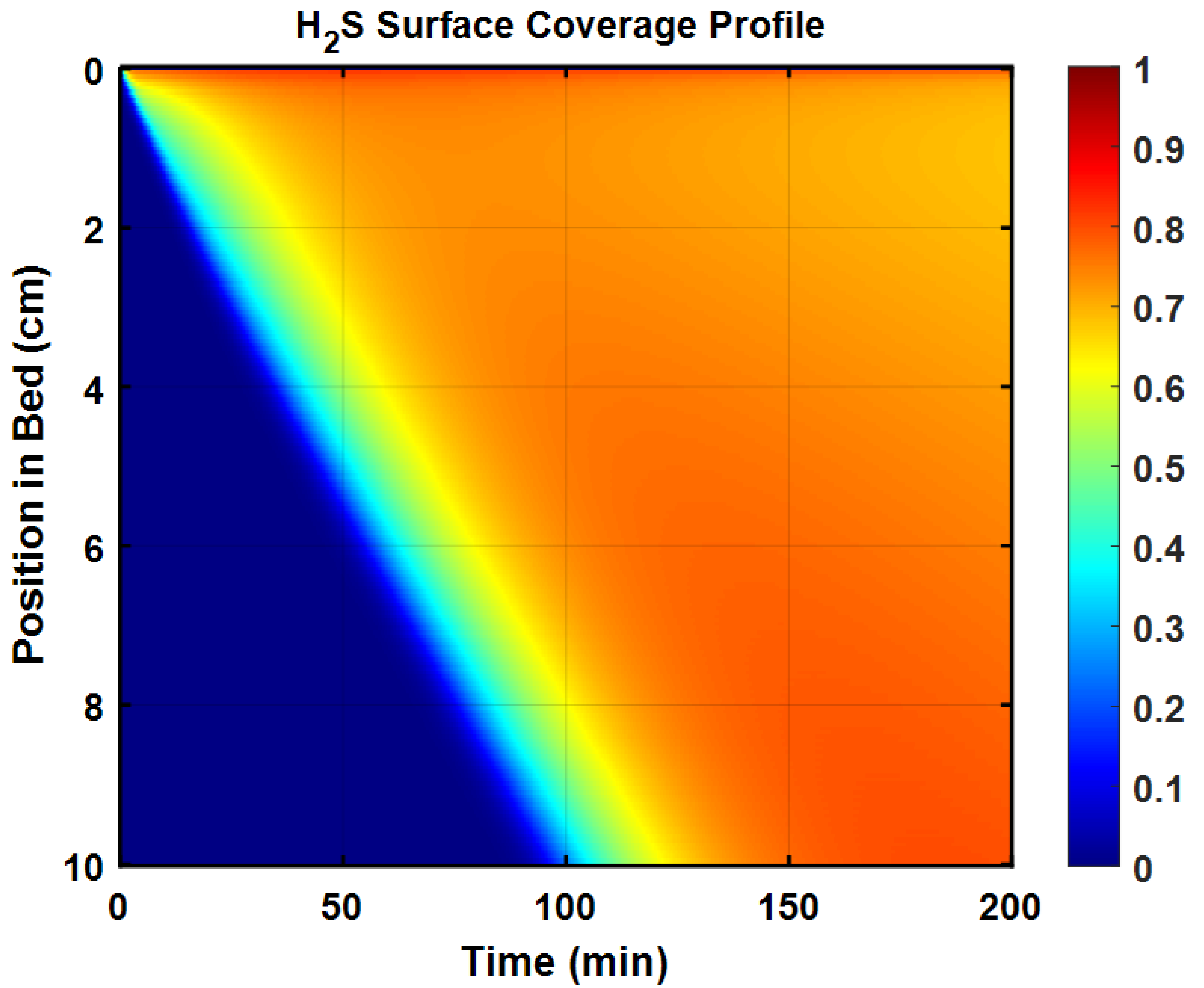
$$CO_2 + H_2S \leftrightharpoons COS + H_2O$$

Feed mixture of H_2S:CO_2=1:1 on 13X at 45°C. Thick line at C/C_0 = 1.

