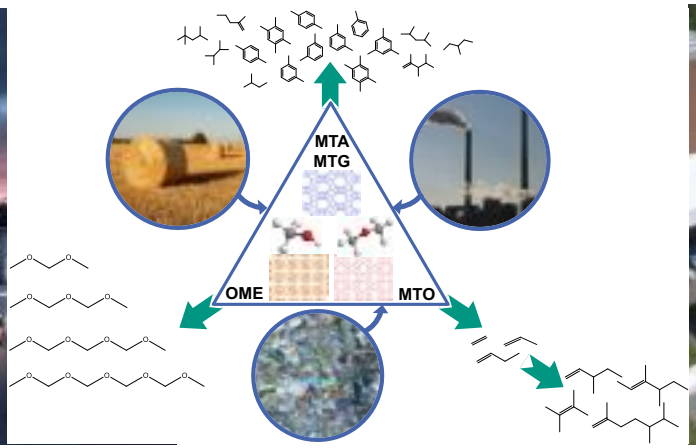
Karlsruher Institut für Technologie

CO_2 to Methanol to Jetfuel – Recent developments at KIT-IKFT

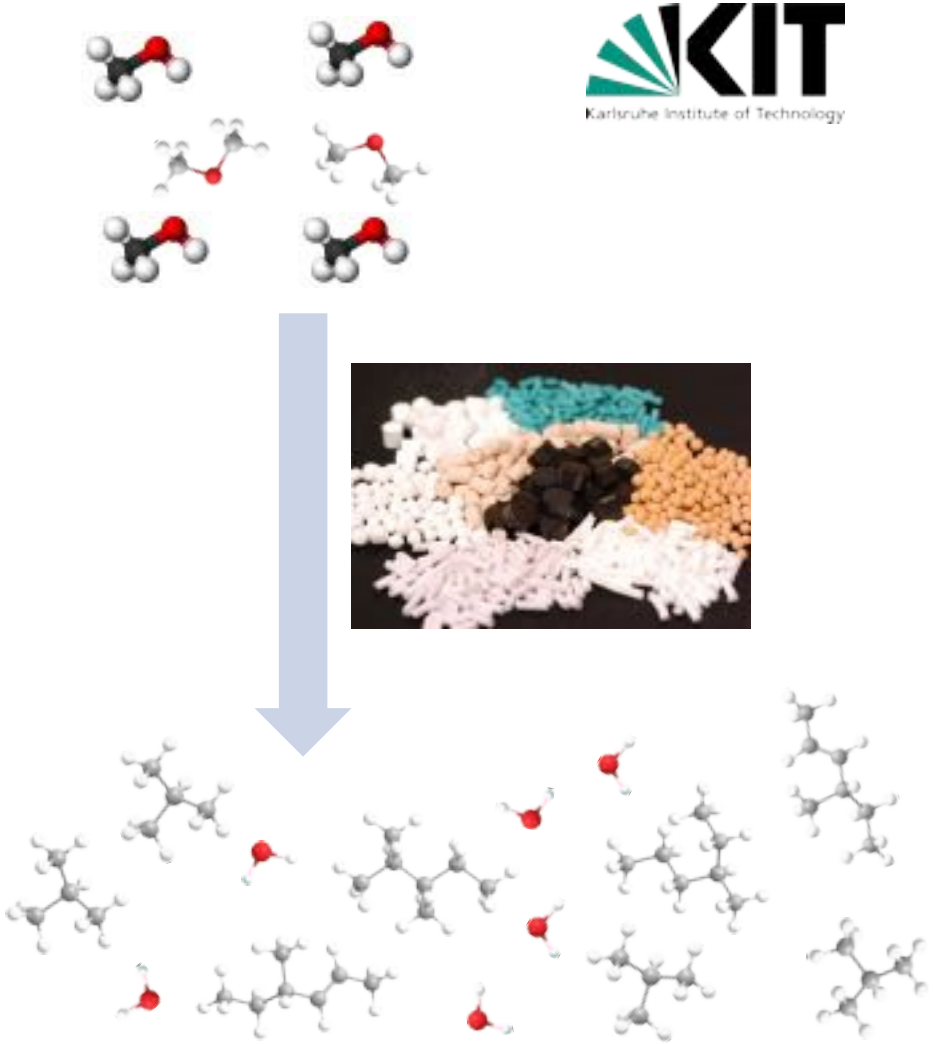
Jörg Sauer, Ulrich Arnold, Stephan Pitter, Moritz Herfet, Lucas Warmuth, Bruno Lacerda de Oliviera Campos Gabriela Rodrigues Niquini, Benjamin Niethammer, Constantin Fuchs

Institute of Catalysis Research and Technology



Content

- Technological background and infrastructure at KIT
  - Main pathways for alternative fuels
  - Fuels from methanol & DME
- Synthesis of methanol from CO_2
- Paraffinic fuels from methanol & DME
  - Modified DtO process for C_2-C_{11} olefins
  - Influence of catalysts and reaction parameters
- (Co-)Oligomerization of olefins
  - Oligomerization of ethylene
  - Co-oligomerization of C_2-C_4 olefins
- Summary & outlook



KIT - Figures and Facts

37 Spinoffs and Startups

5 Campuses – **200** ha area

385 Professors and executive scientists

367 Trainess

22,225 Students

300 Buildings with a usable area of **492,000 m²**

3,100 Doctoral students

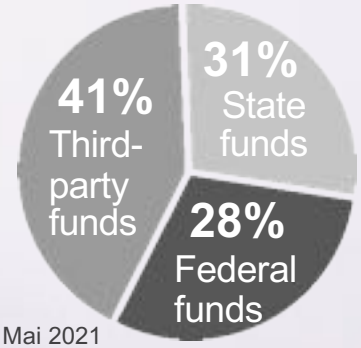
51 Patent applications

9,783 Employees

1,405 international scientists

KIT budget 2021

EUR 1090,7 million



Status: Mai 2021

KIT Excellent again! – Title Regained.

July 19,2019: Success in the funding line „University of Excellence“ of the Excellence Strategy of the Federation and the Federal States

„The Research University in the Helmholtz Association – Living the Change“

Retrospect:

2006

Success in the first round of the Excellence Initiative of the Federation and the States

2009

Foundation of Karlsruhe Institute of Technology

2012

Loss of excellence in the second round of the Excellence Initiative of the Federation and the States

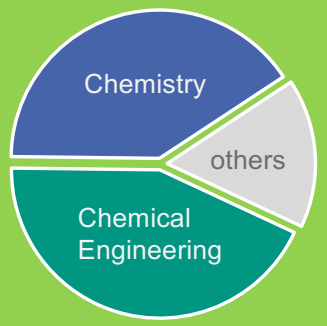
IKFT at a Glance

IKFT develops catalysts and process technologies of catalytic processes for the production of chemical energy carriers based on renewable energy and alternative raw materials. Research spans from the understanding of the processes at the molecular level to the pilot plant stage.

538
Publications since 2017
(peer-reviewed)

102
of which in 2022

128
Staff members



37
PhD students
with

18
being international

6
Scientific departments

7
Faculty Members@KIT

4.845.000 €
R&D Budget
(2021, without personnel)

49 %
of which third-party funded

Experimental research and technological development are complemented by computational catalysis and *operando* techniques to provide a fundamental understanding of catalytic systems under realistic conditions.

The Management Team of IKFT

Jörg Sauer, Director
Catalyst Materials and Process Development

Silke Behrens
Model Systems and Nanoscaled Functional Materials for Catalysis

Olaf Deutschmann
Reaction Kinetics and Reactive Multiphase Flow

Jan-Dierk Grunwaldt
Catalysis and Operando Spectroscopy

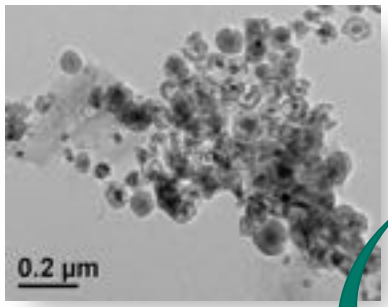
Felix Studt, Director
Theoretical Catalysis

Nicolaus Dahmen, Deputy Director
Scale-up of Processes with Renwable Carbon Sources

Moritz Wolf
Material Synthesis and Scale-up

Stephan Pitter
Scientific Management
Catalysis and Processes for CO_2-Fixation

Our Approach



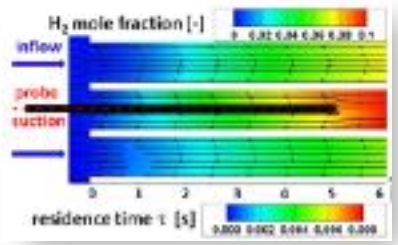
Catalysts

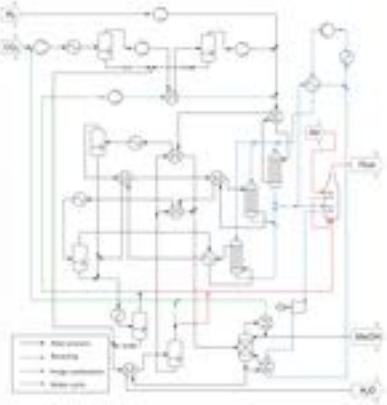
Process Steps

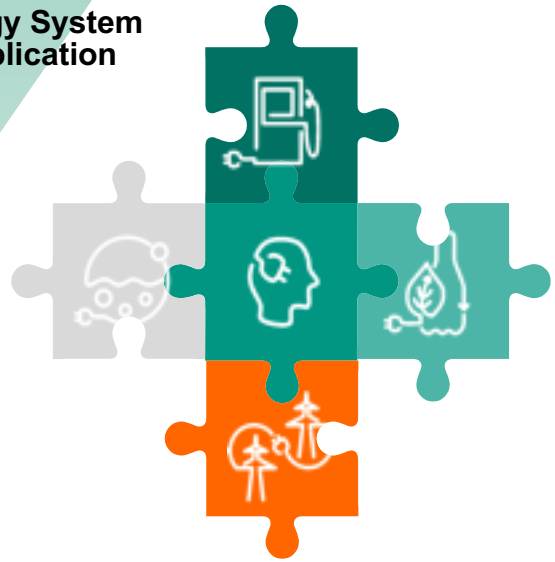
Processes & Plants

Energy System & Application

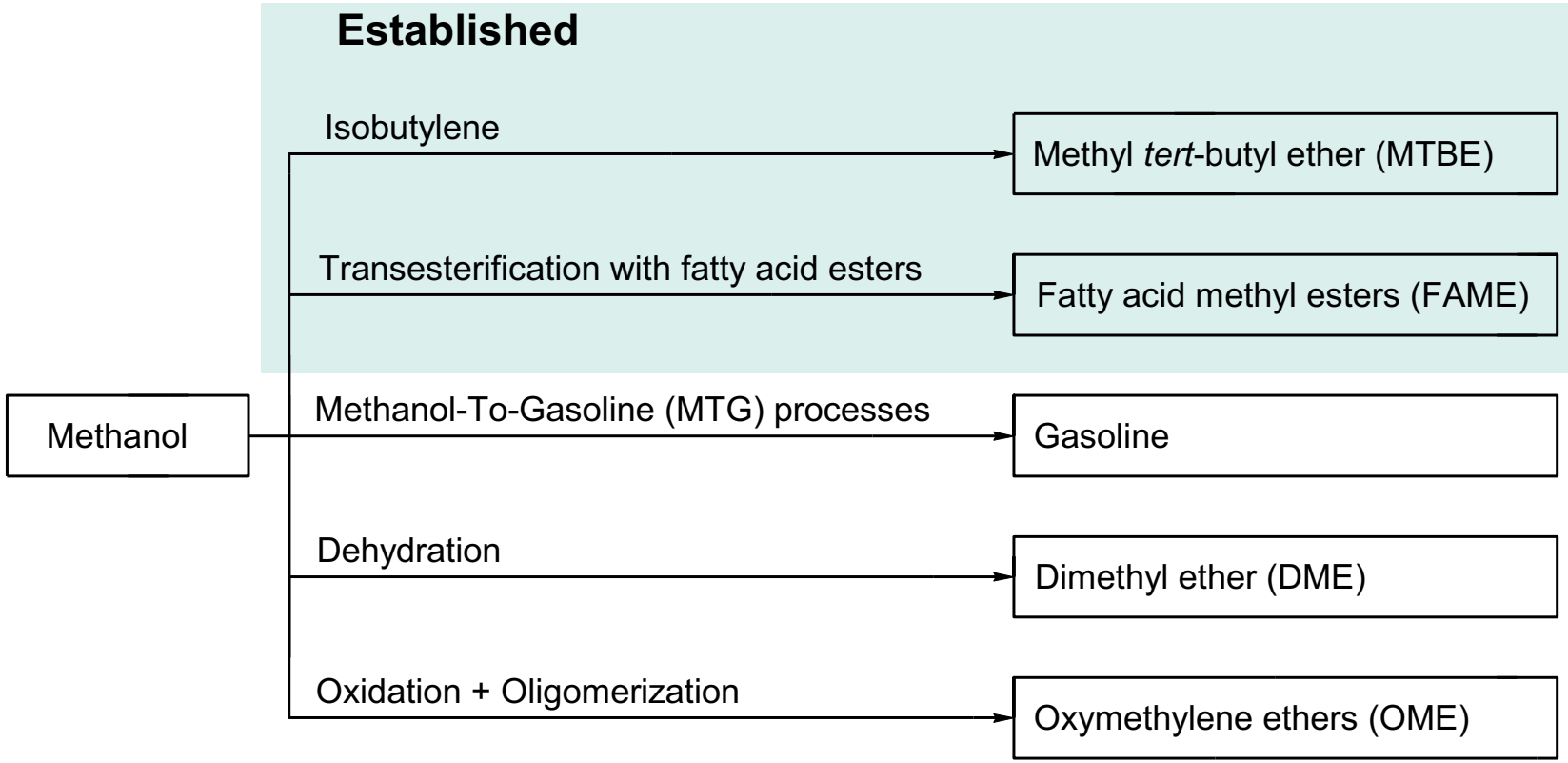
Elementary Processes







Fuels and fuel additives from methanol



F. Asinger, Methanol – Chemie- und Energierohstoff, Springer, Berlin, **1986**.

Potential for direct eMethanol use in MiRO-Refinery:

