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Processes for Advanced Fuel Production from Biomass

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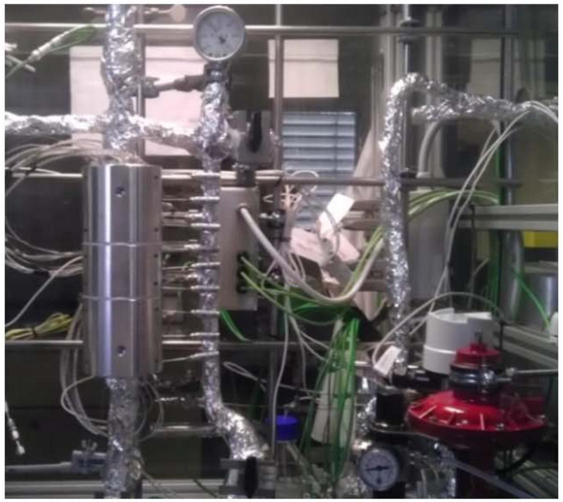
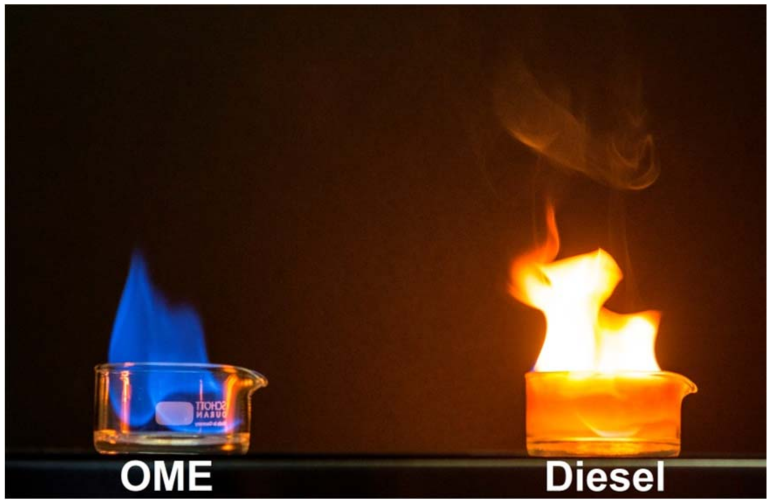
80. Jahrestagung der DPG und DPG-Frühjahrstagung, Regensburg, 6. - 11. März 2016

Institute of Catalysis Research and Technology (IKFT)





Content

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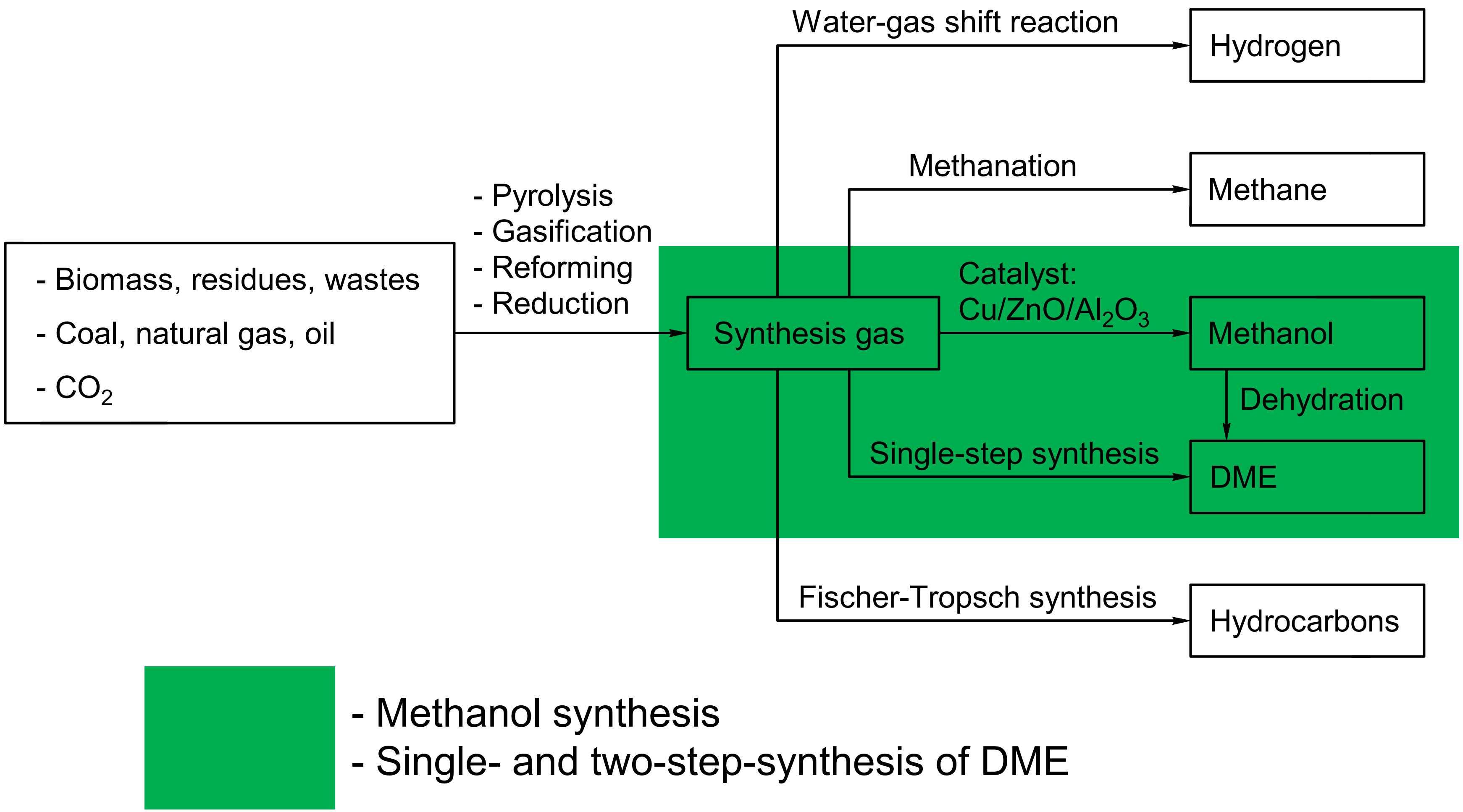
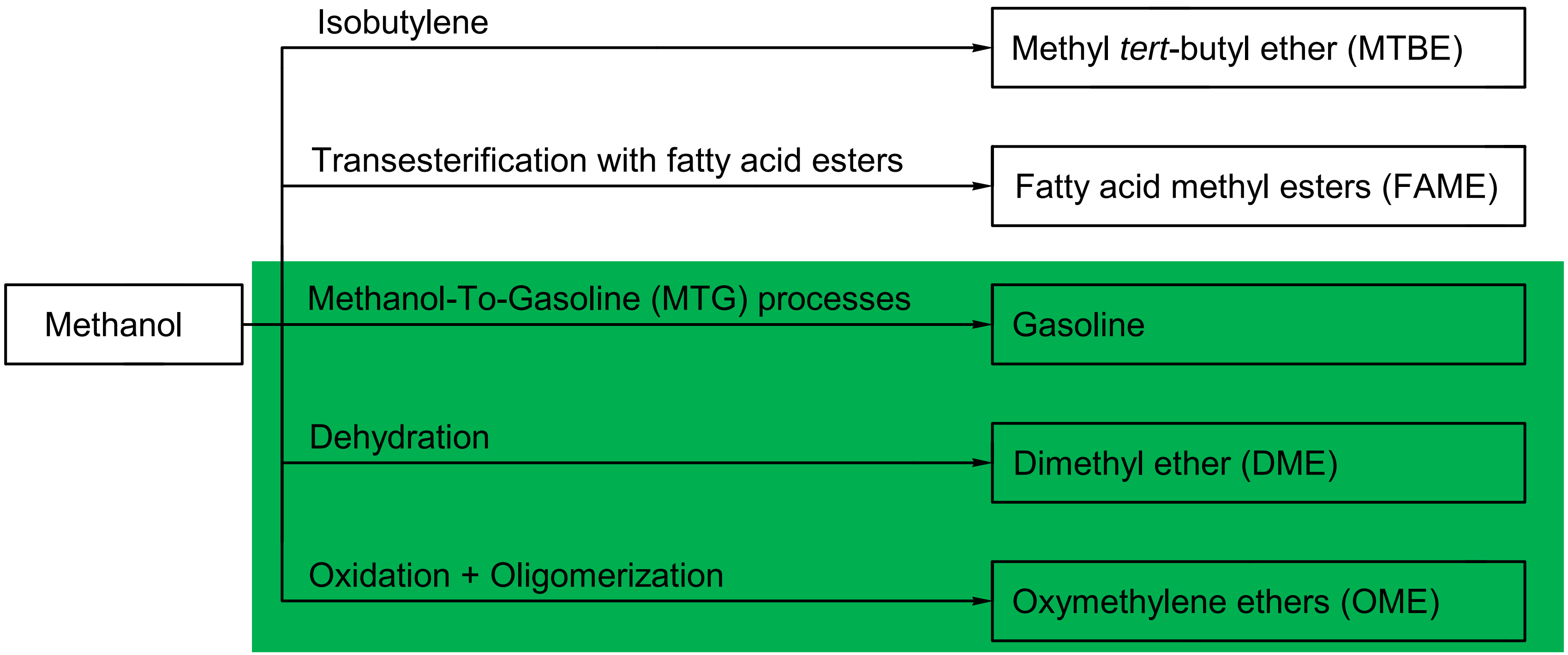
Synthesis of (bio)fuels from various resources: The syngas platform