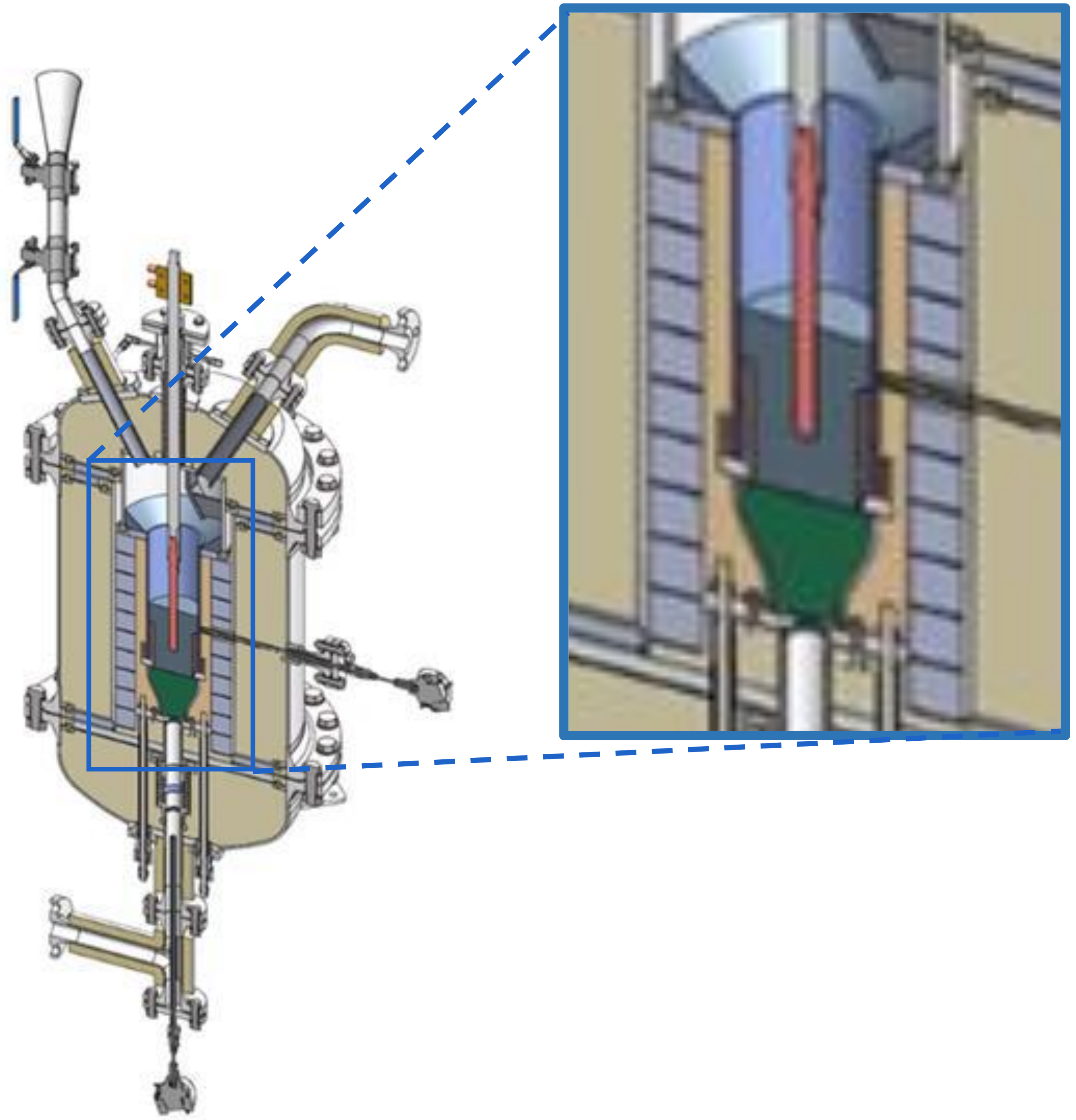


COS synthesis: modeling



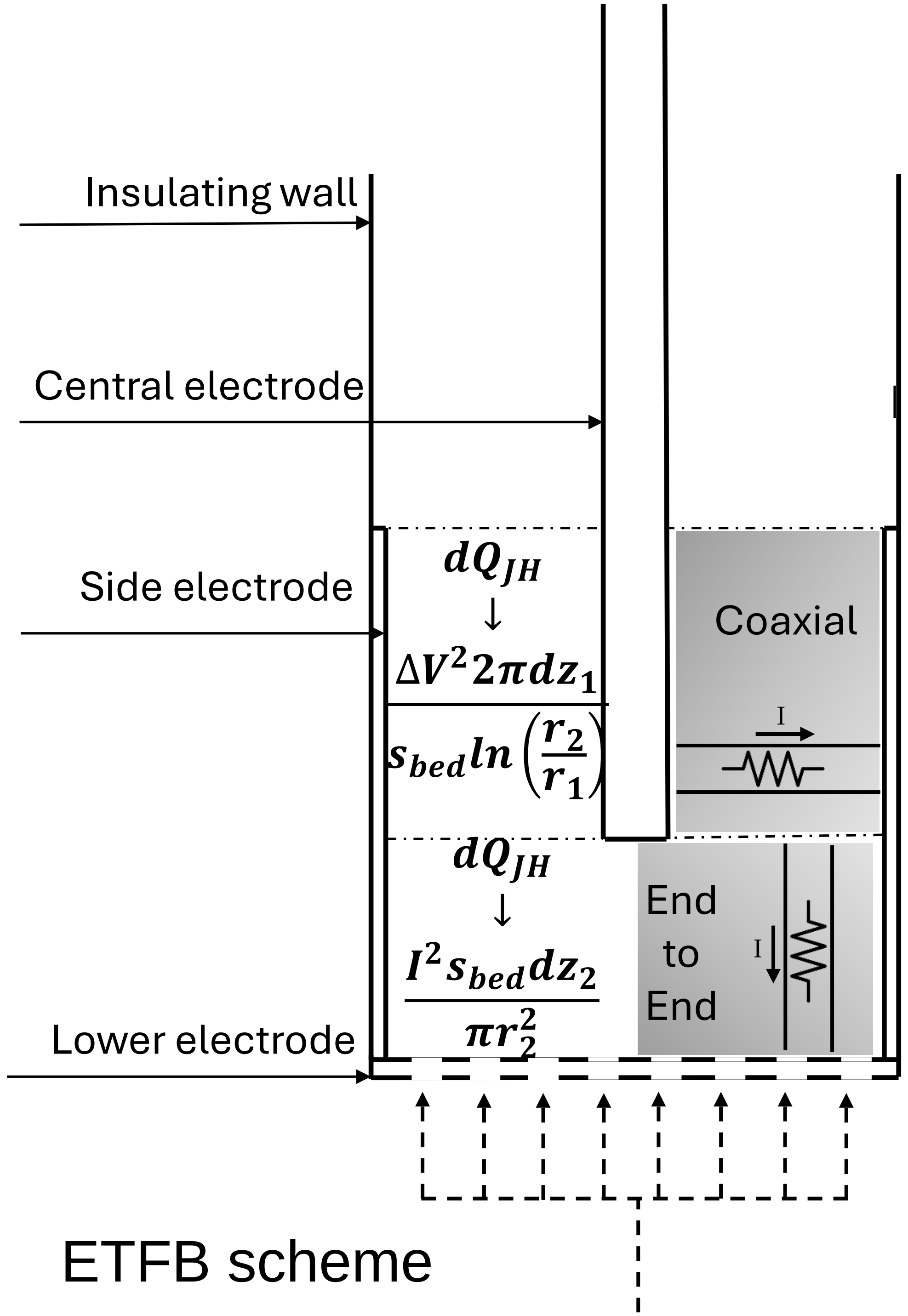


COS decomposition

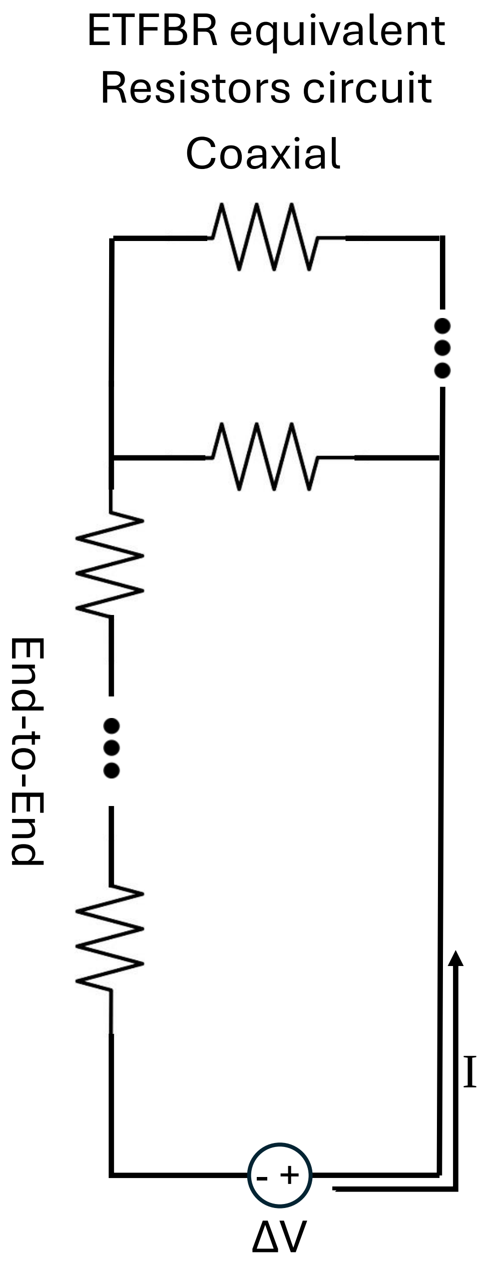


- COS decomposition to CO and sulphur
- temperatures up to 800-1200 °C
- in situ heat generation by joule heating