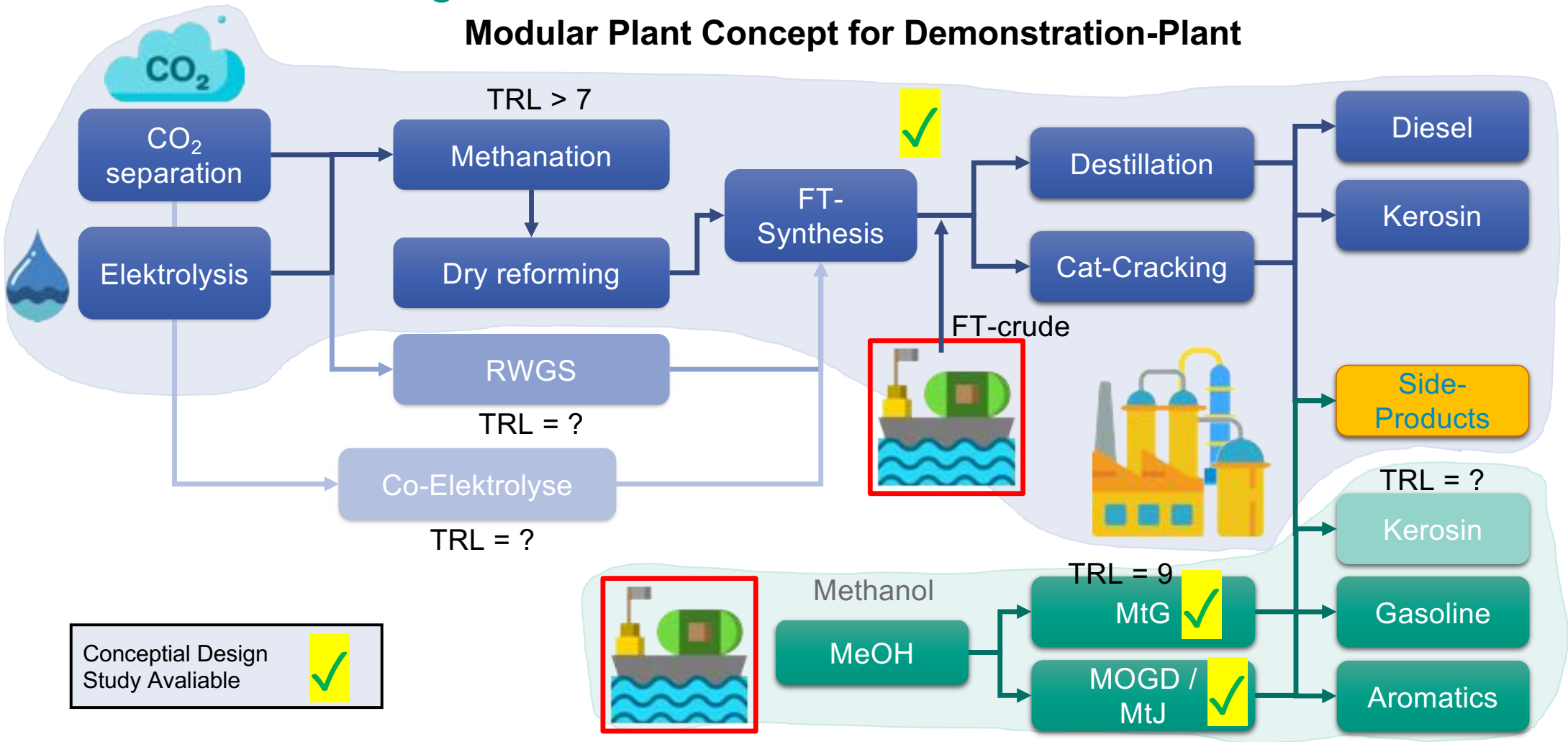
DIN EN 228:2017-08 (Table 1): Oxygen-Content:	3.7% (w/w)
Average Ethanol content of German gasoline 2021:	7.47% (v/v)
Gasoline capacity of MiRO:	5 Mio t/y
=> Maximum Methanol addition (direct or MTBE):	110 000 t/y

Currently Launched Methanol-to-X-Projects – Germany

Project Title	Ministry	Consortial Lead	Project start
M2SAF - Nachhaltiges Kerosin aus Methanol - Methanol to Sustainable Aviation Fuel	BMDV	OMV Deutschland Operations GmbH & Co. KG	08/22
EwOPro - Entwicklung des Olefins-to-Jetfuel-Prozesses	BMWK	Technische Universität Bergakademie Freiberg	03/23
DeCarTrans - Demonstrating a Circular Carbon Economy in Transport Along the Value Chain	BMDV	FEV Europe GmbH	01/23
SAFari - Sustainable Aviation Fuels based on Advanced Reaction and Process Intensification	BMDV	Fraunhofer-Institut für Solare Energiesysteme (ISE)	12/22
REF4FU – Refineries for Future / Erneuerbare Kraftstoffe aus Grünen Raffinerien der Zukunft	BMDV	KIT	12/22

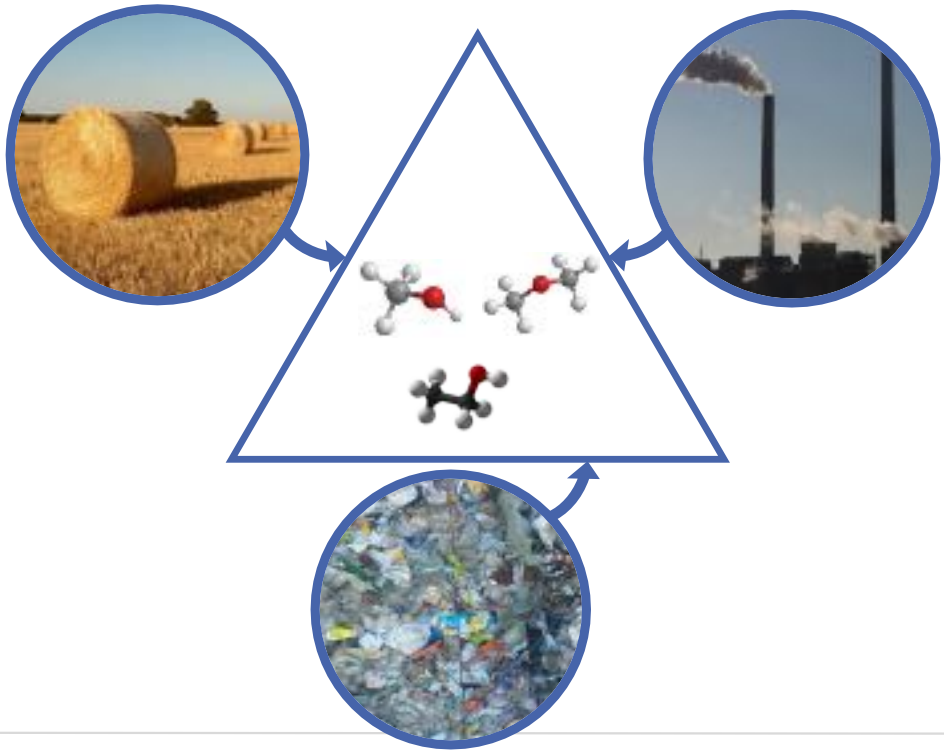
reFuels – Rethinking Fuels

Modular Plant Concept for Demonstration-Plant



Thomas Koch, Olaf Toedter / KIT-IFKM – Nicolaus Dahmen

Methanol-, DME as Key Intermediates



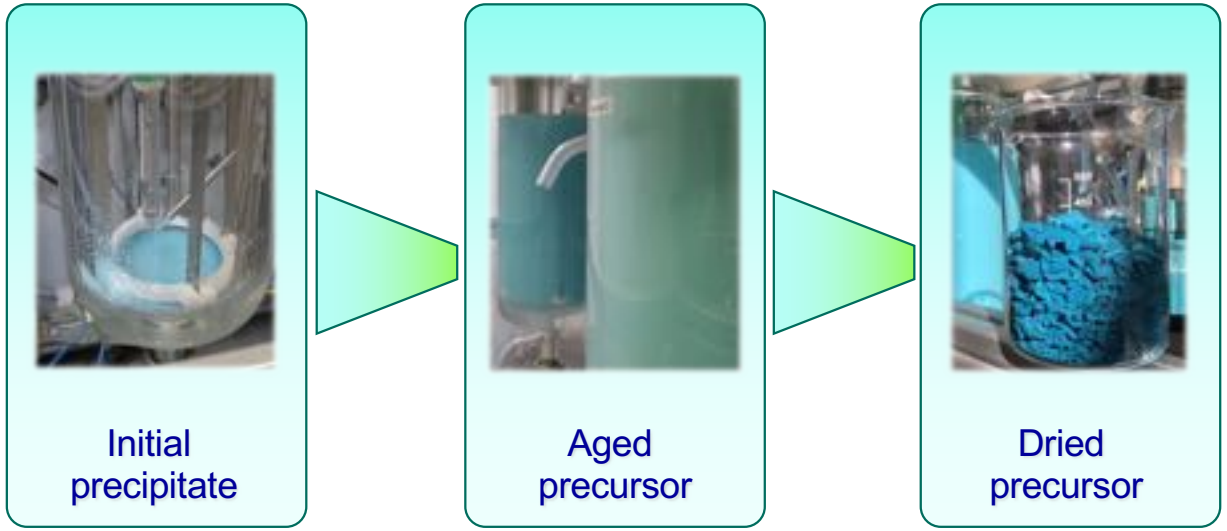
The science of catalyst precursor synthesis

- $Cu(NO_3)_2$
- $Zn(NO_3)_2$
- $M(NO_3)_x$
- $NaHCO_3$ or Na_2CO_3

with M: Al, Zr, others

Parameters:
T, pH, t

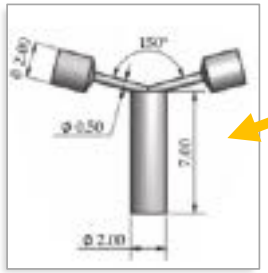
composition,
mixing

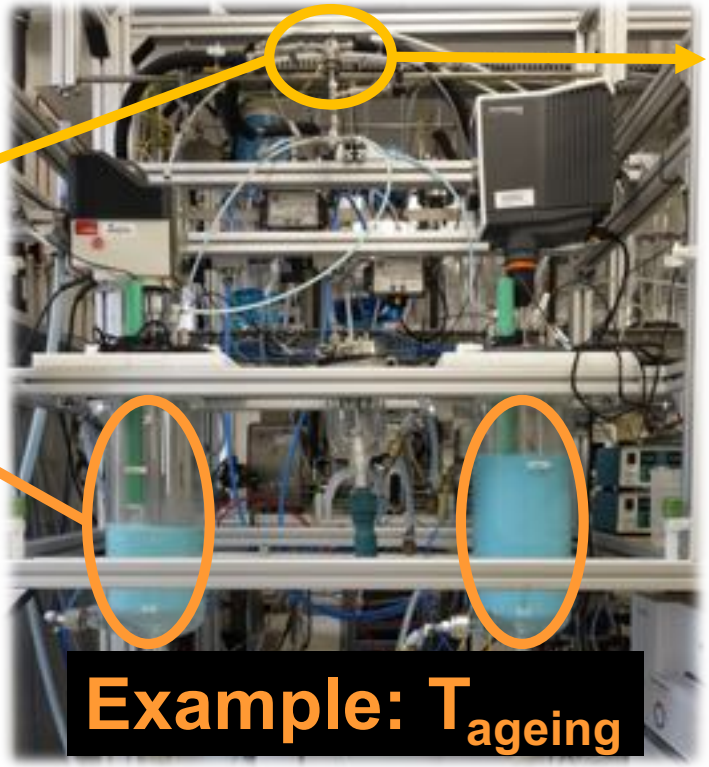


Formation of the crystalline
key phase zincian malachite
$(Cu_{(2-x)}Zn_x)(OH)_2CO_3$
with $0 \leq x \leq 0.31$

a) Behrens, M.; Schlögl, R.; *Z. Anorg. Allg. Chem.* **2013**, *639*, 2683 – 2695.
b) Warmuth, L.; Guse, D.; Kind, M.; Pitter, S. et al. *in preparation.* **2023**.