Synthesis of fuels and fuel additives from (bio)methanol



Legal framework (I)

- From 2015 on: Mandatory reduction of greenhouse gases via biofuels (“Gesetz zur Änderung der Förderung von Biokraftstoffen“, 2009) in Germany:
  - 2015/16: “Klimaschutzquote“ 3.5%
  - 2017/18/19: 4.0%
  - From 2020 on: 6.0%
- From 2017 on: Only biofuels enabling a reduction of greenhouse gases above 50%, with regard to fossil fuels, will be credited (“Biokraftstoff-Nachhaltigkeitsverordnung“, 2009)
- Proposal of the European Commission to change the “Directive 2009/28/EC on the promotion of the use of energy from renewable sources” not adopted yet:
  - Consideration of “Indirect Land-Use-Changes” ILUC
  - Upper limits for first generation biofuels
- …

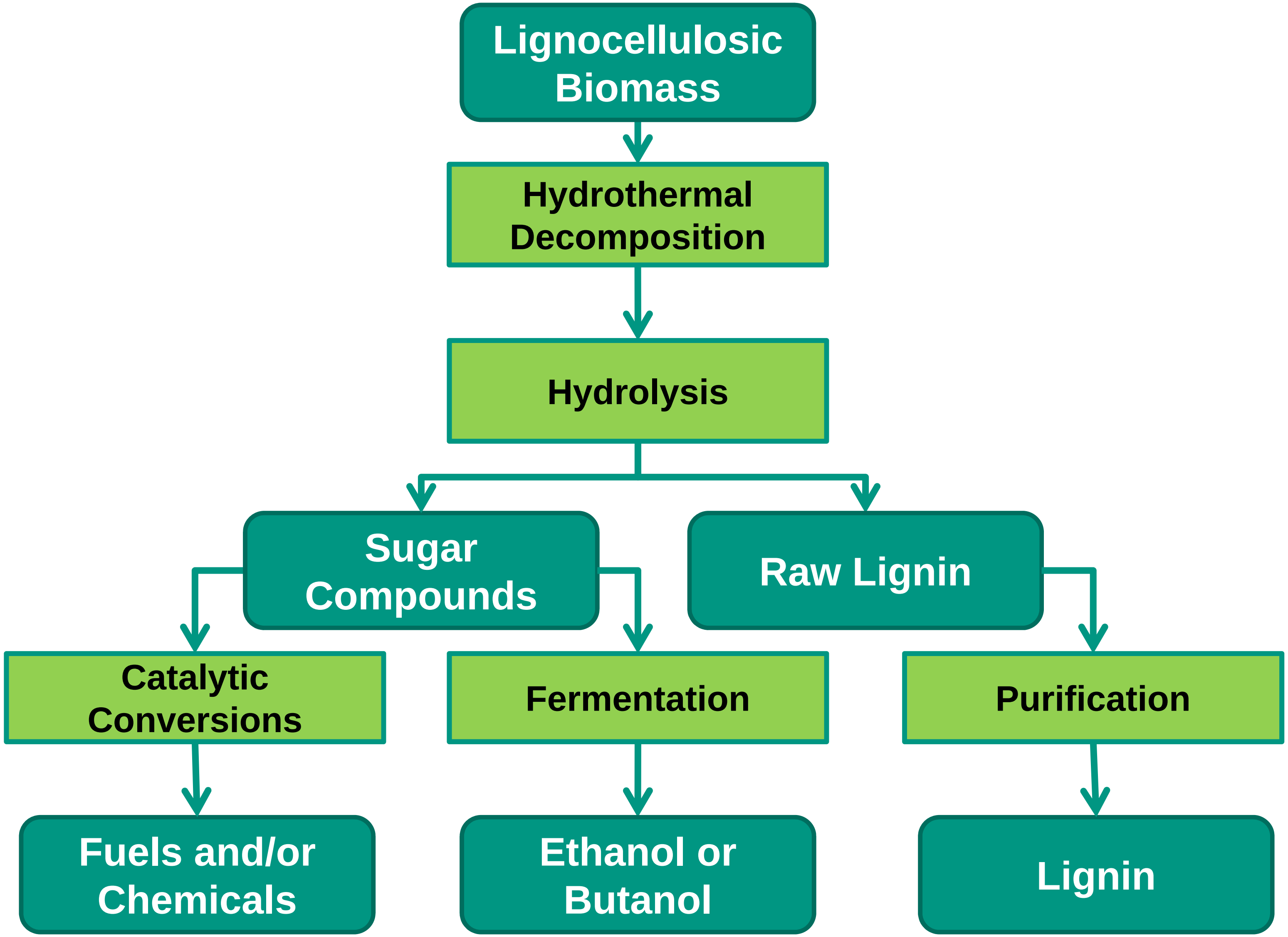
Legal framework (II)