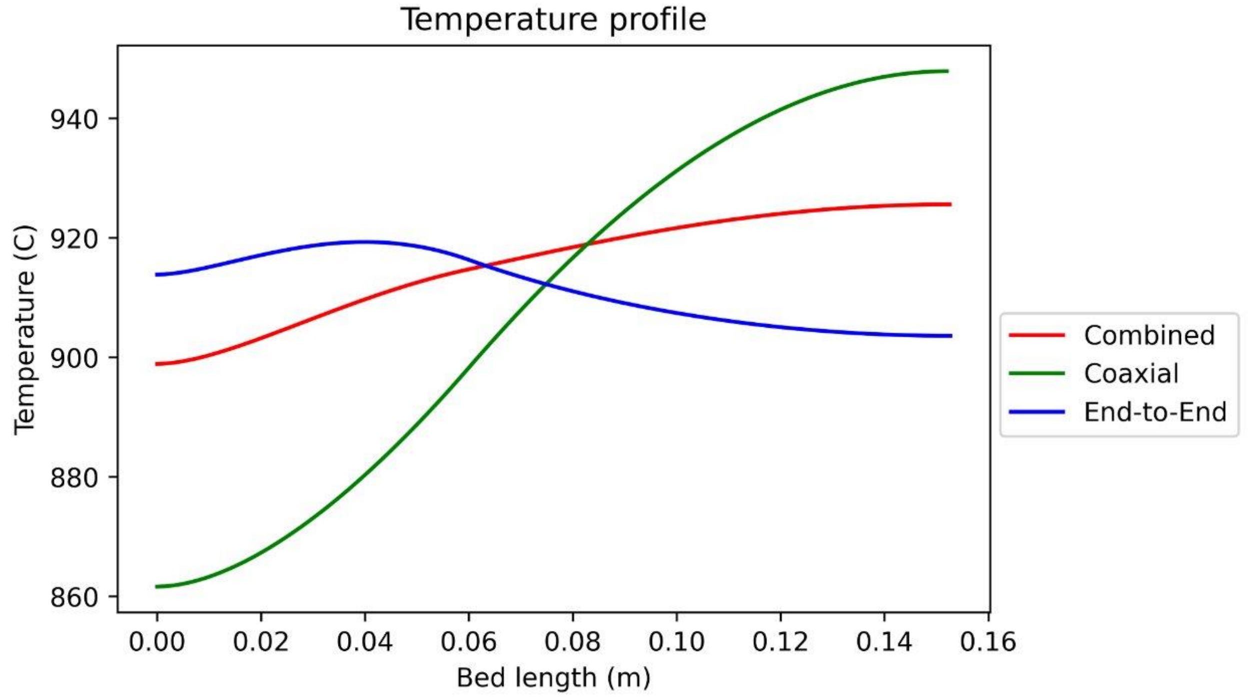
e-CODUCT – ETFB modelling

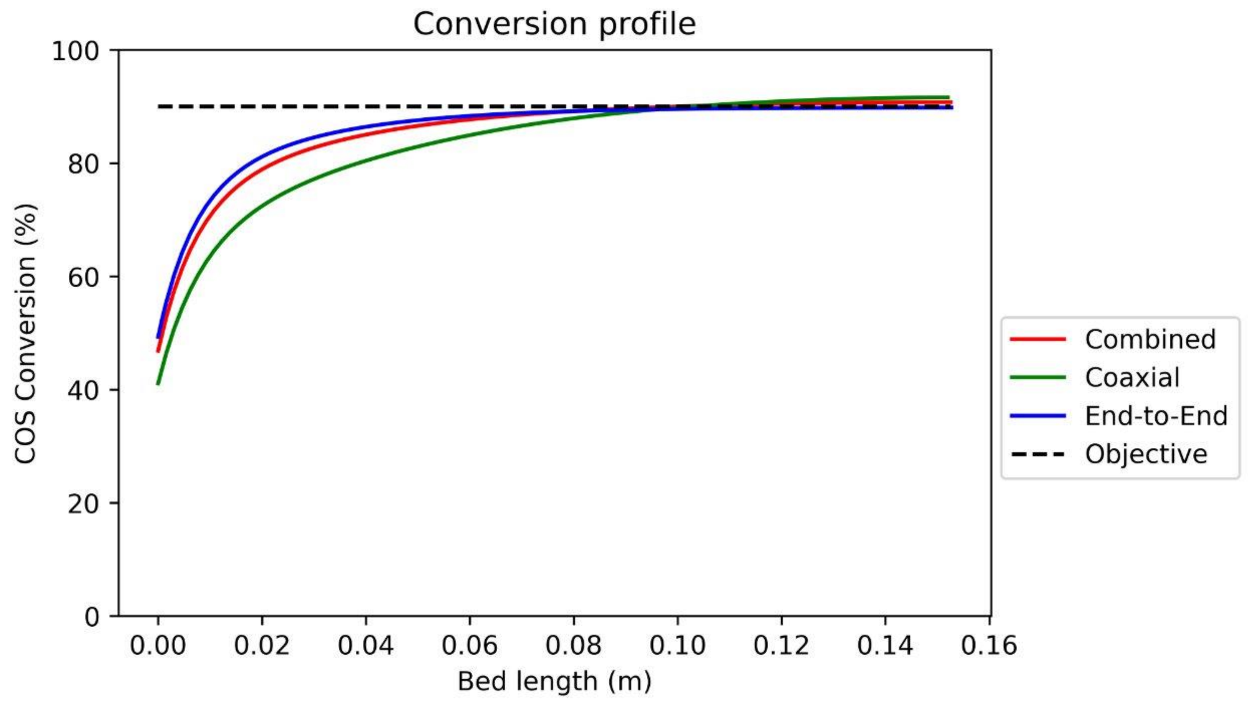


ETFB scheme



Resistor configuration





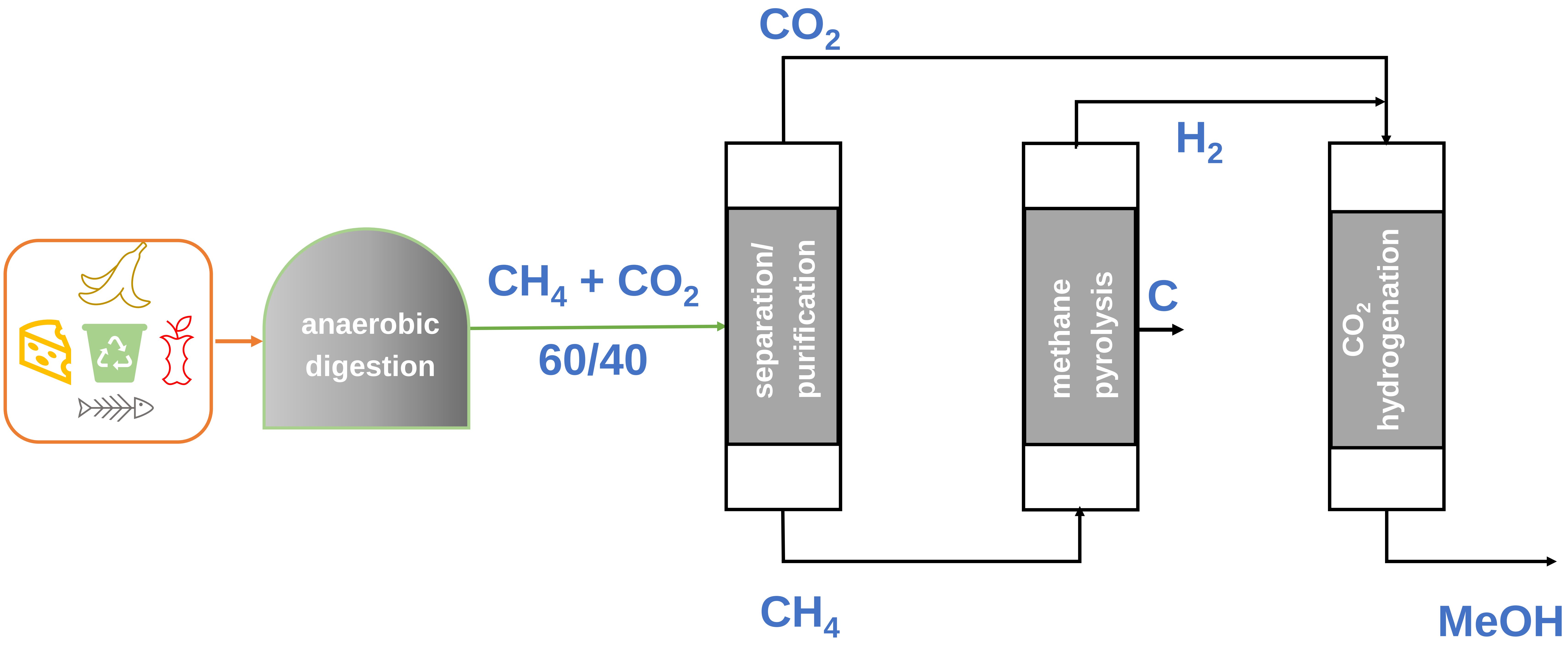
OBIWAN: context

- biogas ($CH_4 + CO_2$) valorization
  - calorific
  - to chemicals/(sustainable) aviation fuels