Modification of co-precipitation process



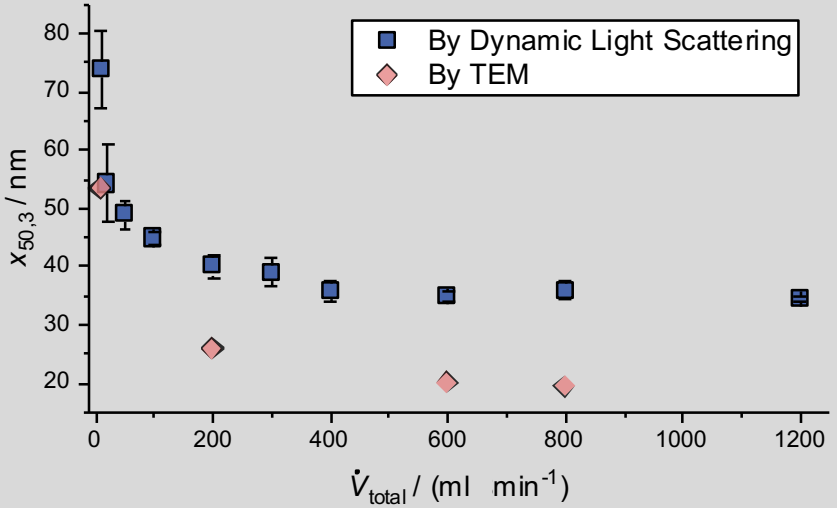


Batch-wise aging in two parallel stirred tank reactors (5 L) with optimized mixing equipment:

- Enabling time separation and separate acquisition of precipitation and aging

Continuously operating, micro-structured Y-mixer:

- Turbulent mixing with initial precipitation in an extremely short period of time



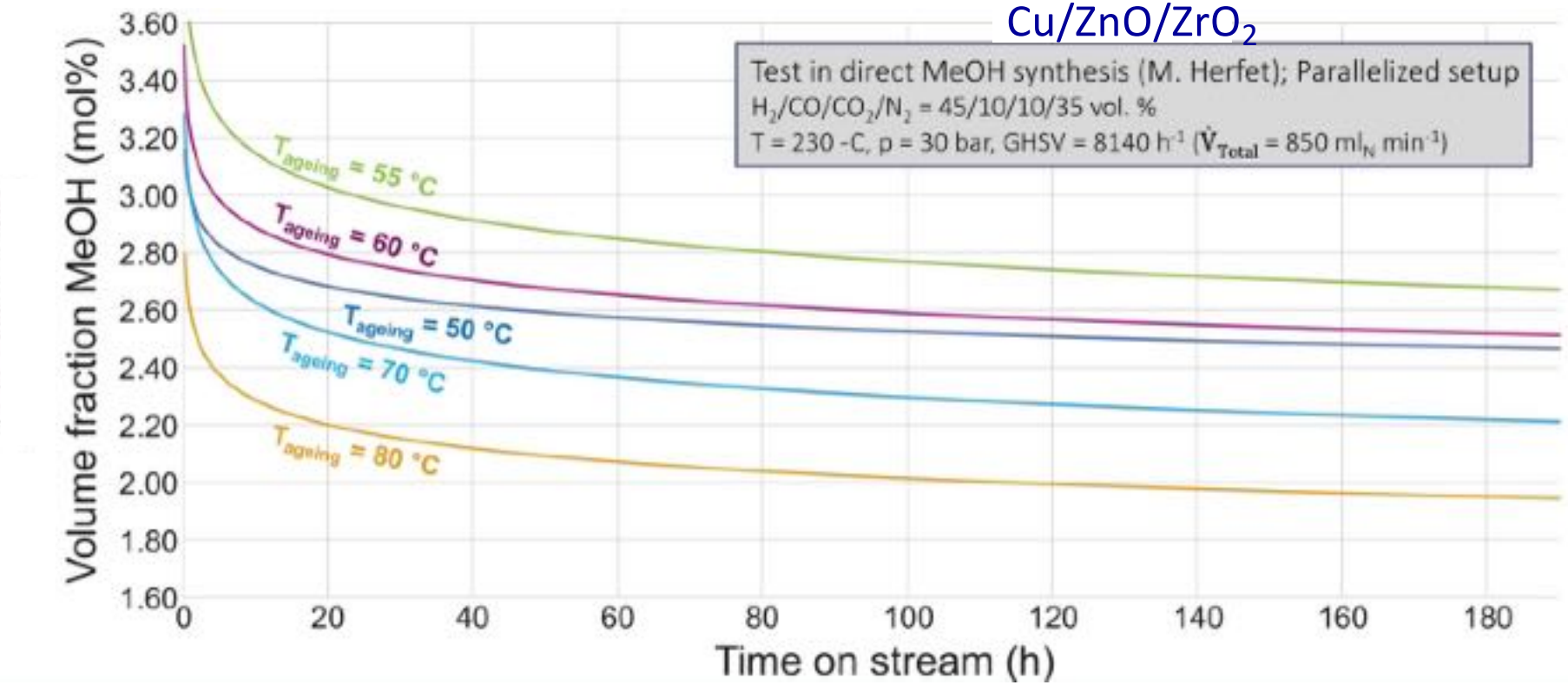
a) Polierer, S.; Guse, D.;, Wild, S.; Herrera Delgado, K.; Otto, T. N.; Zevaco, T. A.; Kind, M; Sauer, .J.; Studt, F.; Pitter, S.; *Catalysts* **2020**, *10*, 816.
b) D. Guse, L. Warmuth, F. Kreißig, S. Pitter, M. Kind in *The Role of Catalysis for the Energy-Transition* (Hrsg.: DGMK e.V.), **2022**.

Mathias Kind + David Guse / KIT-TVT – Stephan Pitter – Lucas Warmuth

Institute of Catalysis Research and Technology (IKFT)

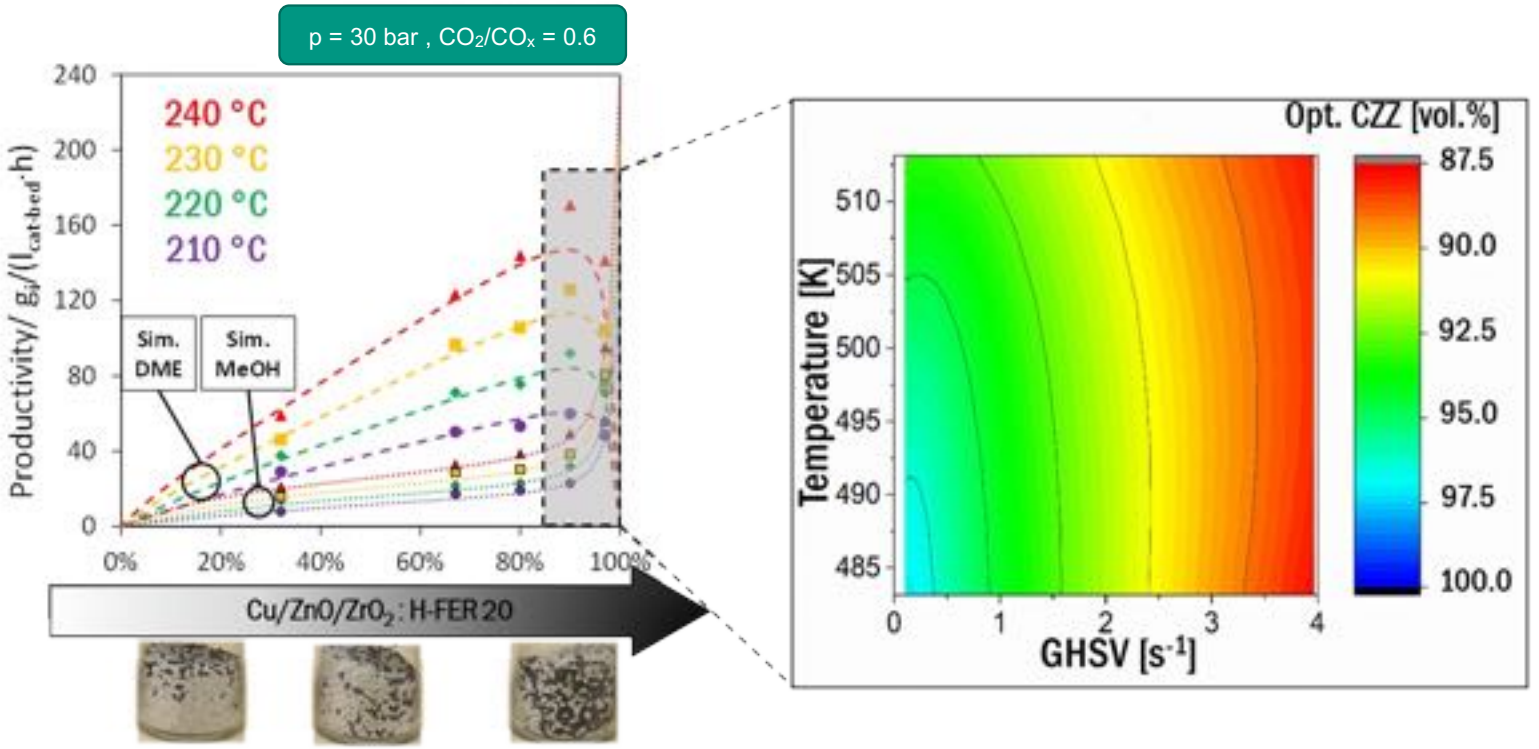
The "chemical memory" begins at an early stage

Case study on precursor suspension ageing temperature



Polierer, S.; Herfet, M.; Warmuth, L.; Pitter, S. et al. *in preparation*. **2023**.

Model-based optimization of CZZ/H-FER-20 bed composition for the direct DME synthesis



Extrapolation over a broader GHSV, including industrially relevant process conditions

The optimum CZZ amount depends on GHSV, temperature and CO_2/CO_x ratio

The CZZ optimum amount is mostly affected by the GHSV

S.Wild, et.al. *React. Chem.* Eng. 2022, 7, 943

e-XPlore Demonstration Unit

Construction: 2020-2022
Start operation: 2023

Methanol synthesis via CO/CO_2

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$

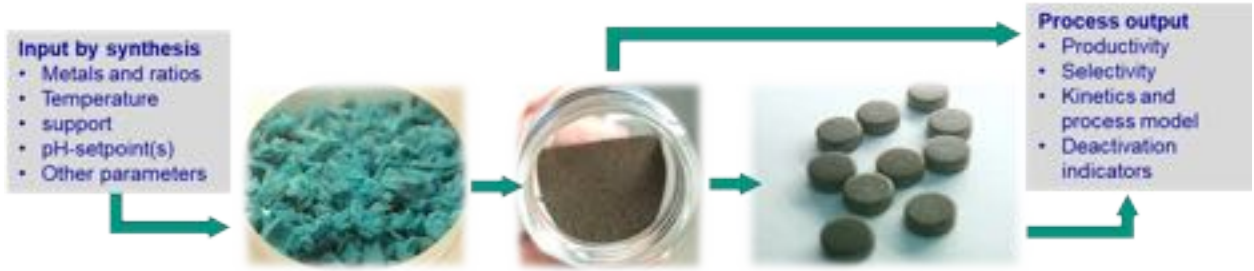
Methanol dehydration

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$$

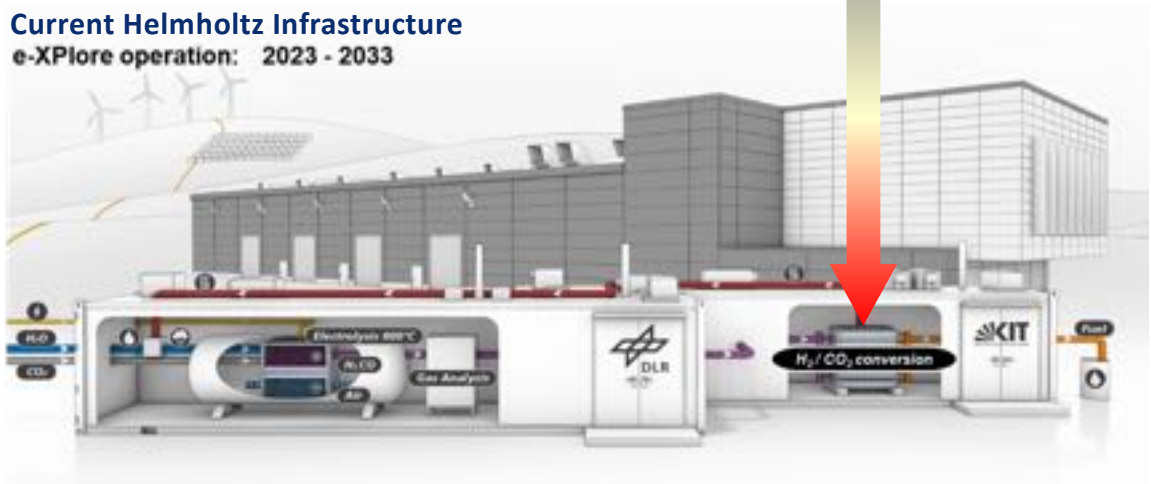
Oxymethylene ether synthesis

$$CH_3OCH_3 + HCHO \rightleftharpoons OME_x$$

Integrating improved MeOH catalysts in H_2-based and CO_2-neutral value chains



Guse, D.; Polierer, S.; Wild, S.; Pitter, S.; Kind, M.; *Chem. Ing. Tech.* **2022**, 94, 314.