- Gasoline: DIN EN 228
  - ROZ > 95
  - Density 720 – 775 kg/m³
  - Aromatic compounds < 35% (v/v)
  - Oxygen content < 3.7% (w/w)
  - Ethers (5 or more C-atoms) < 22% (v/v)
  - Other oxygen containing compounds < 15% (v/v)

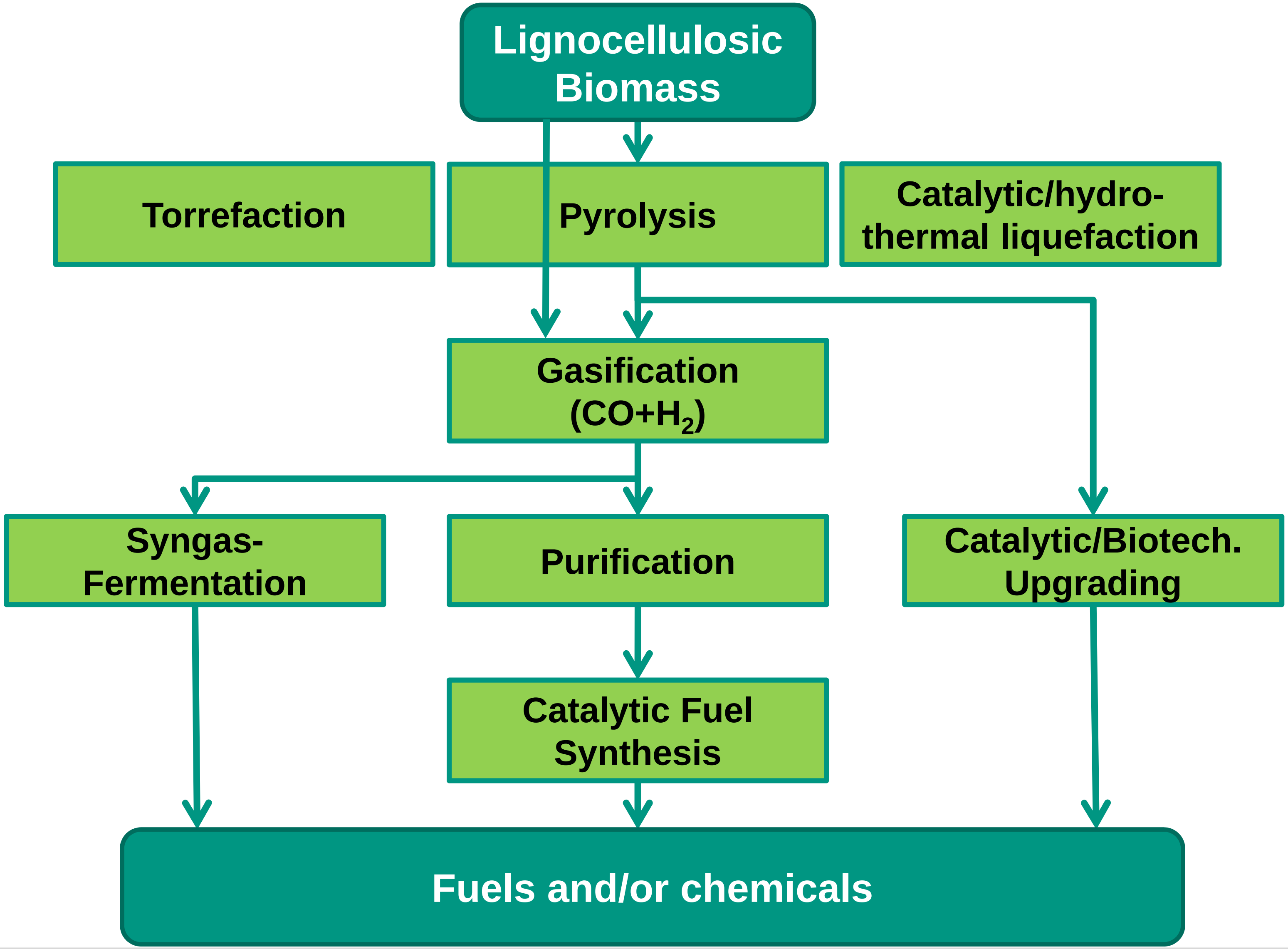
- Diesel fuel: DIN EN 590
  - Cetane number > 51
  - Density 820 – 845 kg/m³
  - Boiling range 250 °C (65%) … 360 °C (95%)
  - No limit for O-content so far

Content

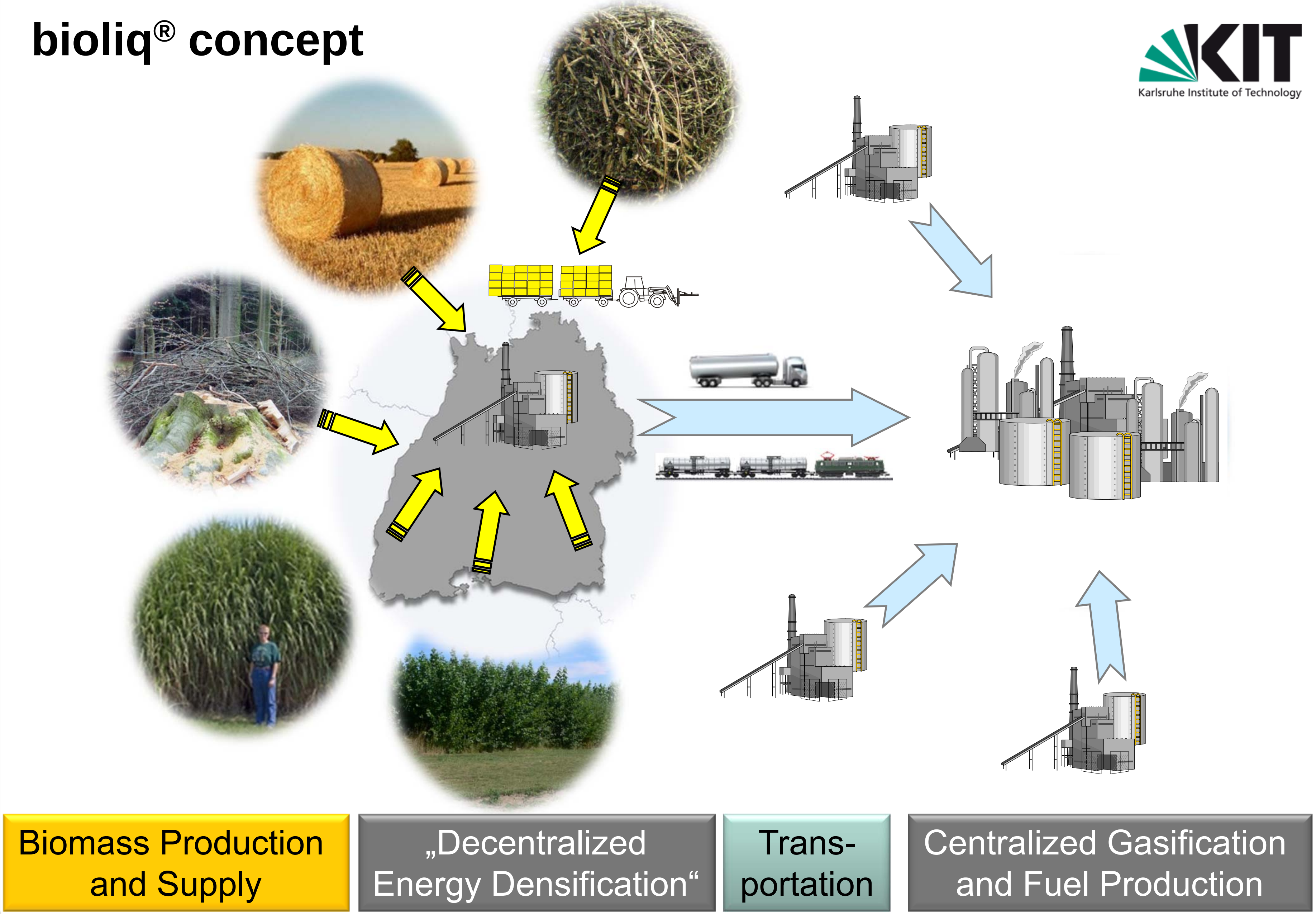
The Lignocellulose Hydrolysis Value Chains