GHENT UNIVERSITY

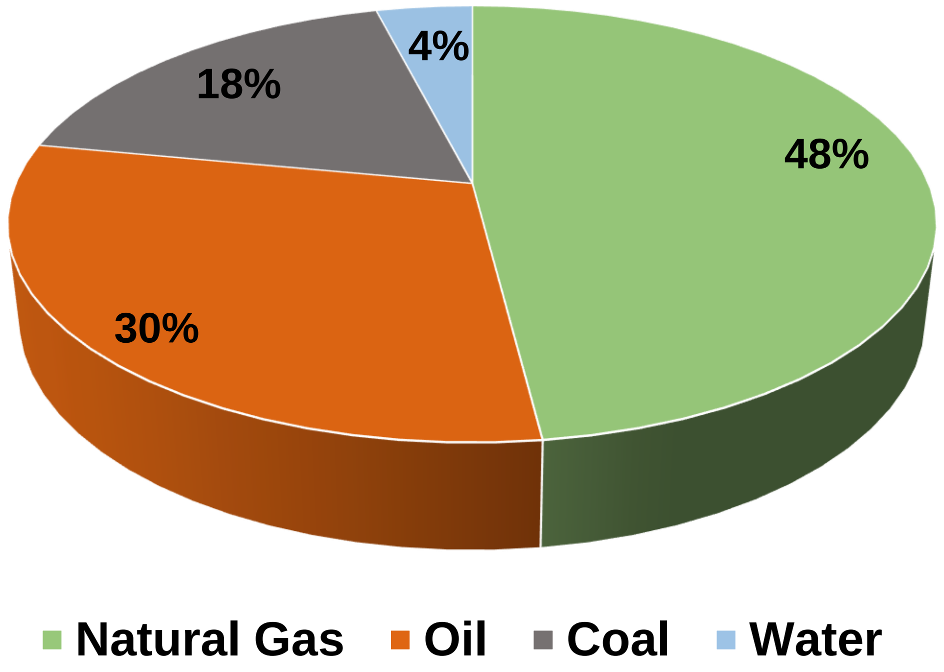
LCT DRIVING CHEMICAL TECHNOLOGY

OBIWAN: process lay-out



hydrogen production (from methane)

H_2 production sources



$$SMR: \quad CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H = 206 \frac{kJ}{mol}$$

$$DMR: \quad CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad \Delta H = 247 \frac{kJ}{mol}$$

$$POM: \quad CH_4 + O_2 \leftrightarrow CO + 2H_2O \quad \Delta H = -36 \frac{kJ}{mol}$$

$$MP: \quad CH_4 \leftrightarrow C + 2H_2 \quad \Delta H = 74 \frac{kJ}{mol}$$

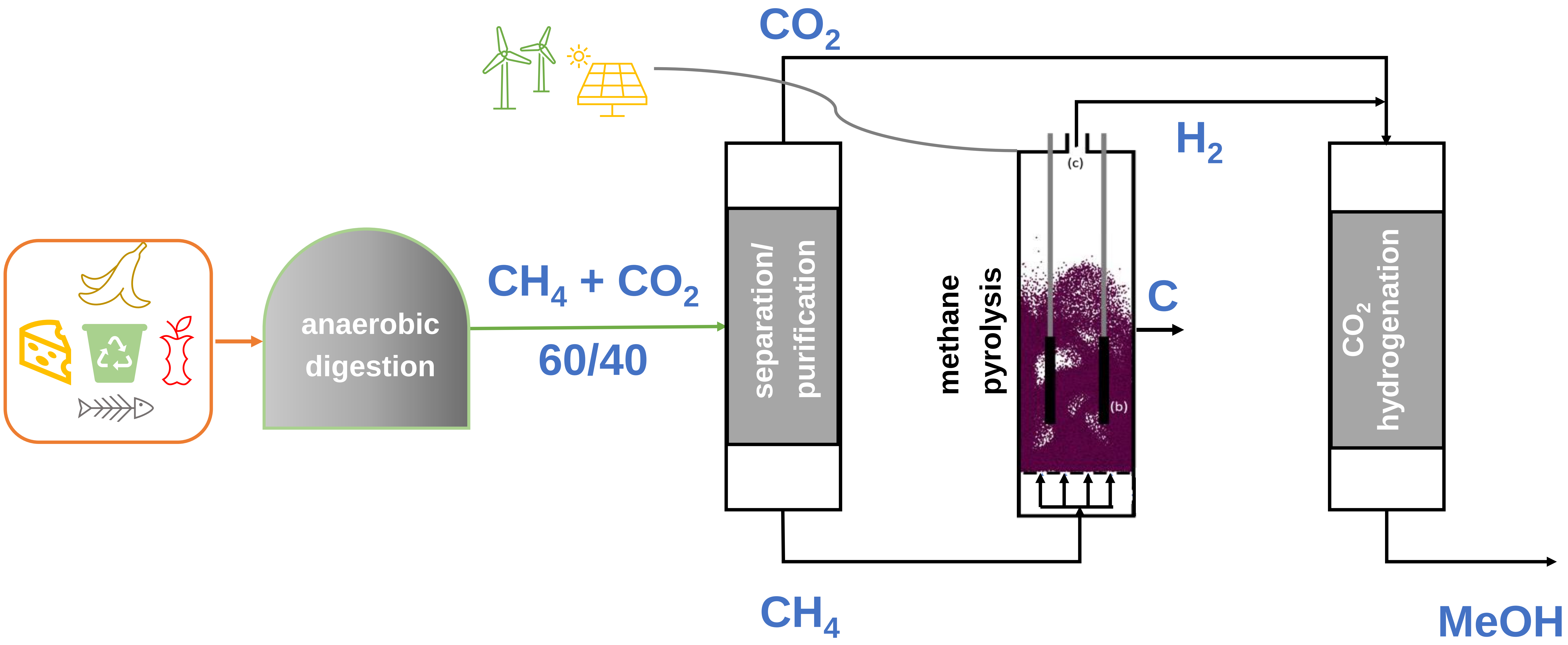
Methane Pyrolysis on carbonaceous catalyst:

- ☐ less energy intensive
- ☐ no greenhouse gas emission
- ☐ high purity H_2
- ☐ cheap & sulfur resistant catalyst

GHENT UNIVERSITY

LCT DRIVING CHEMICAL TECHNOLOGY

OBIWAN: process lay-out



outline

- introduction
- methane valorization – C123
- electrification
- e-CODUCT
- OBIWAN
- conclusions