Catalyst development and scale-up

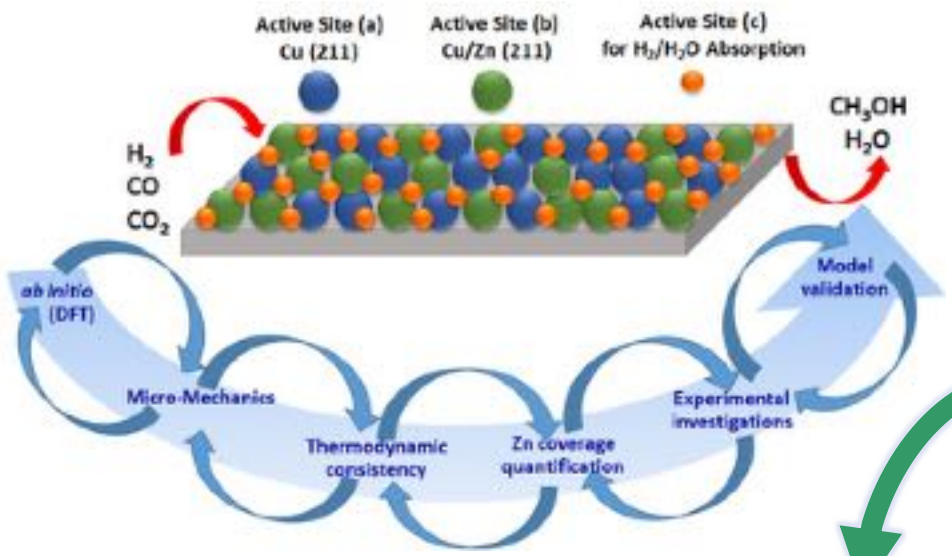
- Accelerated material design for preparation process being similar to technical catalyst manufacturing
- Access to catalysts in kg scale

Process development

- with information on spatially resolved catalyst activity under technically relevant process conditions

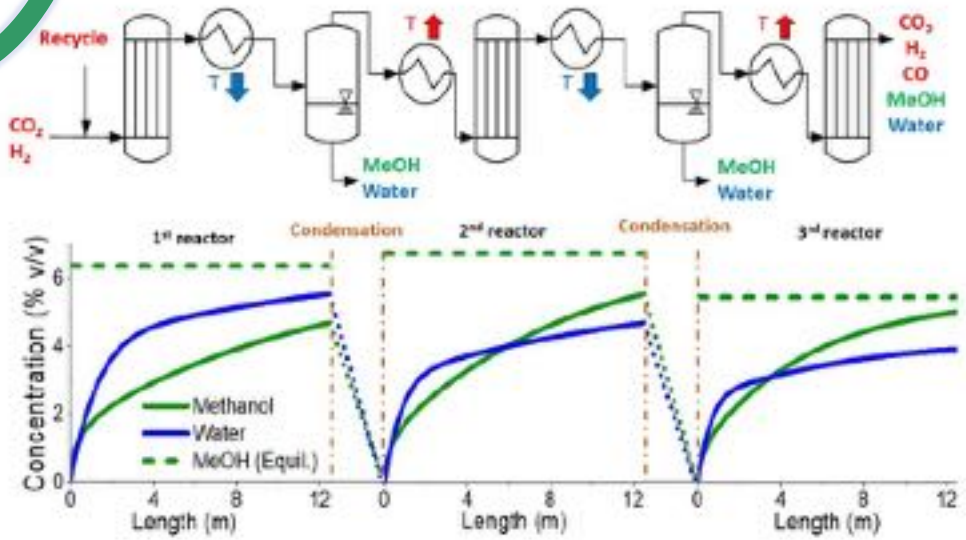
- Manufacturer: Reacnostics
- Completion: Q3 2023
- Profile reactor for catalyst studies
- Conventinal shell and tube reactor

Modeling kinetics / process of MeOH synthesis



Fundamentals of MeOH formation

- Experimental and theory based microkinetic modeling provides key insights into the reaction mechanism.

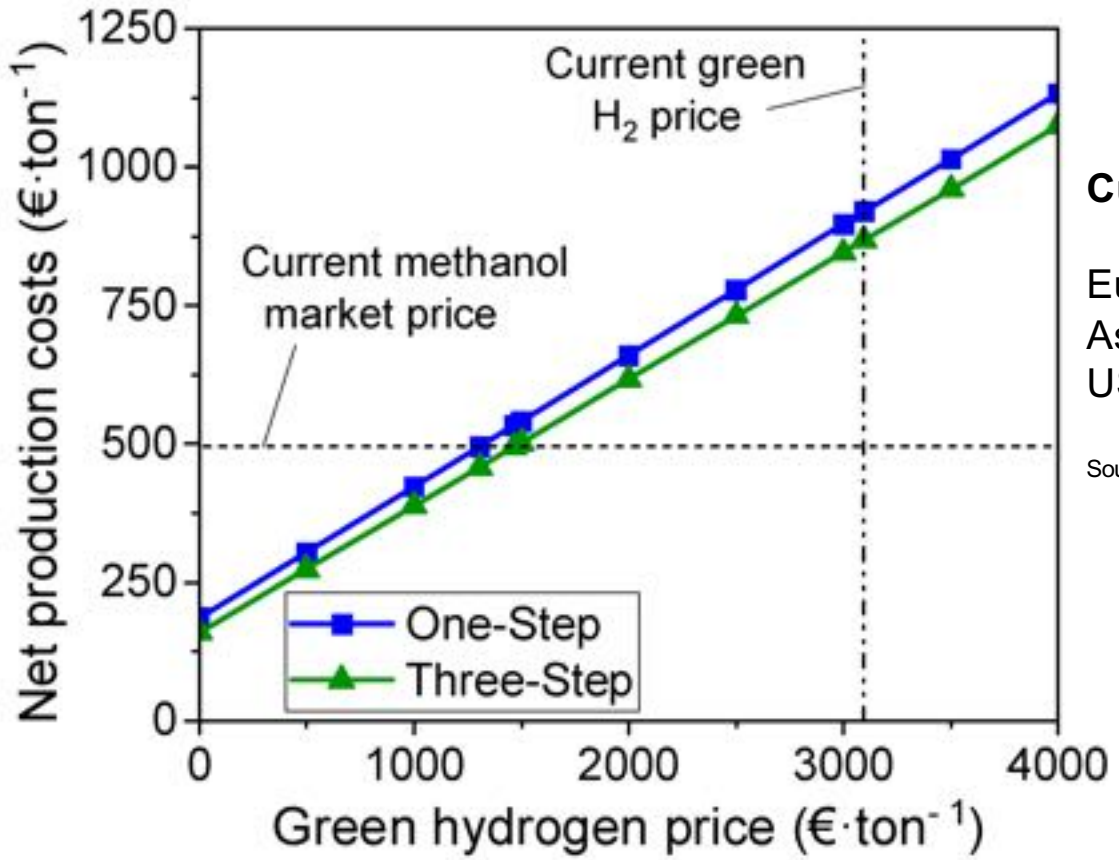


Use in Process Development

- Derived formal kinetic model accurately described a wide operating region.
- Intermediate condensation steps (figure right) significantly improve process efficiency.

a) Lacerda de Oliveira Campos, B.; John, K.; Beeskow, P.; Herrera Delgado, K.; Pitter, S.; Dahmen, N.; Sauer, J. *Processes* **2022**, 10, 1535. b) Wild, S.; Lacerda de Oliveira Campos, B.; Zevaco, T. A.; Guse, D.; Kind, M.; Pitter, S.; Herrera Delgado, K.; Sauer, J.; *Reaction chemistry & engineering* **2022**, 7, 943.

Production Costs of Methanol 1-Step- vs. 3-Step-Process (-5,7%)



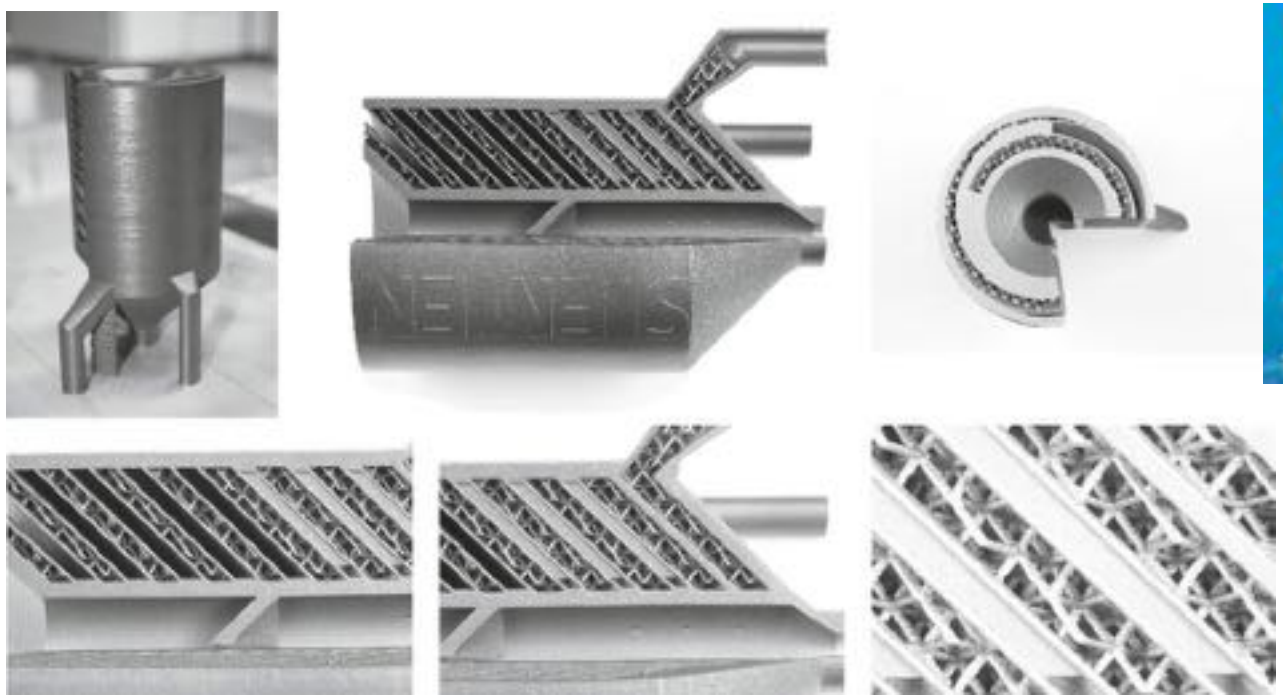
Current Methanol Prices:

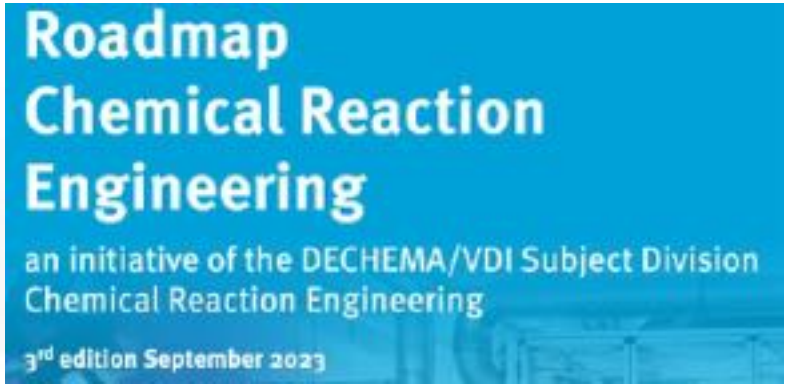
Europe:	395 EUR
Asia:	293 EUR
USA:	480 EUR

Source: Methanex.com, 2023-09-02

Lacerda de Oliveira Campos, B.; John, K.; Beeskow, P.; Herrera Delgado, K.; Pitter, S.; Dahmen, N.; Sauer, J. *Processes* **2022**, 10, 1535

3D-Printing Offers new Design-Options for Reactor-Design
Project „3D-Process“ of Evonik, Siemens, KIT