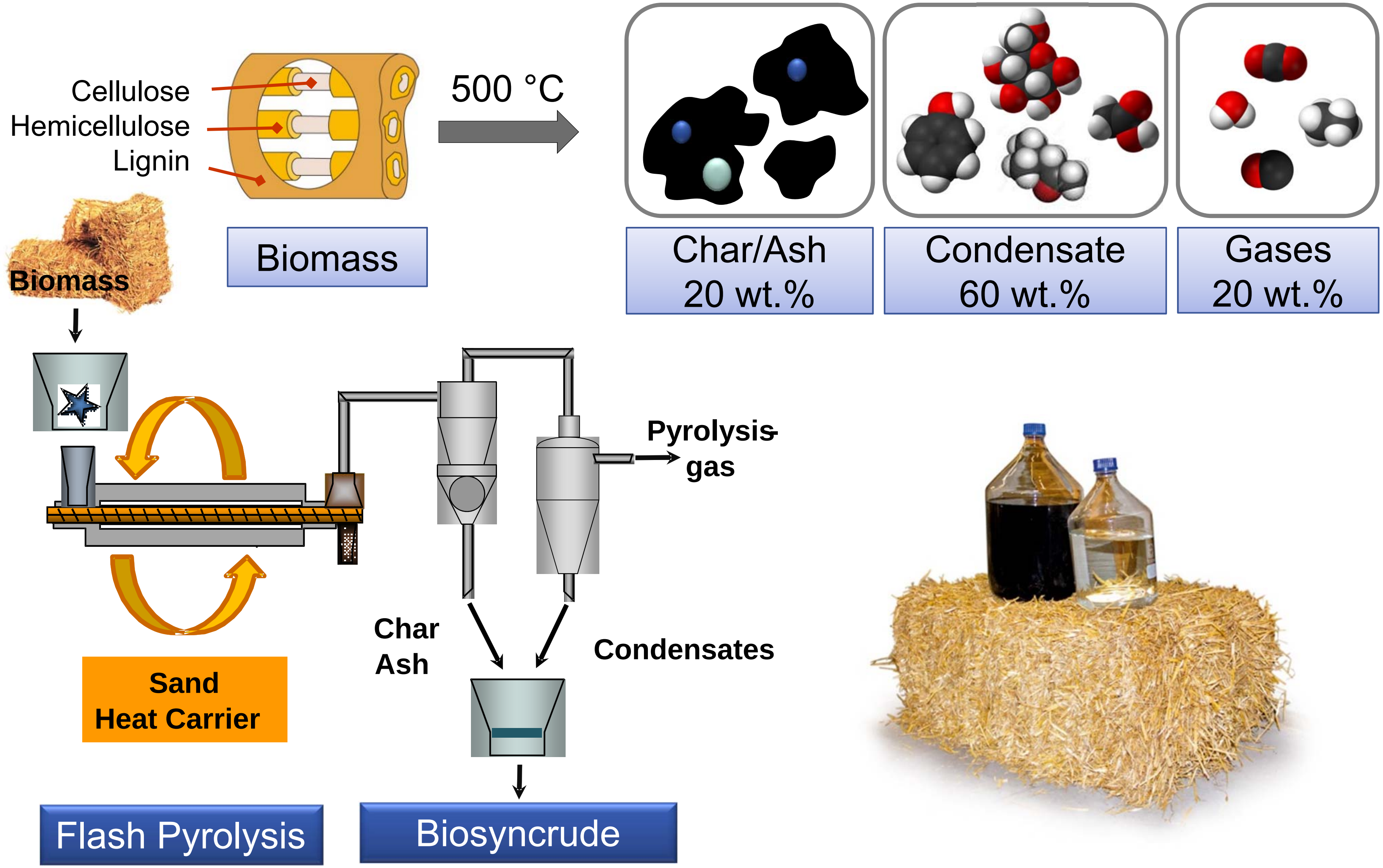
The thermochemical BtL value chain



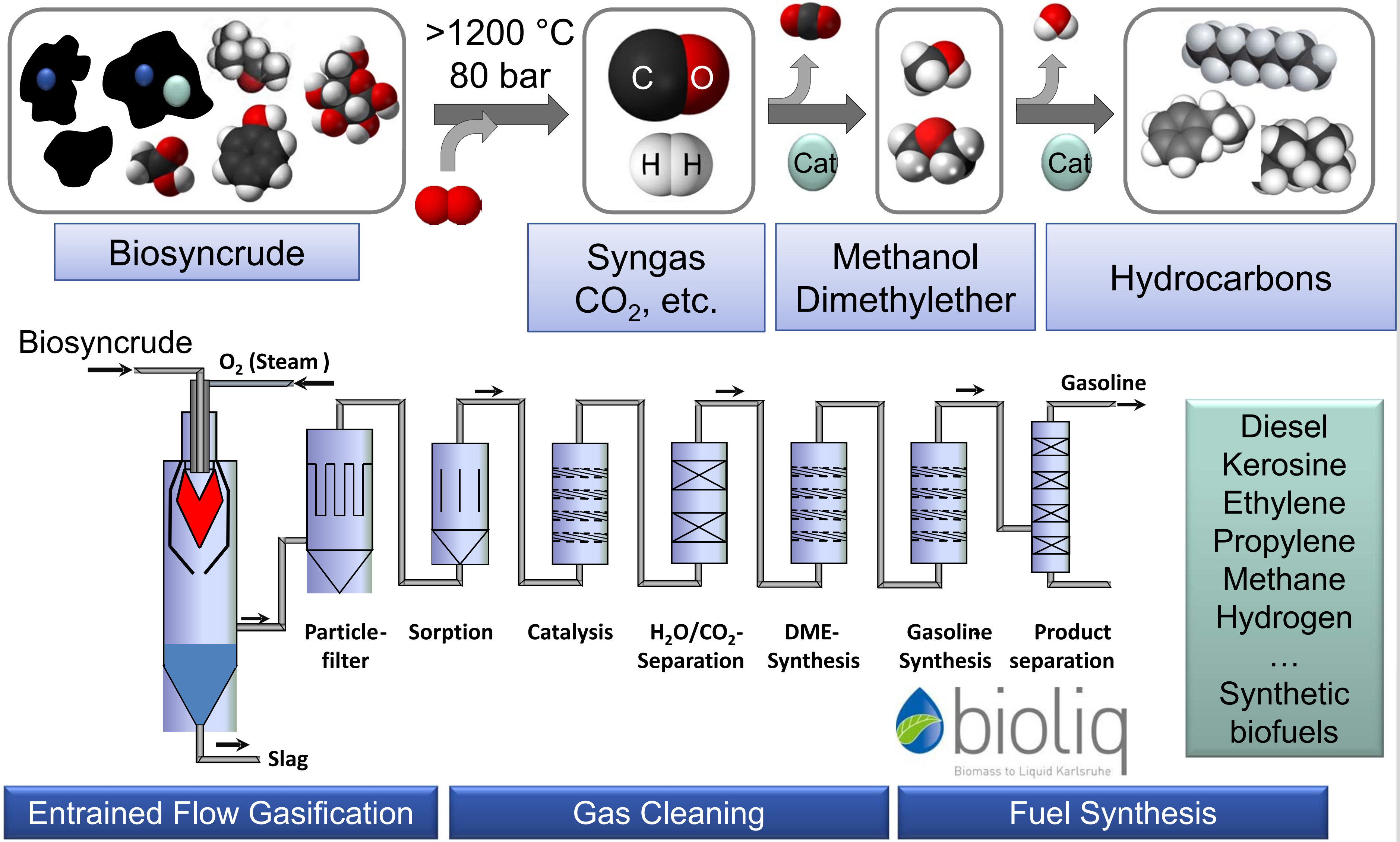
bioliq® concept



Chemistry and technology – decentralized



Chemistry and technology – centralized



bioliq® pilot plant at KIT

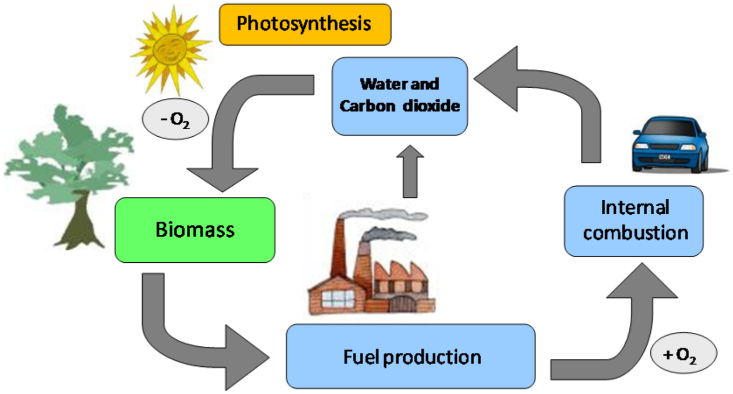
Fast Pyrolysis Biosyncrude-Production	Gasification Syngas-Production	Gas-Cleaning and Fuel Synthesis

Technical Validation & **Platform for Research**