C123
VALORISING METHANE RESOURCES

e-CODUCT

GHENT
UNIVERSITY

LCT
DRIVING CHEMICAL TECHNOLOGY

conclusions, opportunities and perspectives

- from a linear to a circular economy
  - catalysis
  - reactors
  - processes
  - **kinetics**
- fundamental model-based optimization
  - quantitative assessment
  - validation qualitative understanding

conclusions, opportunities and perspectives

- (natural) gas valorization: OCoM process concept
  - combination chemical reactions
  - feedstock composition
- chemical reactor electrification
  - more than connecting an electric heater to the grid
  - reasoning from the inside
  - CO_2 emission reduction
  - integration in a process
  - …

conclusions, opportunities and perspectives

- challenges
  - few large-scale vs many small-scale applications
  - electricity availability
  - impact on the chemistry
  - …

acknowledgments

The e-CODUCT project is funded under Horizon Europe Grant Agreement n°101058100

Interreg

Cofinancé par
l'Union Européenne
Medegefinancierd door
de Europese Unie

France – Wallonie – Vlaanderen

GHENT
UNIVERSITY

LCT
DRIVING CHEMICAL TECHNOLOGY

acknowledgements (2)

GHENT UNIVERSITY

AGENTSCHAP INNOVEREN & ONDERNEMEN

fwo

Interreg

Cofinancé par l'Union Européenne
Medegefinancierd door de Europese Unie

France – Wallonie – Vlaanderen

erc
European Research Council

GHENT UNIVERSITY

LCT
DRIVING CHEMICAL TECHNOLOGY

Horizon Europe

JM

bp

TotalEnergies

ExxonMobil

EASTMAN

BASF
We create chemistry

oleon
A NATURAL CHEMISTRY

ifp Energies nouvelles

janssen
PHARMACEUTICAL COMPANIES OF Johnson&Johnson

Tessenderlo Group
EVERY MOLECULE COUNTS

acknowledgements (3)

(former) post docs

Ana Bjelic

Jeroen Lauwaert

Jeroen Poissonnier

Pedro Mendes

Sebastien Siradze

Soroush Zare

Zahra Mohammadbagheri

(former) PhD students

Alejandro Romero Limones

Alexandra Bouriakova

Anoop Chakkingal

Bert Biesemans

Beruk Alemu Bekele

Bram Van Wettere

Carlos Alvarado Camacho

César Pernalete

Kevin De Ras

Klaus Jacobs

Laura Pirro

Loïc Eloi

Lucas Ivan Garbarino

Maria Herrero Manzano

Marie-Elisabeth Lissens

Nebojsa Korica

Noor Aljammal

Pieter Janssens

Raman Ghassemi

Reza Monjezi

Tom Vandevyvere

Willem De Meyer

Wout Callewaert

Yonggang Cheng

GHENT UNIVERSITY

LCT DRIVING CHEMICAL TECHNOLOGY

12th International Symposium on Catalysis in Multiphase Reactors
&
11th International Symposium on Multifunctional Reactors

CONFERENCE THEME

Multiscale modeling and experimentation

Reactor design
Process development
Low carbon technology
Renewable chemicals
Polymer design
Catalysis and kinetics

8-11 SEPTEMBER 2024

Ghent, Belgium

Abstract Submission
Deadline: 24 February 2024

MORE INFO

www.camure.ugent.be

SCIENTIFIC COMMITTEE

Chairman of the symposium

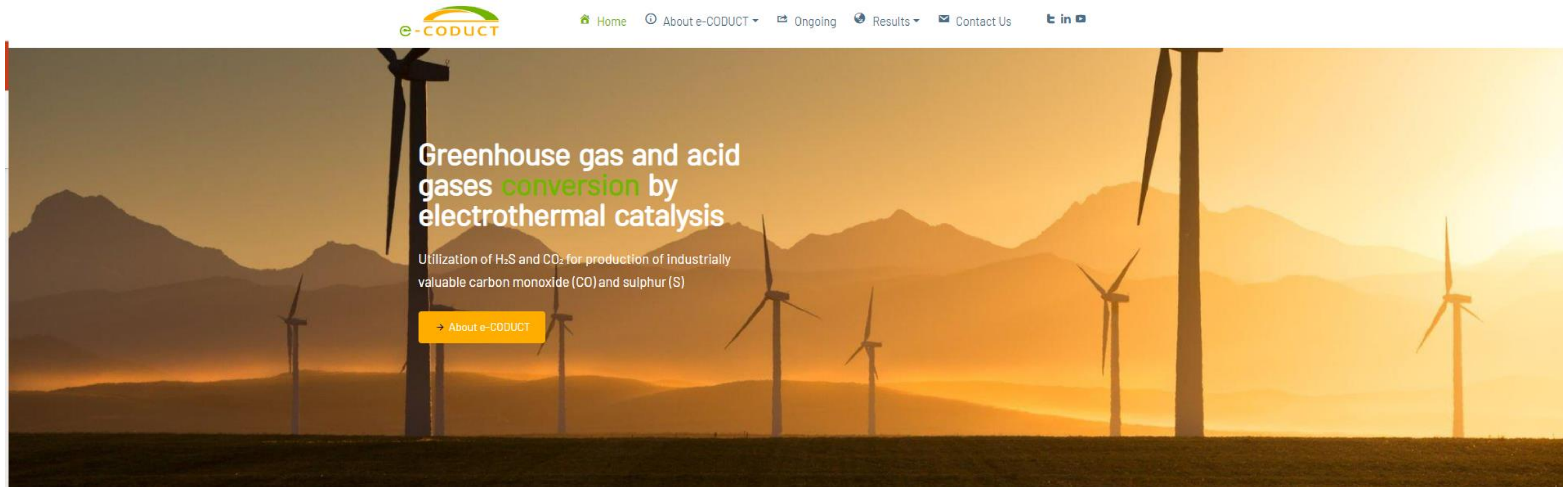
prof. dr. ir. Joris THYBAUT

Co-chairmen of the symposium

prof. dr. ir. Kevin VAN GEEM
prof. dr. ir. Mark SAEYS

GHENT UNIVERSITY
FACULTY OF ENGINEERING AND ARCHITECTURE
LCT

e-CODUCT: Want to know more?!



Greenhouse gas and acid gases conversion by electrothermal catalysis

Utilization of H_2S and CO_2 for production of industrially valuable carbon monoxide (CO) and sulphur (S)