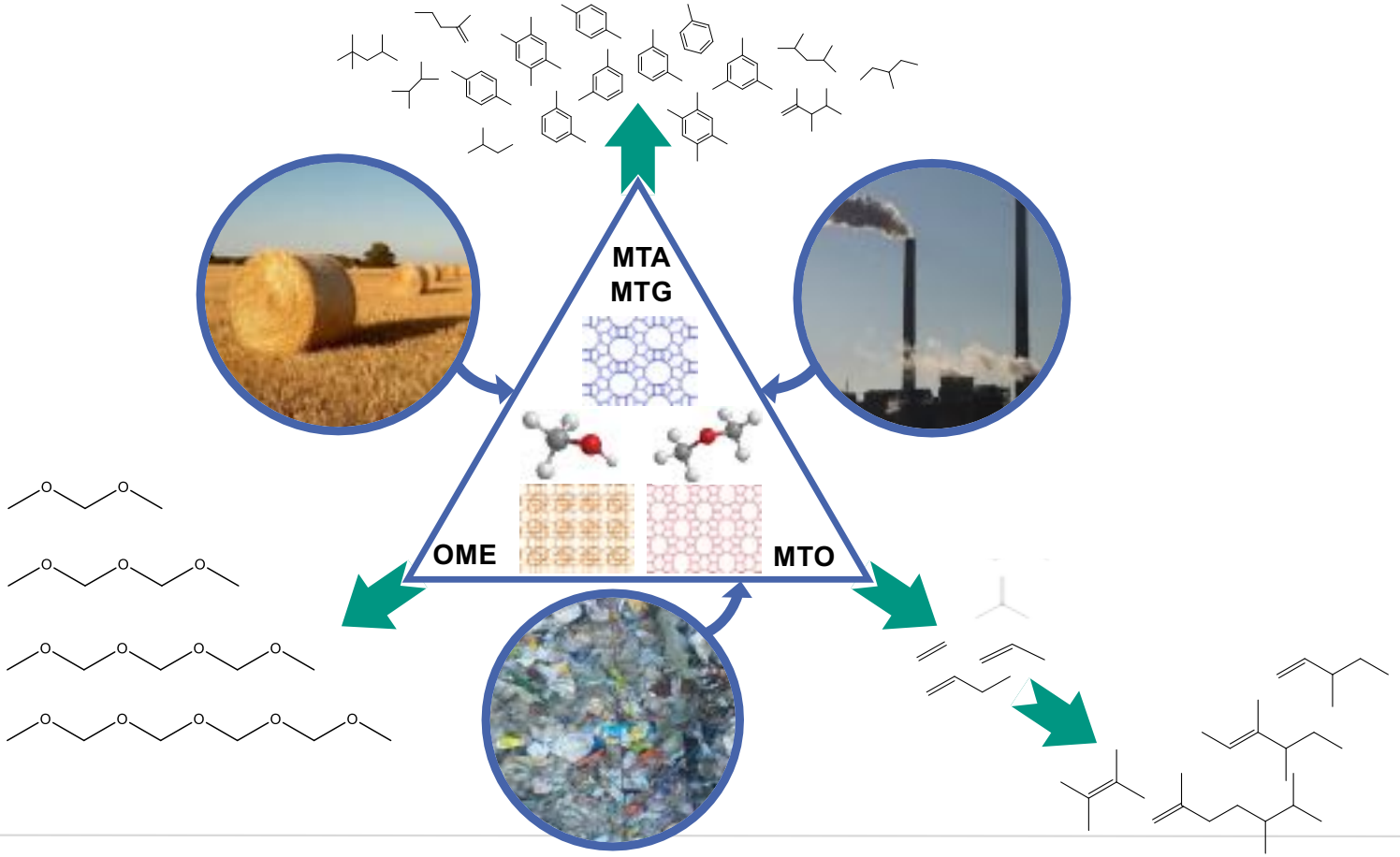
https://dechema.de/dechema_media/Downloads/Positionspapiere/2023+Roadmap+%E2%80%9EChemical+Reaction+Engineering_+engl_-p-20009528.pdf

Jastram, A., Schaack, S. and Kiener, C. (2022). Chemie Ingenieur Technik, 94: 948-957.

Stephan Pitter – Karla Herrera Delgado – Gabriela Niquini

Institute of Catalysis Research and Technology (IKFT)

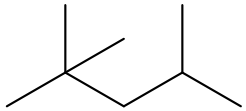
Methanol and DME as Key-Intermediates for CO_2-Neutral Petrochemistry and Fuel Production



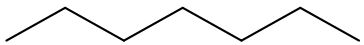
Paraffinic fuels: Production and properties of paraffinic gasoline

- Known technology => Catpoly Process from UOP, 1930 (olefin oligomerization)
- Gasoline without aromatics => Cleaner combustion
- Properties like common gasoline => Compatibility with materials
  => Similar energy content
  => Similar viscosity, density …
  => No changes in logistics and infrastructure

- Molecular structure: Purely paraffinic



Octane number$_{\text{iso-octane}}$ = 100

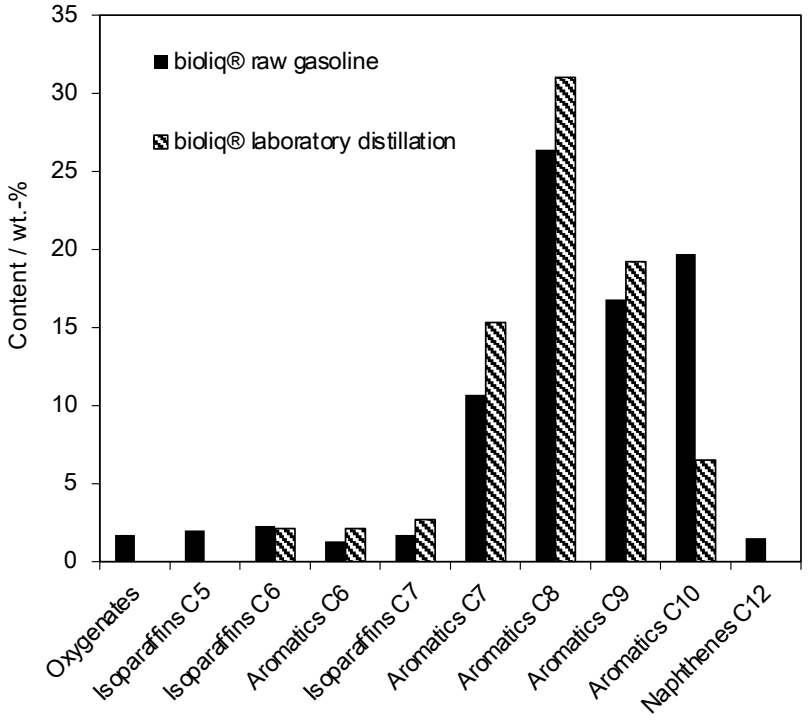


Octane number$_{\text{n-heptane}}$ = 0

- High branching needed to reach high octane numbers; compensation of missing aromatics

Gasoline from MTG- and DTG-processes

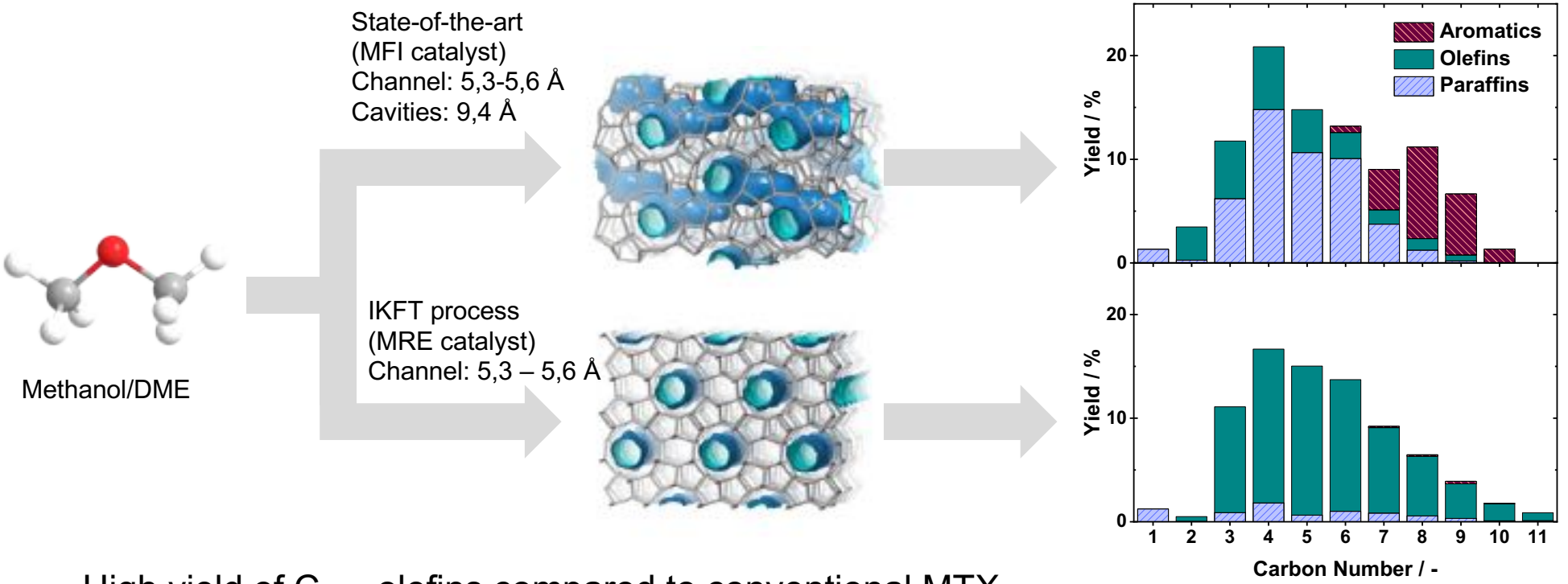
- Example: Gasoline from the DTG unit of the bioliq® process at KIT (MFI zeolite catalyst)
  - Product spectrum dominated by aromatics
  - High share of heavy gasoline
  - Work-up necessary
  - Distillation to remove high-boiling aromatics
  - Blending with conventional gasoline
  - Blends with 10% bioliq® gasoline within EN228 specification
  - Further improvement of fuel quality by chemical treatment



T. Michler, N. Wippermann, O. Toedter, B. Niethammer, T. Otto, U. Arnold, S. Pitter, T. Koch, J. Sauer, Gasoline from the bioliq® process: Production, characterization and performance, *Fuel Process. Technol.* **2020**, *206*, 106476. DOI: 10.1016/j.fuproc.2020.106476

T. Michler, N. Wippermann, O. T. Michler, B. Niethammer, C. Fuchs, O. Toedter, U. Arnold, T. Koch, J. Sauer, Further Development of Gasoline from the bioliq® Process with Focus on Particulate and Hydrocarbon Emissions, *Fuels* **2022**, *4*, 205-220. DOI: 10.3390/fuels4020013

New concept for the conversion of methanol/DME to C_{2-11} olefins



High yield of C_{2-11} olefins compared to conventional MTX processes

B. Niethammer, U. Arnold, J. Sauer, *Appl. Catal., A* **2023**, *651*, 119021. DOI: 10.1016/j.apcata.2023.119021

Properties of Catalysts from MFI-, *MRE-, TON-Structure

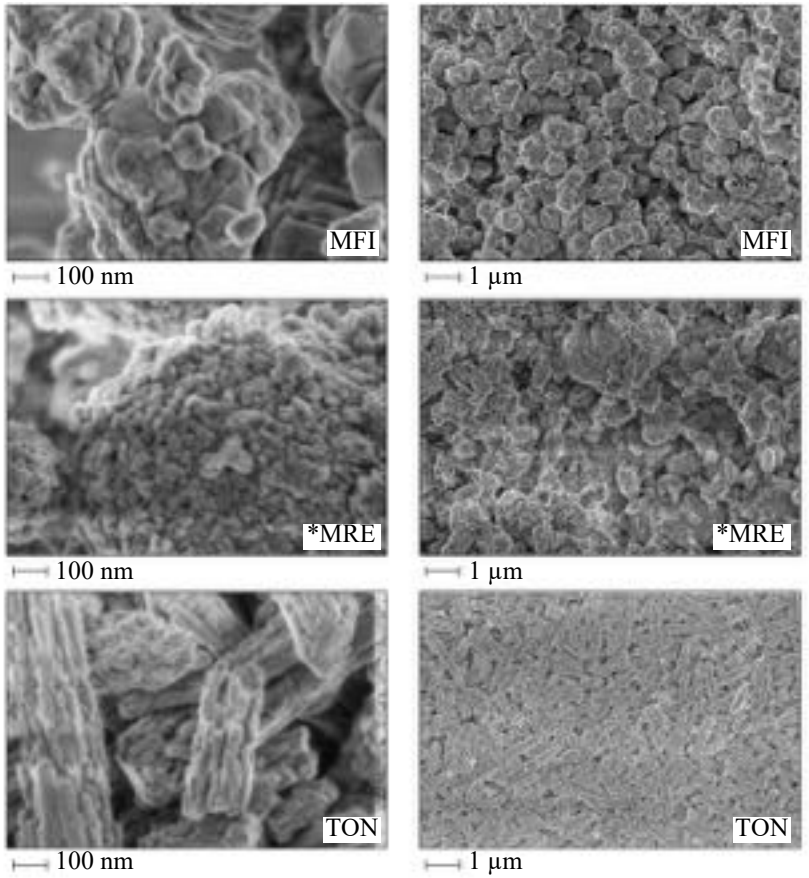
	MFI	*MRE	TON
Si/Al ratio (mol mol^{-1})[a]	40.2	73.5	50.4
BET area (m^2 g^{-1})	459	195	228
External/internal surface[b]	0.18	0.59	0.27
Micropore volume (cm^3 g^{-1})[c]	0.22	0.07	0.10
Brønsted acid sites (µmol g^{-1})[d]	235	97	170
Lewis acid sites (µmol g^{-1})[d]	37	24	22