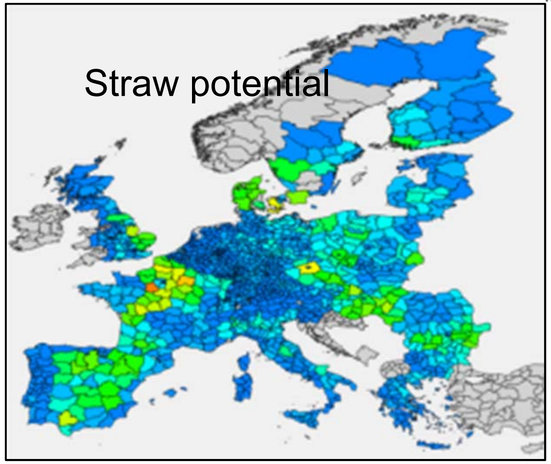
- Mass and energy balances
- Scale-up
- Stability and availability
- Production costs

- Improved insights in processes
- Optimization and development
- Diagnostics, modelling, simulation
- New applications of products

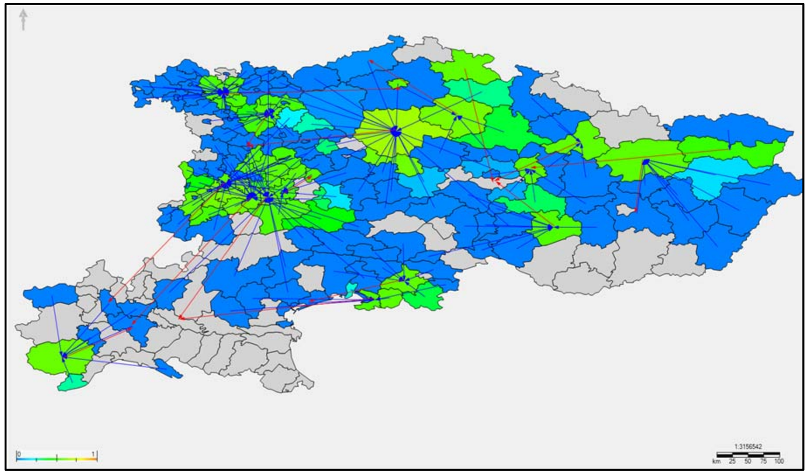
Systems analysis



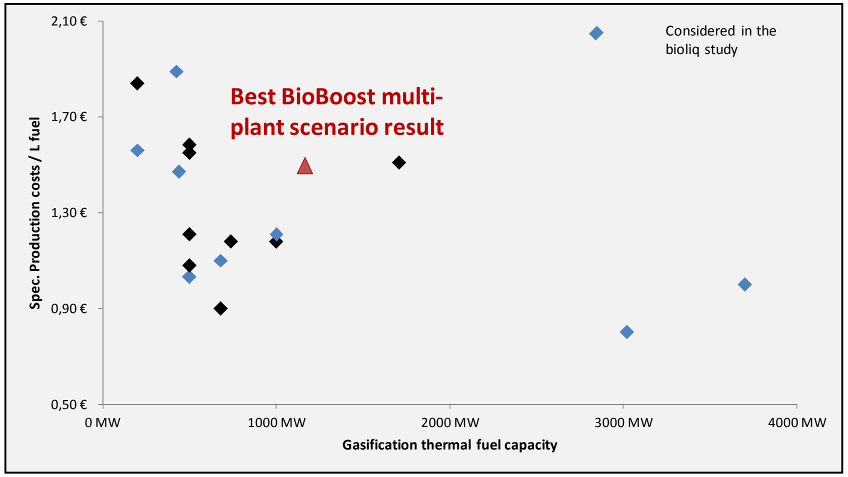
Life Cycle Assessment,
CO_2 reduction potential > 84 %