Website: https://e-coduct.eu/

LinkedIn: @e-coduct project
https://www.linkedin.com/in/ecoduct/

Twitter: @eCODUCT2022
https://twitter.com/eCODUCT2022

YouTube: @ecoduct2022
https://www.youtube.com/@ecoduct2022/about

#e-CODUCT #HorizonEurope #CO2Reduction #innovation #technology

GHENT UNIVERSITY

LCT DRIVING CHEMICAL TECHNOLOGY

LABORATORY FOR CHEMICAL TECHNOLOGY

Technologiepark 125, 9052 Ghent, Belgium

E info.lct@ugent.be
T 003293311757

https://www.lct.ugent.be

GHENT
UNIVERSITY

LCT
DRIVING CHEMICAL TECHNOLOGY

Modified ER Mechanism

Eley-Rideal with CO_2 & COS adsorption

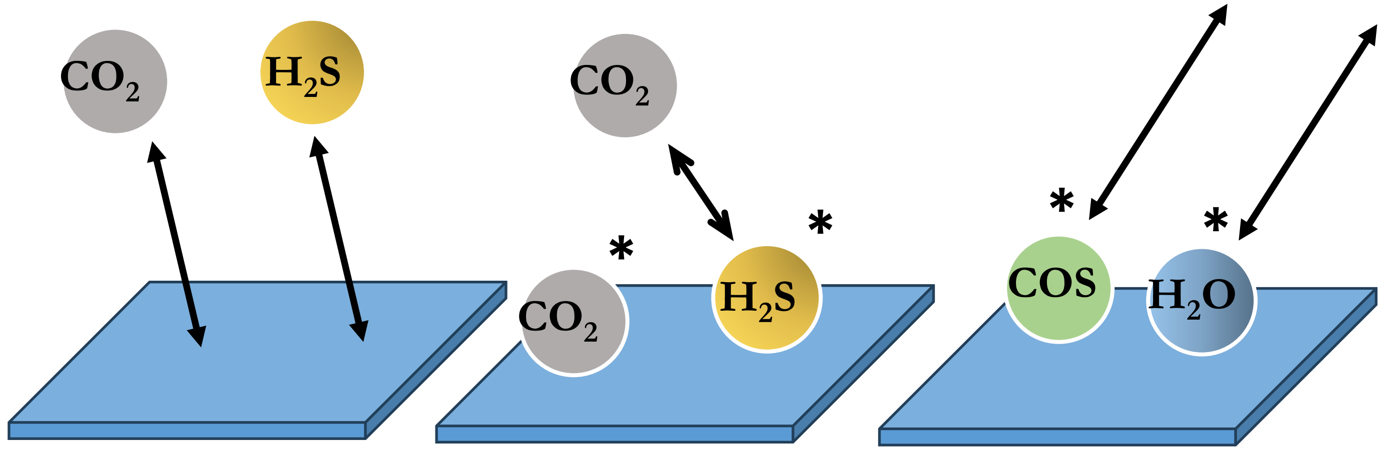
$H_2S + * \leftrightarrows H_2S*$ $r_1 = k_1^+ C_{H_2S}\theta_* - k_1^- \theta_{H_2S}$

$H_2S* + CO_2 \leftrightarrows COS + H_2O*$ $r_2 = k_2^+ C_{CO_2}\theta_{H_2S}\theta_* - k_2^- \theta_{H_2O}\ \theta_{*COS}$

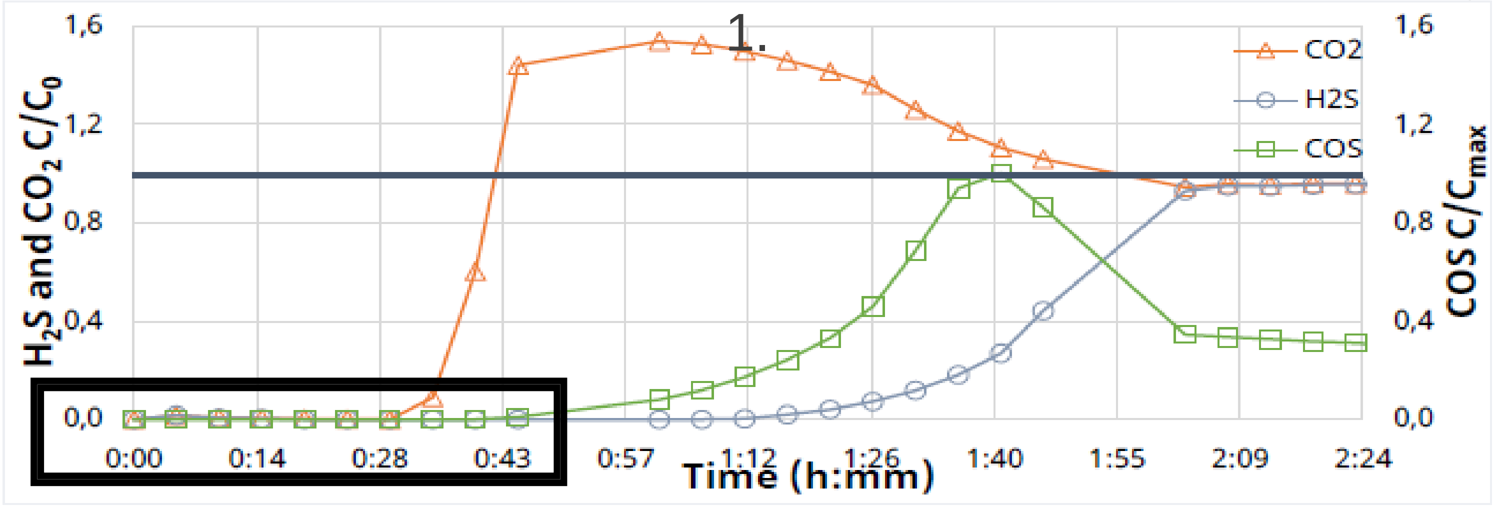
$H_2O * \leftrightarrows H_2O + *$ $r_3 = k_3^+ \theta_{H_2O} - k_3^- C_{H_2O}\theta_*$

$COS + * \leftrightarrows COS *$ $r_4 = k_4^+ \theta_{COS} - k_4^-\ C_{COS}\ \theta_*$

$CO_2 + * \leftrightarrows CO_2*$ $r_5 = k_5^+ C_{CO_2}\theta_* - k_5^- \theta_{CO_2}$



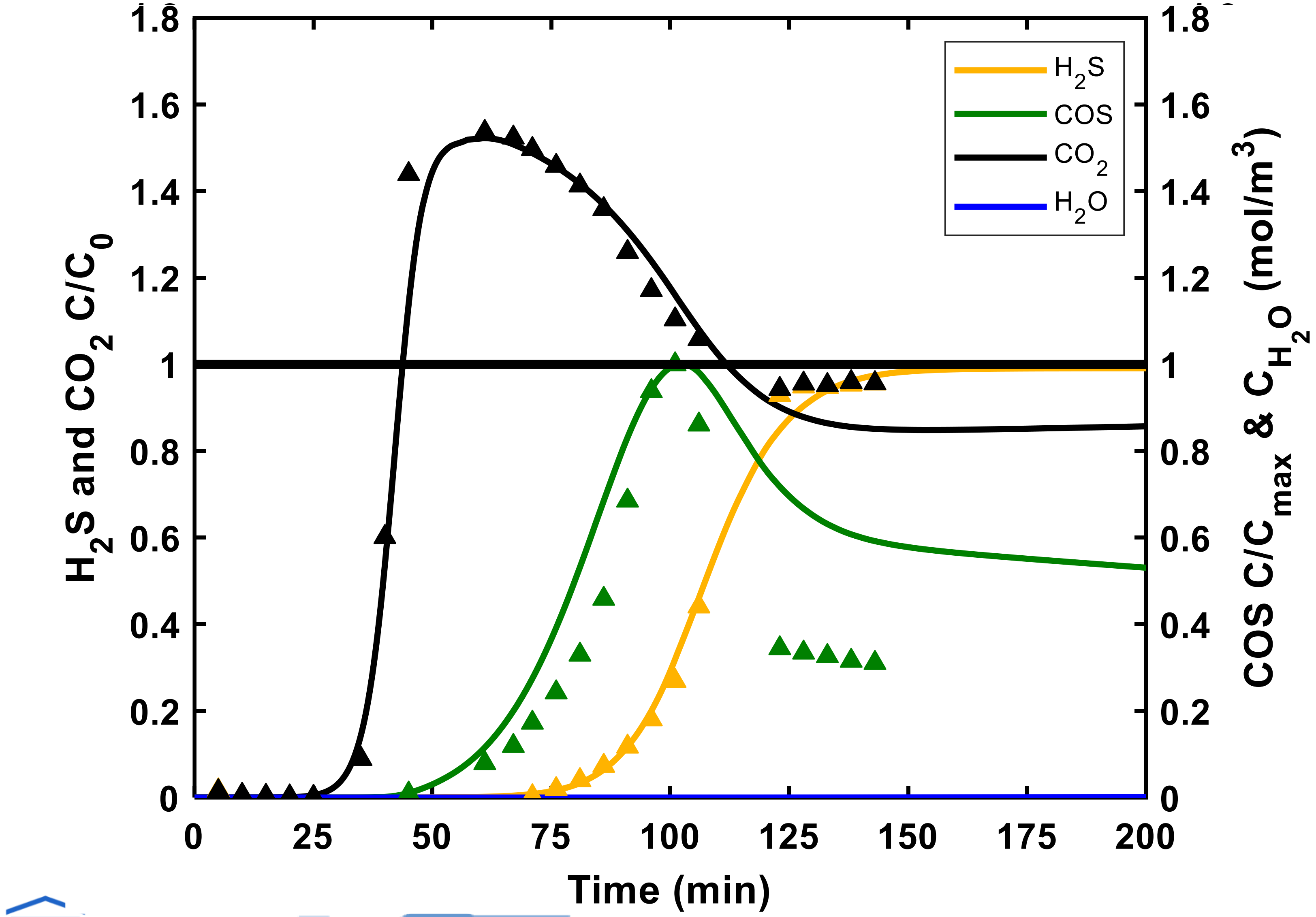
Feed mixture of H_2S:CO_2=1:1 on 13X at 45°C. Thick line at C/C_0 = 1.