[a] ICP-OES

[b] t-plot

[c] NLDFT

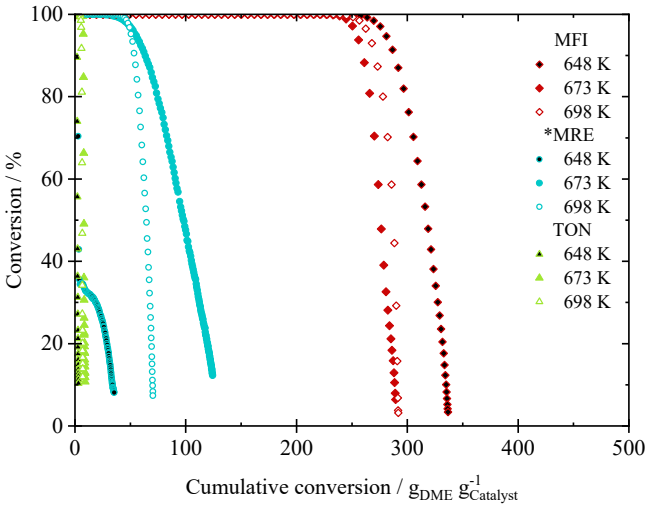
[d] Pyridine FTIR



B. Niethammer, U. Arnold, J. Sauer, *Appl. Catal., A* **2023**, *651*, 119021. DOI: 10.1016/j.apcata.2023.119021

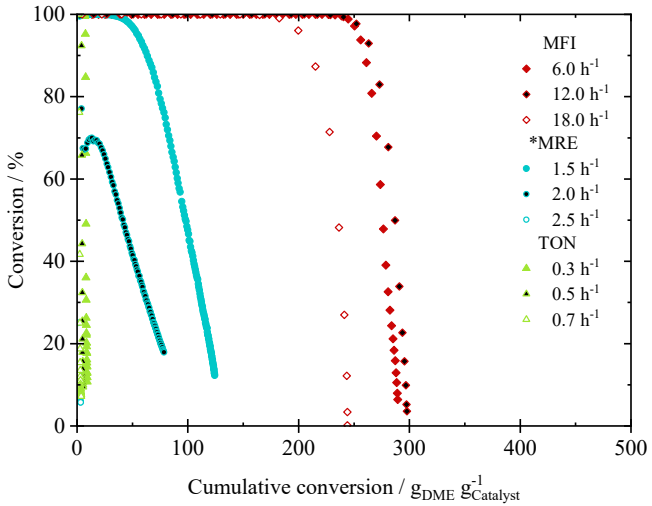
Influence of reaction conditions

Influence of temperature



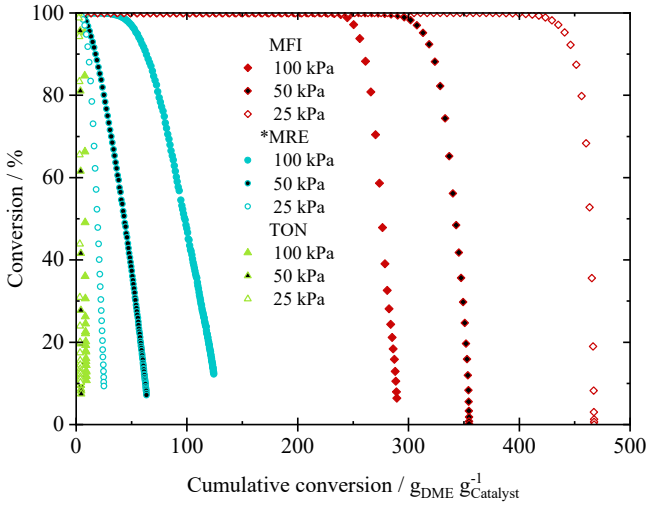
Fixed reaction parameters:
p_{DME} = 100 kPa
WHSV = 6.0 h^{-1} (MFI), 1.5 h^{-1} (*MRE), 0.3 h^{-1} (TON)

Influence of space velocity



T = 673 K
p_{DME} = 100 kPa

Influence of pressure



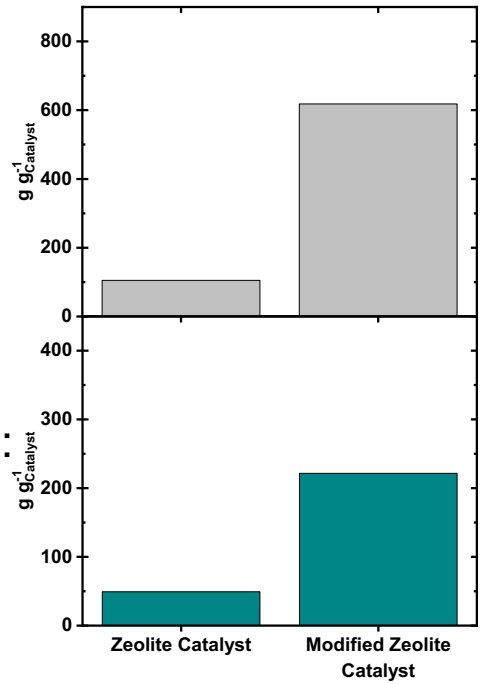
T = 673 K
WHSV = 6.0 h^{-1} (MFI), 1.5 h^{-1} (*MRE) and 0.3 h^{-1} (TON)

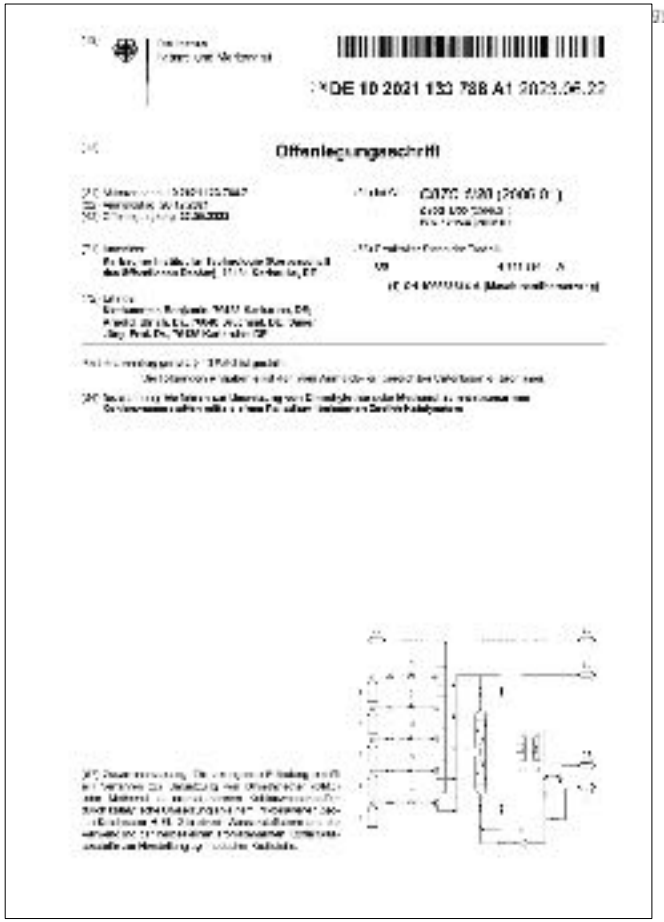
Suitable reaction conditions in the case of *MRE: T = 673 K, WHSV = 1.5 h^{-1}, p_{DME} = 100 kPa

Enhancing catalyst activity and stability be metal loading

Cumulative DME conversion:

Yield of C_{5-11} olefins:

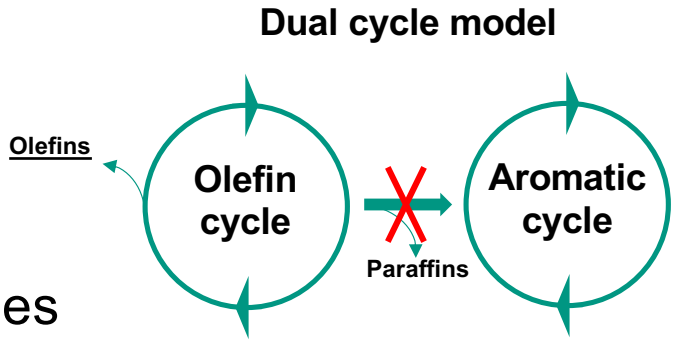




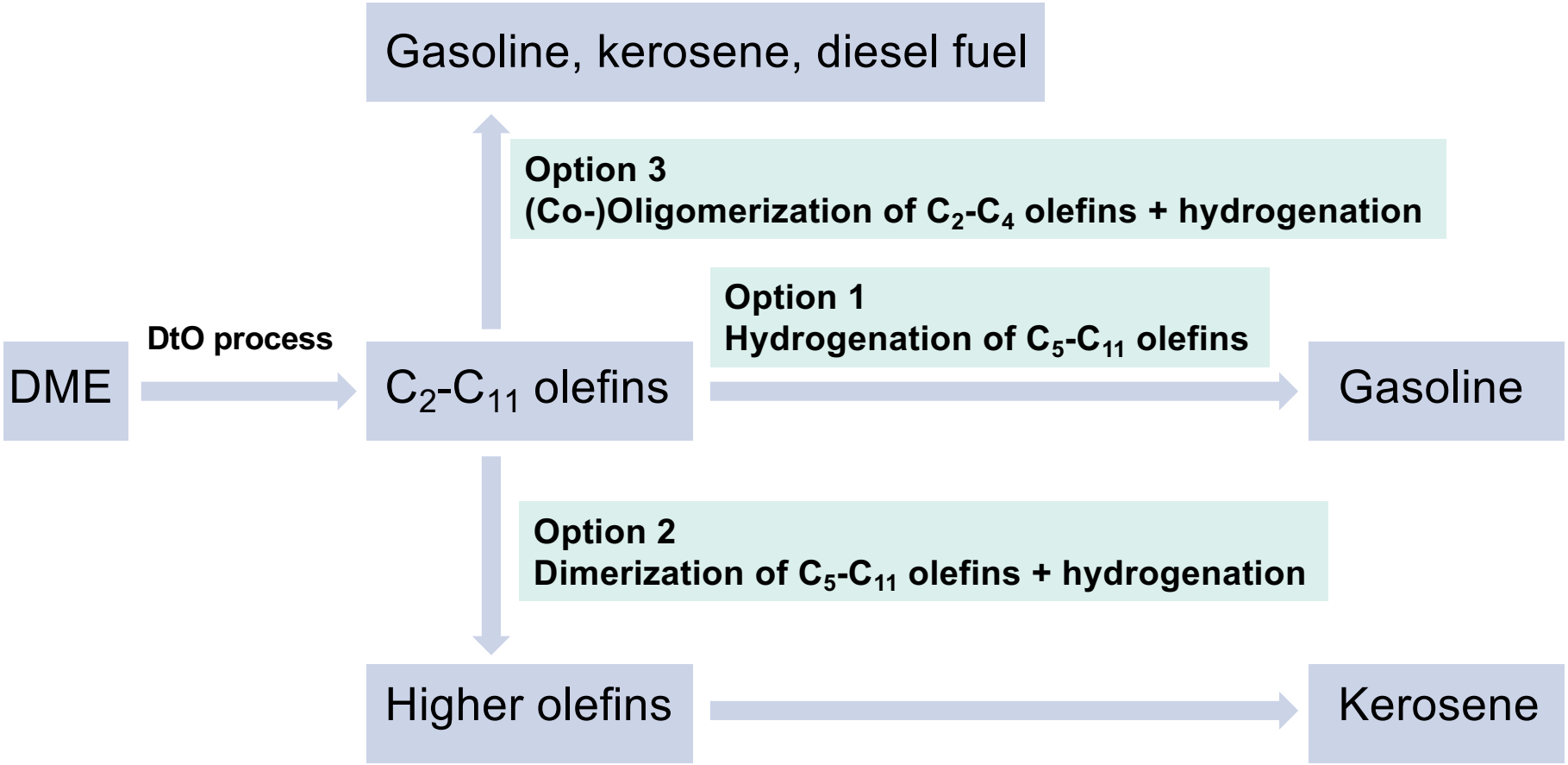
- Catalyst & process modification:
  - Metal loading on catalyst & co-feeding of H_2
  - Increase of catalyst activity and stability
  - High yield of C_{5-11} olefins remains

Reaction mechanism

- Dual cycle model is generally accepted
  - Formation of olefins in the olefin cycle
  - Formation of aromatics in the aromatic cycle
  - Formation of paraffins by interaction of both cycles
- Catalyst shape selectivity suppresses formation of aromatics
- Olefins become the dominating product species
- Manifold possibilities for further processing of the resulting olefins