Sustainable resource potential



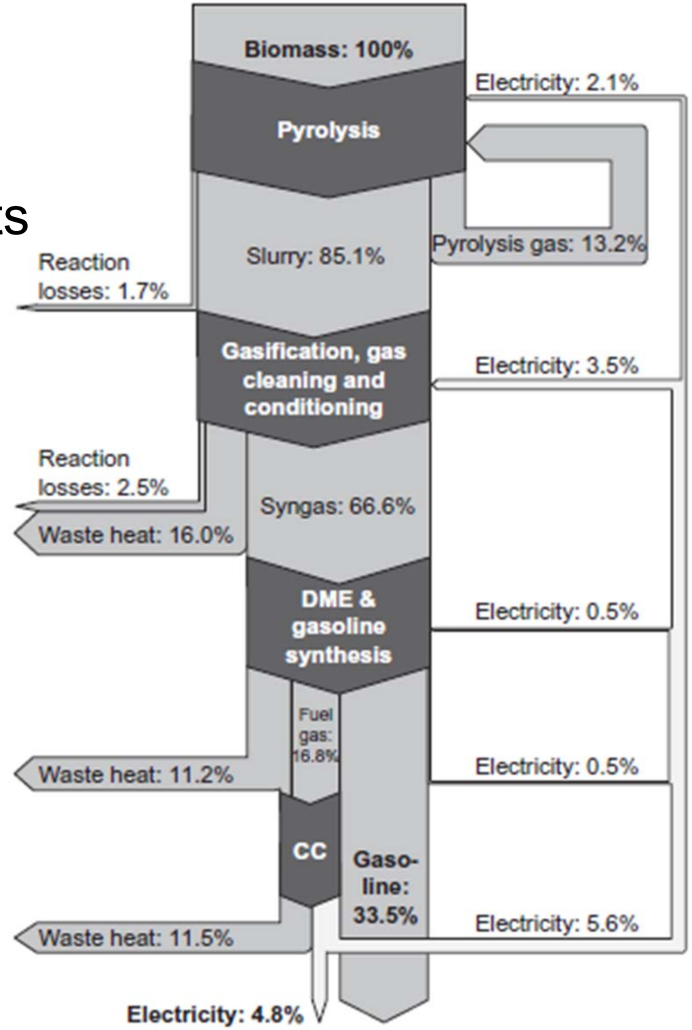
Simulation of transport/
conversion scenarios



Production costs @
process efficiencies of 39 ±6 %

Systems analysis

- Biomass potential and availability
  - Regional
  - National
  - EU 27+Switzerland NUTS 3 level
- integrated vs. central/de-centralized concepts
  - Plant configurations
  - Logistic models
  - Site optimization
- http://iung.neogis.pl/navigator/
- Techno-economic assessment (1-1,8 €/kg)
- Life cycle assessment
- Comparative studies to other processes
  - Studies: FNR IER Freiberg, Wuppertal Institute, IFEU, DENA………



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DME as an alternative diesel fuel

	DME	Diesel	Methanol	Ethanol	Methyl-*tert*-butyl-ether (MTBE)	Gasoline
Boiling point (°C)	−25	160-360	64	78	55	38-210
LHV (kJ/g)	27.6	41.7	20.0	26.9	38.3	43.5
Octane number (RON)	–	–	108.7	108.6	109	>95
Cetane number	>55	>51	–	–	–	–
Sulfur content (ppm)	0	<10	0	0	0	<10

=> High cetane number, similar to diesel fuel

DME as an alternative diesel fuel

- **Properties**
  - Colorless, flammable gas
  - Readily liquefiable
  - Non-toxic, non-carcinogenic and non-mutagenic
- **Advantages:**
  - Clean combustion (soot-free, reduced NO_x-/SO_x emissions)
  - No sophisticated engine modification necessary
  - No elaborate modification of fuel supply infrastructure
- **Challenges:**
  - Lower heating value
  - Low fuel viscosity
  - Costs (e.g. adaption of sealing materials)