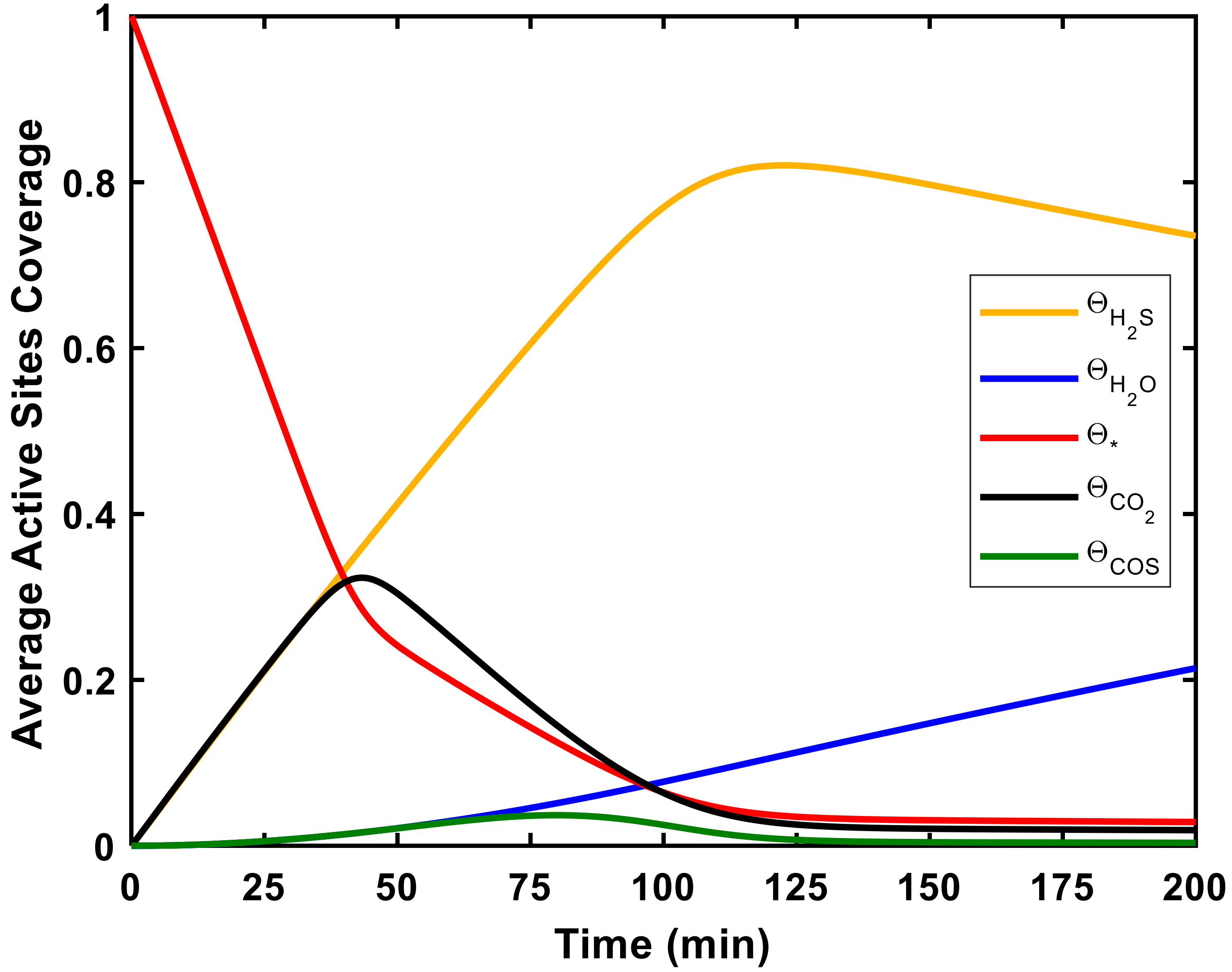


CO_2 and COS retention is accounted

Modified ER Mechanism: Results

Feed mixture of $H_2S:CO_2$=1:1 on 13X at 45°C. Thick line at C/C_0 = 1.