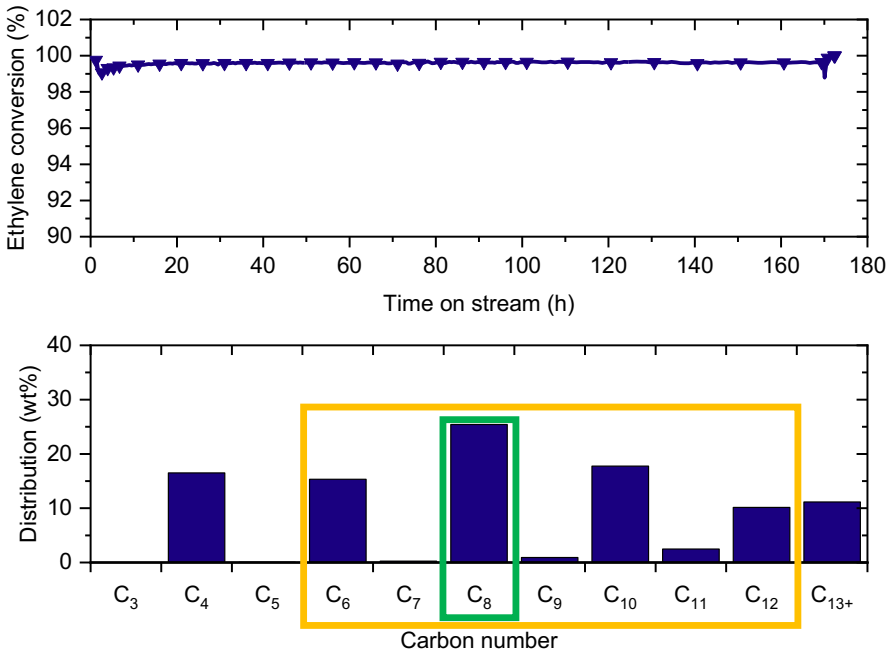


Modified DtO process and downstream olefin conversion



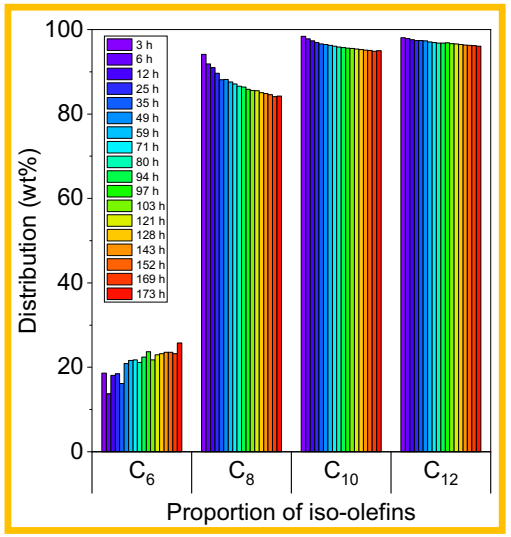
Option 3: (Co-)Oligomerization of C_2-C_4 olefins

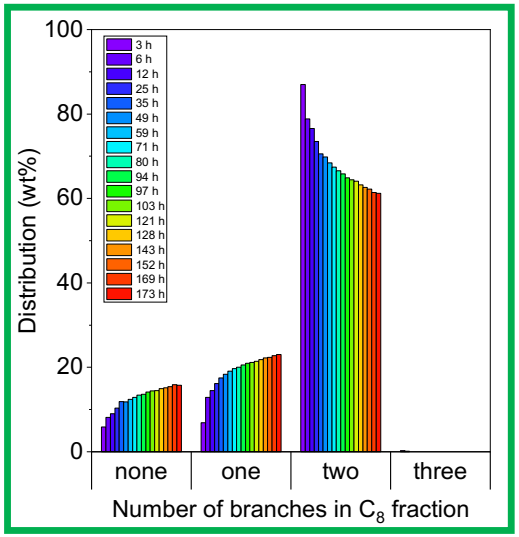
Ethylene oligomerization over 5% Ni-SiO_2-Al_2O_3



Reaction conditions: t = 173 h, T = 120 °C, $p_{ethylene}$ = 50 bar, WHSV = 8 h^{-1}

Isomers in the C_6-C_{12} range

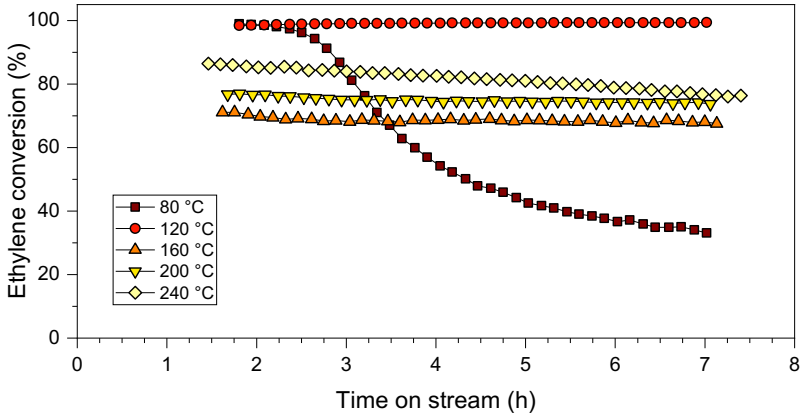


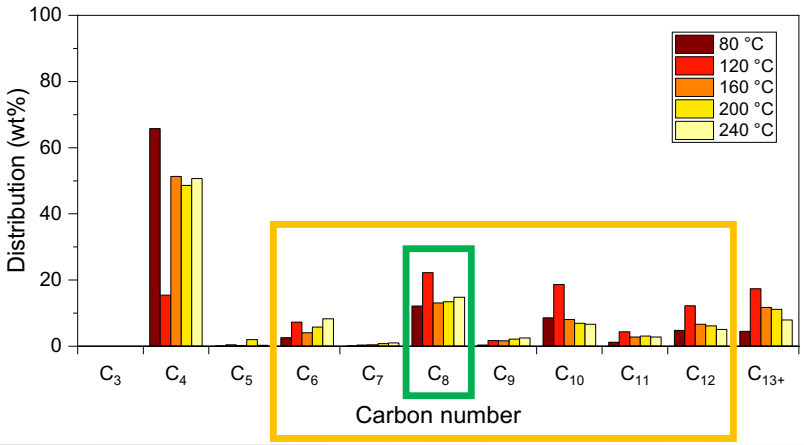


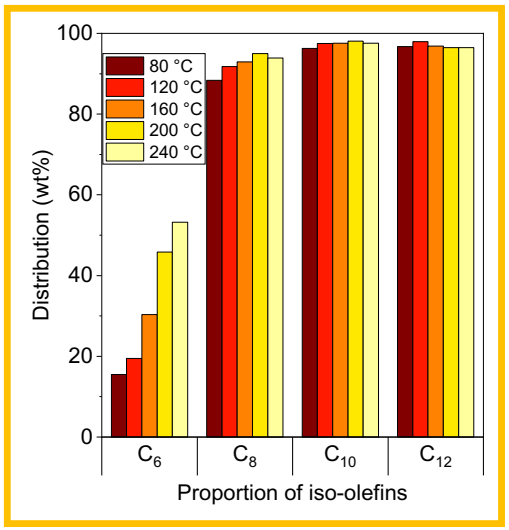
- High share of iso-olefins
- High share of double branched octanes
- Changes in branching over time on stream

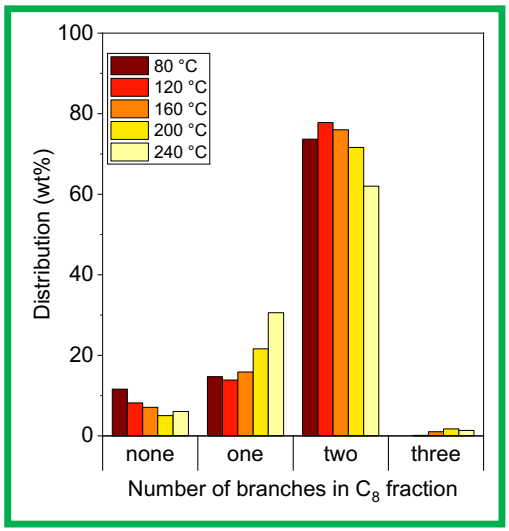
M. Betz, C. Fuchs, U. Arnold, T.A. Zevaco, J. Sauer, Production of hydrocarbon fuels by heterogeneously catalyzed oligomerization of ethylene: Tuning of the product distribution, *Biomass Bioenergy* **2022**, *166*, 106595. DOI: 10.1016/j.biombioe.2022.106595

Influence of temperature on ethylene oligomerization







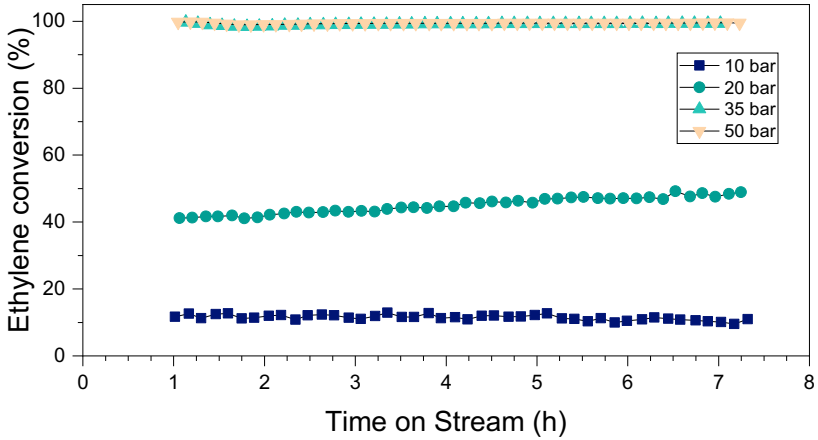


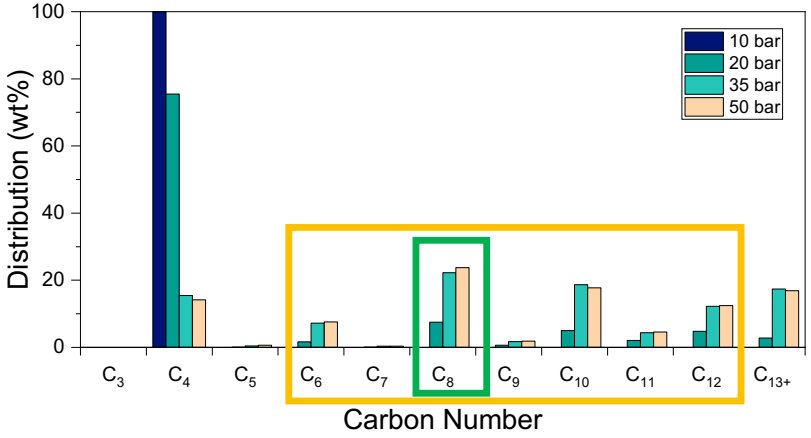
Fixed parameters:

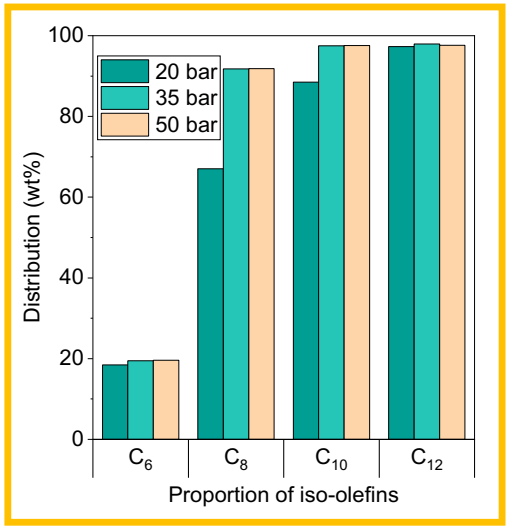
$p_{ethylene}$ = 35 bar, WHSV = 8 h^{-1}