Isuzu DME Diesel Truck

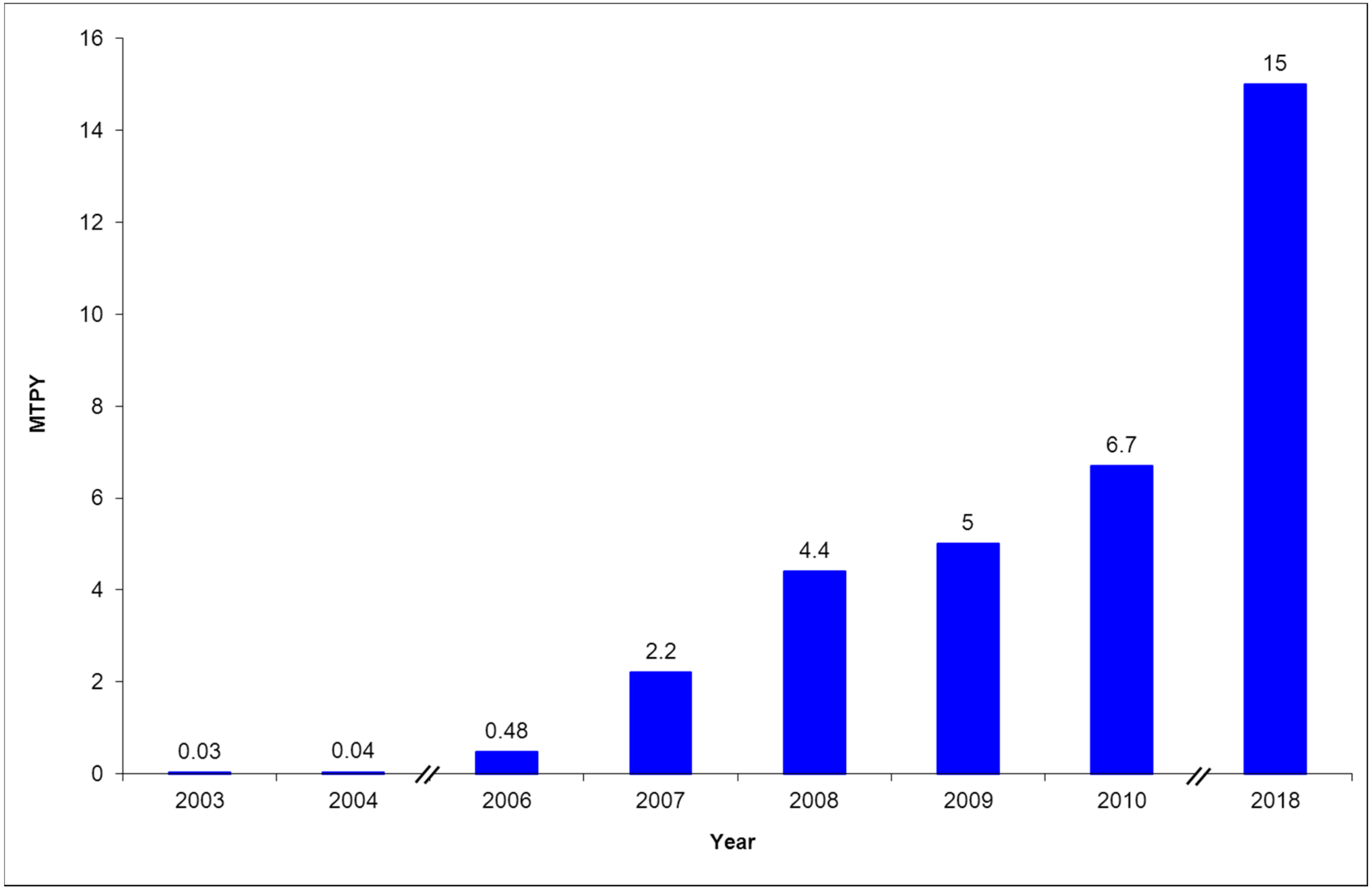
Nissan NTSL DME Diesel Truck

SAIC DME Diesel Bus

Volvo Diesel Trucks

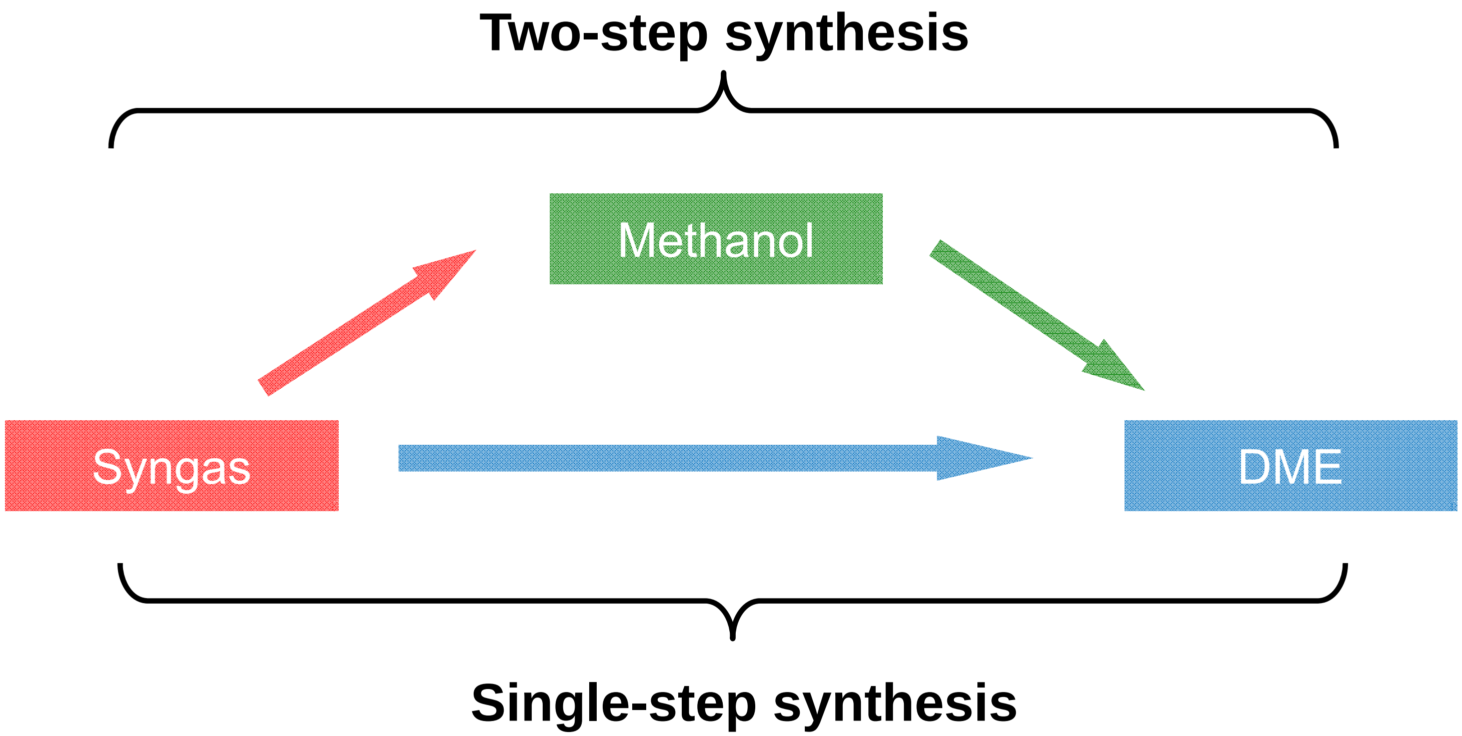
T.A. Semelsberger, R.L. Borup, H.L. Greene, J. Power Sources 2006, 156, 497-511.

Global DME production capacity



J.A. Taupy, DME Industry and Association Overview,
4th International DME Conference. Stockholm, Sweden, September 6-9, 2010.

DME synthesis



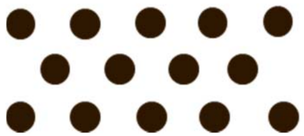
$$4\,H_2 + 2\,CO \longrightarrow 2\,CH_3OH$$
$$2\,CH_3OH \longrightarrow CH_3OCH_3 + H_2O$$
$$CO + H_2O \longrightarrow CO_2 + H_2$$

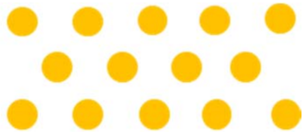
$$3\,H_2 + 3\,CO \longrightarrow CH_3OCH_3 + CO_2$$

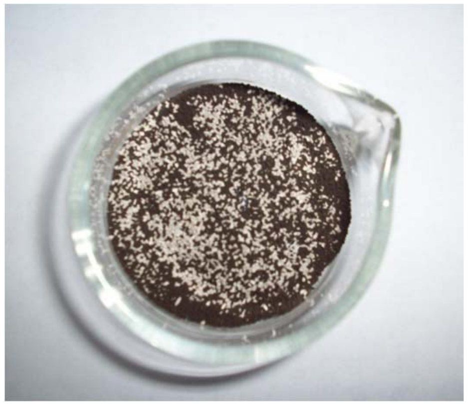
Catalyst systems for single-step synthesis

Syngas → Hydrogenation → Methanol → Dehydration → DME

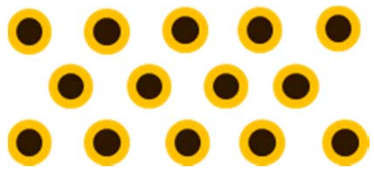
Catalyst: $Cu/ZnO/Al_2O_3$ γ-Aluminium oxide or zeolite







Admixed systems or **Bifunctional catalysts**



R. Ahmad, D. Schrempp, S. Behrens, J. Sauer, M. Döring, U. Arnold, Fuel Process. Technol. 2014, 121, 38-46.

Oxymethylene dimethyl ethers (OMEs) as fuels and fuel additives

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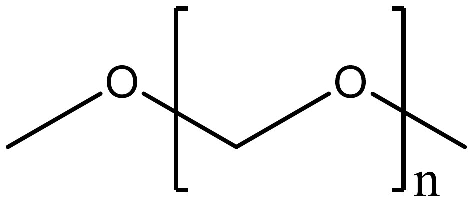
- **Why oxymethylene ethers?**
  - Absence of carbon-carbon bonds => Soot-free combustion
  - Similar vapour pressure as conventional diesel
  - unlimited miscibility with diesel
  - Non-toxic, non-corrosive