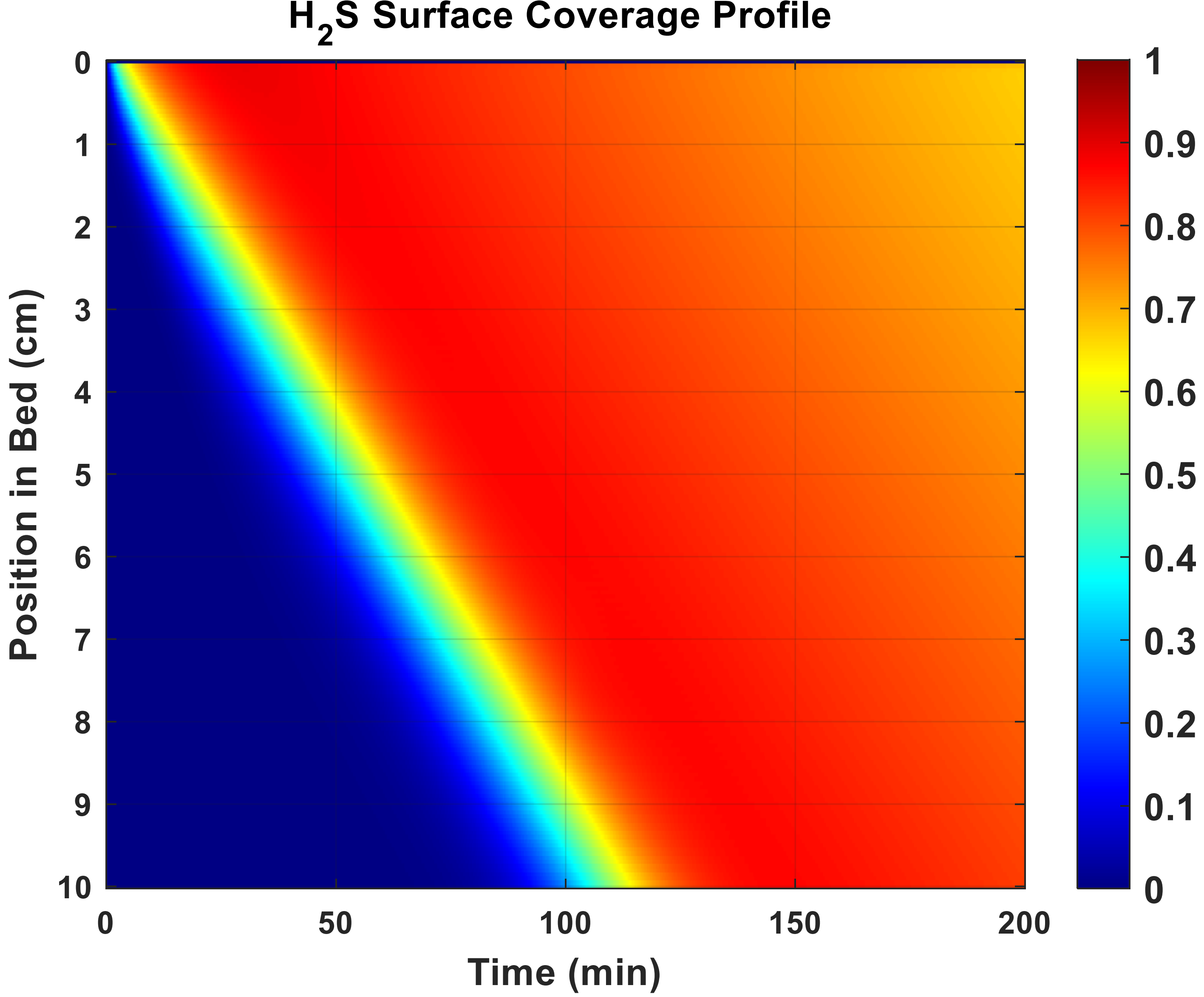




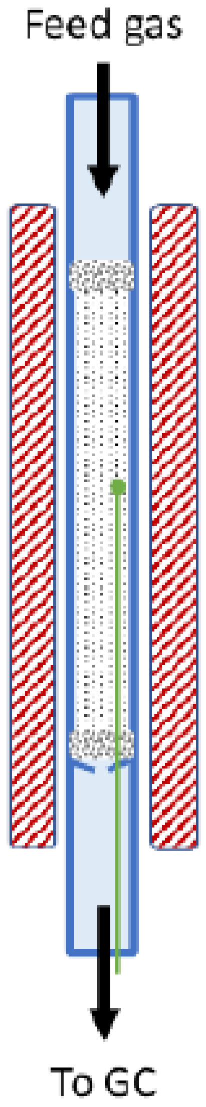
$k_{H_2S}^{ads}$	$k_{H_2S}^{des}$	k_r^f	k_r^r	$k_{H_2O}^{des}$	$k_{H_2O}^{ads}$	$k_{CO_2}^{ads}$	$k_{CO_2}^{des}$	k_{COS}^{des}	k_{COS}^{ads}
1E-3	1.8E-4	5.5E-6	1E-7	1E-4	1	6E-4	4E-3	3E-3	1E-3

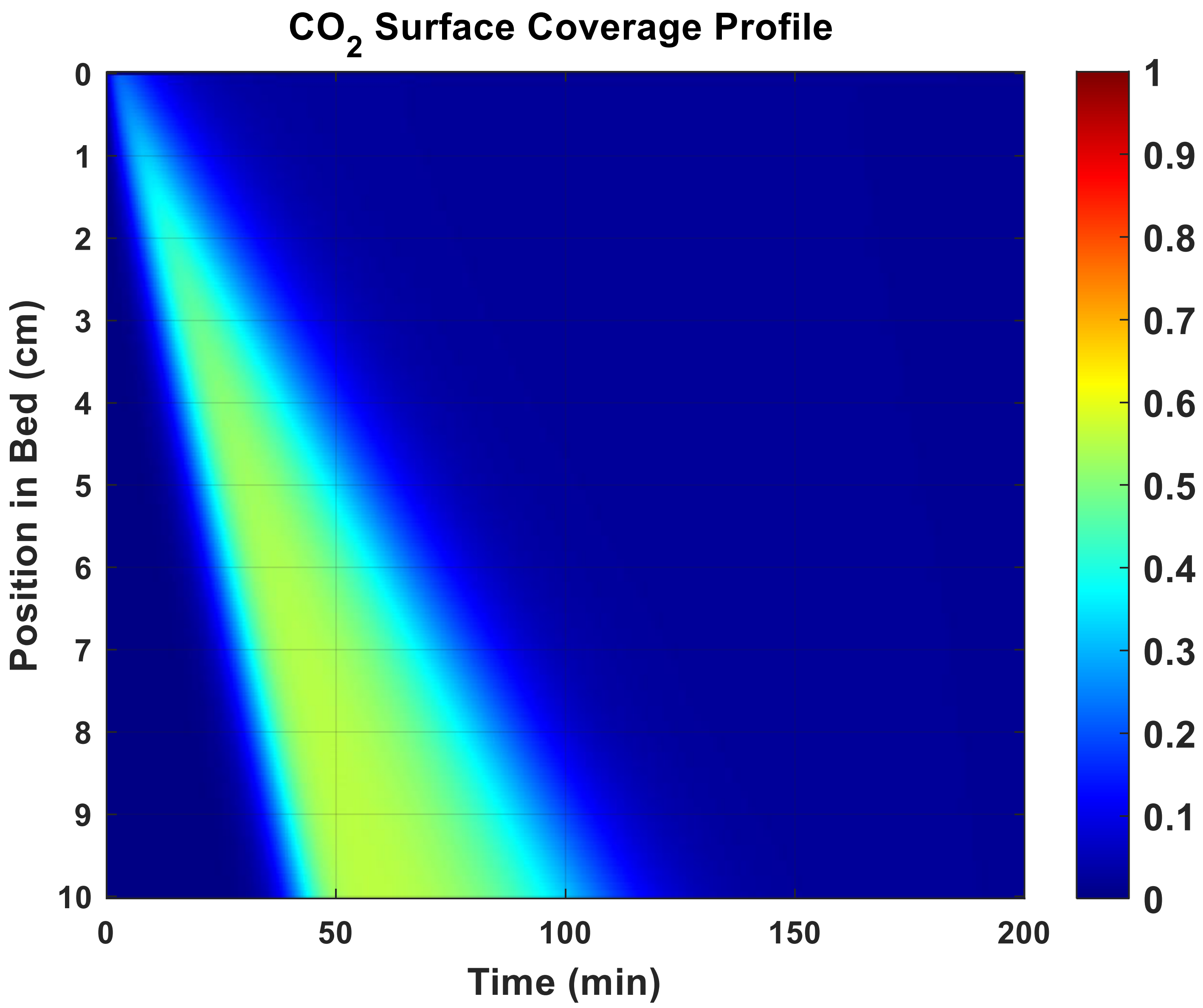
Modified ER Mechanism: Results – Reactant Profiles

Feed mixture of H_2S:CO_2=1:1 on 13X at 45°C. Thick line at C/C_0 = 1.



H_2S Surface Coverage Profile





CO_2 Surface Coverage Profile

Modified ER Mechanism: Results – Product Profiles

Feed mixture of H_2S:CO_2=1:1 on 13X at 45°C. Thick line at C/C_0 = 1.