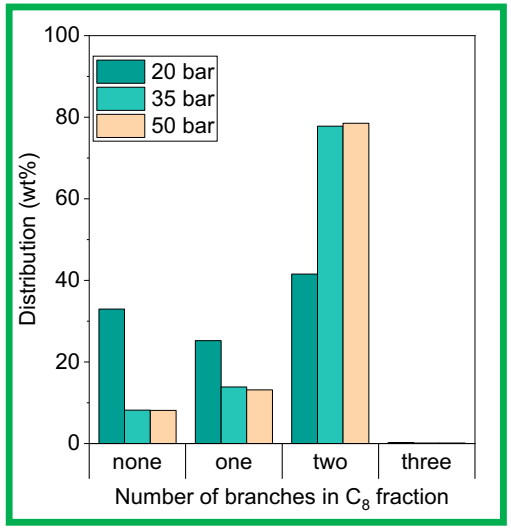
⇒ Favorable temperature: 120 °C

Influence of pressure on ethylene oligomerization









Fixed parameters:
T = 120 °C, WHSV = 8 h^{-1}

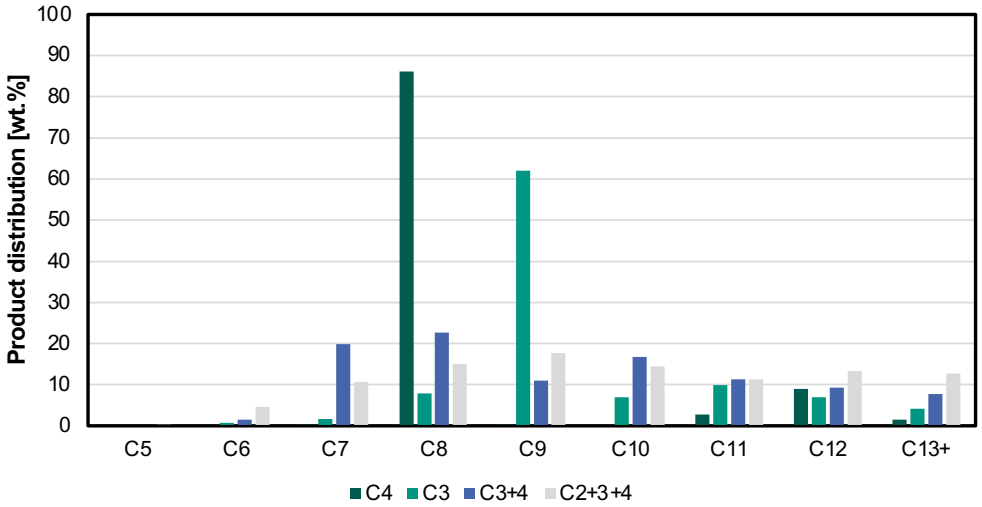
⇒ Favorable pressure: > 35 bar

Co-oligomerization of C_2-C_4 olefins

Parameters:
T = 120 °C, WHSV = 4 h^{-1}
$P_{olefins}$=32 bar

Catalyst:
SIRALOX 40 with 5 wt % Ni

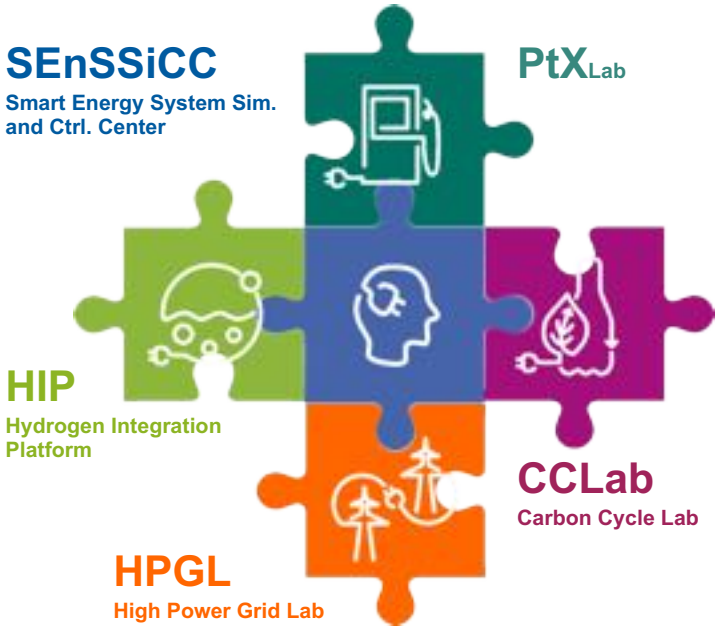
Typical product distributions

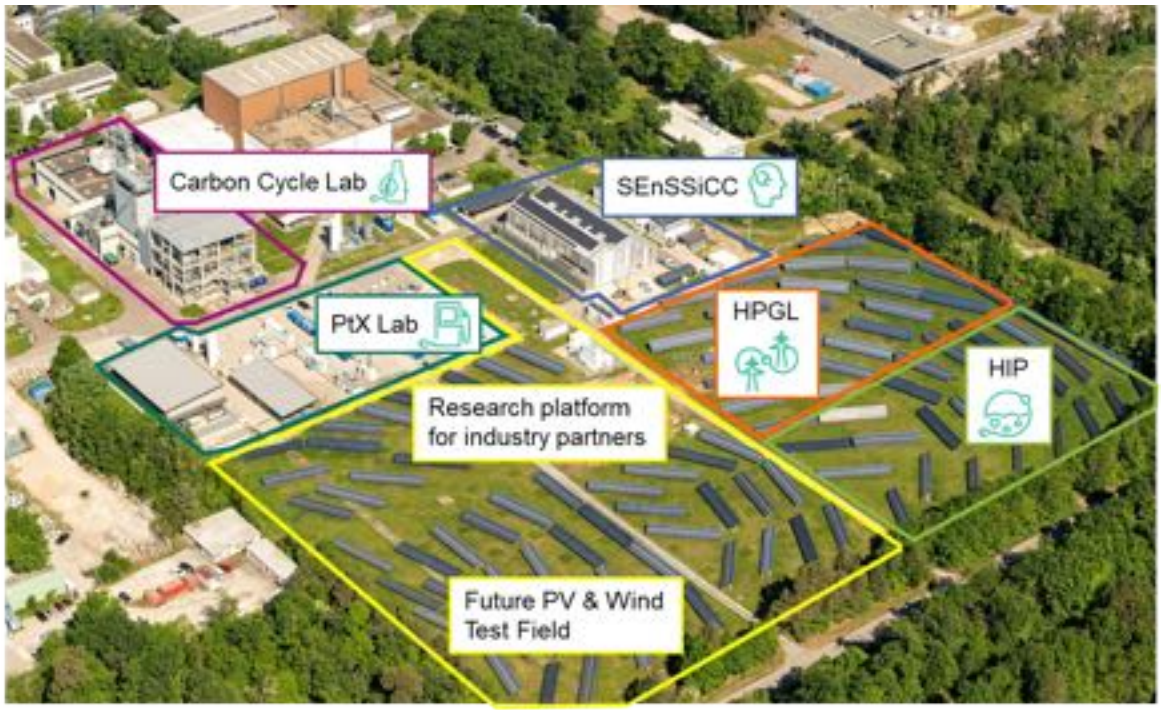


C. Fuchs, U. Arnold, J. Sauer, (Co-)Oligomerization of Olefins to Hydrocarbon Fuels: Influence of Feed Composition and Pressure, *Chem. Ing. Tech.* **2023**, *95(5)*, 651-657. DOI: 10.1002/cite.202200209

Energy Lab

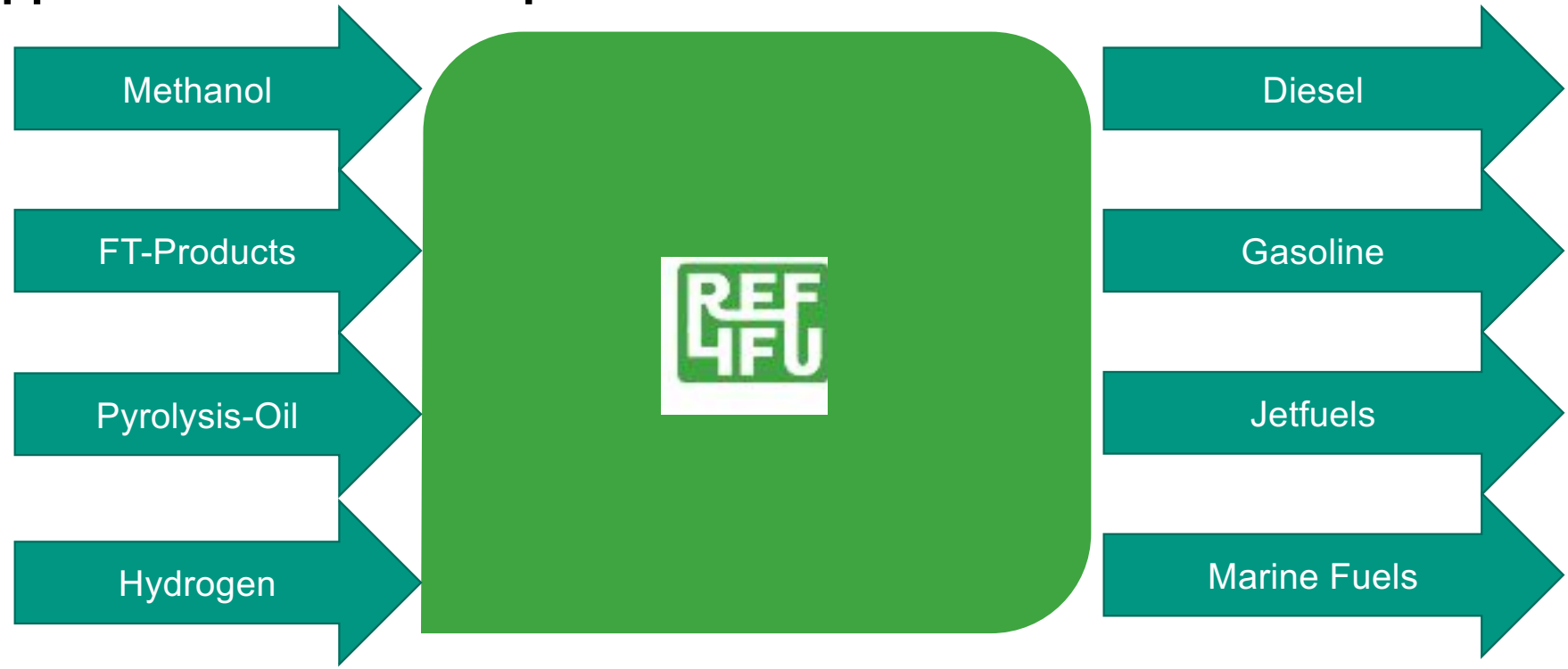
Flexible “plug-and-play platform” for coupled flows of energy - material - information



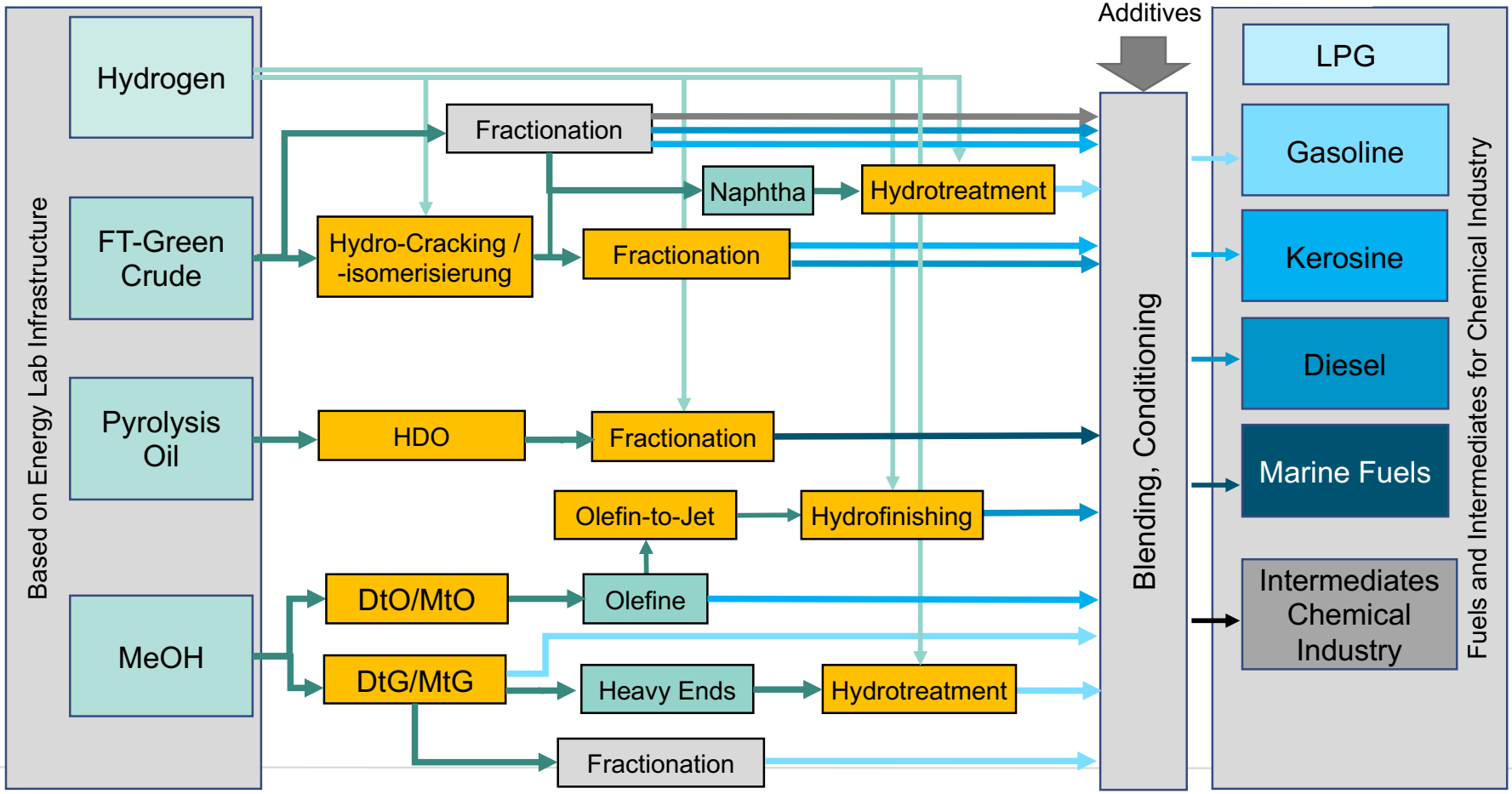


Energy Lab is the central research infrastructure of the Energy Research at KIT with the goal to respond in agile way to the highly dynamic challenges, exceptional and social boundary conditions of the Energy Transition.

Linking Energy Carriers with Applications from Transportation Sector



Value Chains in REF4FU



Summary & Outlook

- Closing the anthropogenic carbon cycle requires access to cheap carbon sources and hydrogen
- The „Methanol Economy“ is a concept for import of energy carriers and hydrogen equivalents which should be suitable for highly populated industrial countries
- The product quality of future fuels and chemicals has a tremendous impact on their environmental footprint
- Catalysis and Reaction Engineering supply us with tools to develop efficient conversion processes
- Incorporating the scale-up from TRL 2 to 5 into academic research opens up interesting new research topics

Acknowledgements

HELMHOLTZ Energy Research Programme MTET

Bundesministerium für Wirtschaft und Klimaschutz/ Projektträger Jülich
3D-PROCESS - Disruptive reactor concepts through additive manufacturing: From digital design to industrial implementation

Strategiedialog Automobilwirtschaft BW und Ministerium für Verkehr BW
reFuels – Rethinking fuels

Bundesministerium für Digitales und Verkehr / Fachagentur Nachwachsende Rohstoffe
Renewable Fuels from green refineries of the future

Bundesministerium für Bildung und Forschung / Projektträger Jülich
Kopernikus Project Power-to-X