Properties	OME 3	OME 4	OME 5	Diesel [EN 590]
Molecular weight [g/mol]	136	166	196	–
Density [kg/l, 20 °C]	1.03	1.07	1.11	0.82-0.84 (15 °C)
Oxygen content [wt.%]	47.0	48.1	48.9	–
LHV [MJ/kg]	19.6	19.0	18.5	42.6
LHV [MJ/l]	20.2	20.3	20.5	35.3
Autoignition point [°C]	235	235	240	~220
Flash point [°C]	54	88	115	>55
Boiling point [°C]	156	202	242	170-390
Cetane number	124	148	180	>51

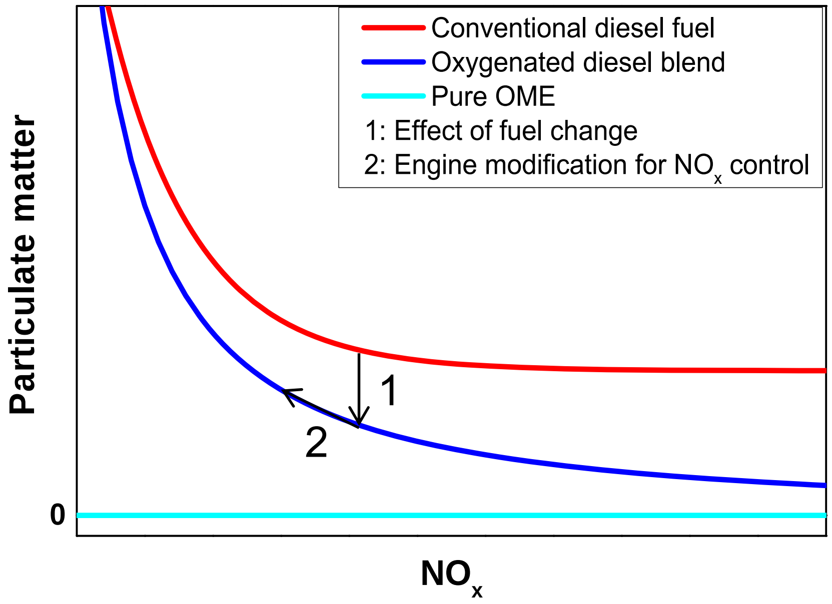


B. Lumpp, D. Rothe, C. Pastötter, R. Lämmermann, E. Jacob, MTZ - Motortechnische Zeitschrift 2011, 72, 198-202.

Why oxymethylene ethers?

NO_x-particle-trade-off:

- OME: Soot-free combustion
- Blend: 20% OME
  → soot decreases about 50%
- Possibility to reduce the charge cycle
  → decreases NO_x



- M. Härtl, P. Seidenspinner, G. Wachtmeister, E. Jacob, MTZ - Motortechnische Zeitschrift 2014, 75, 68-73.
- A.S. Cheng, R.W. Dibble, B.A. Buchholz, SAE Special Publications, Vol. 1716, 47-58, SAE Paper 2002-01-1705, 2002.

Combustion of OME and Diesel

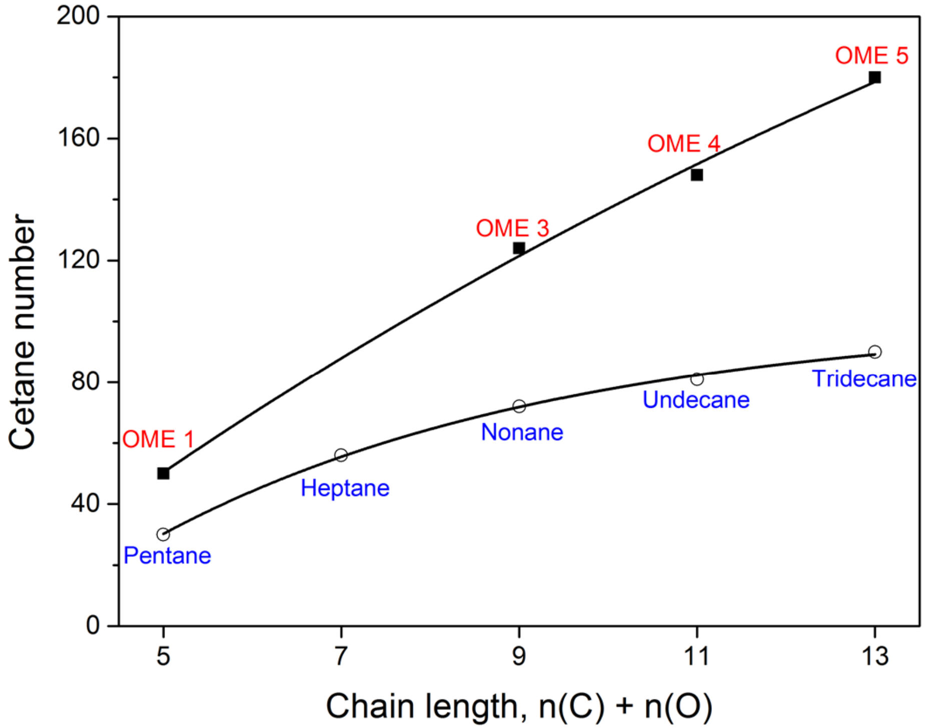
From DME to POMs – which chain length is appropriate?

- Most suitable OMEs for fuel applications: OME-3, OME-4 and OME-5
- Polymeric OMEs: Commercially available plastics (POMs)

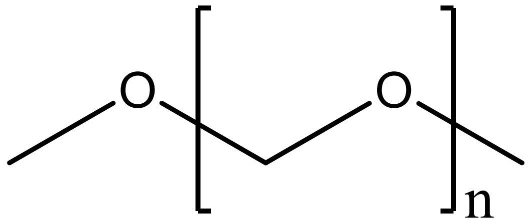
DME:	CH_3-O-CH_3
OME-1:	CH_3-O-CH_2O-CH_3
OME-2:	CH_3-O-CH_2OCH_2O-CH_3
OME-3:	CH_3-O-CH_2OCH_2OCH_2O-CH_3
OME-4:	CH_3-O-CH_2OCH_2OCH_2OCH_2O-CH_3
OME-5:	CH_3-O-CH_2OCH_2OCH_2OCH_2OCH_2O-CH_3
OME-6:	CH_3-O-CH_2OCH_2OCH_2OCH_2OCH_2OCH_2O-CH_3
OME-6+n:	CH_3-O-CH_2OCH_2OCH_2OCH_2OCH_2OCH_2O$(CH_2O)_n$-CH_3

(Re)Investigation of fuel properties with high purity OME samples

- OME synthesis from dimethoxymethane and trioxane
- Purification by rectification: 99.9+% purity
- Determination of fundamental fuel parameters, e.g. cetane numbers:



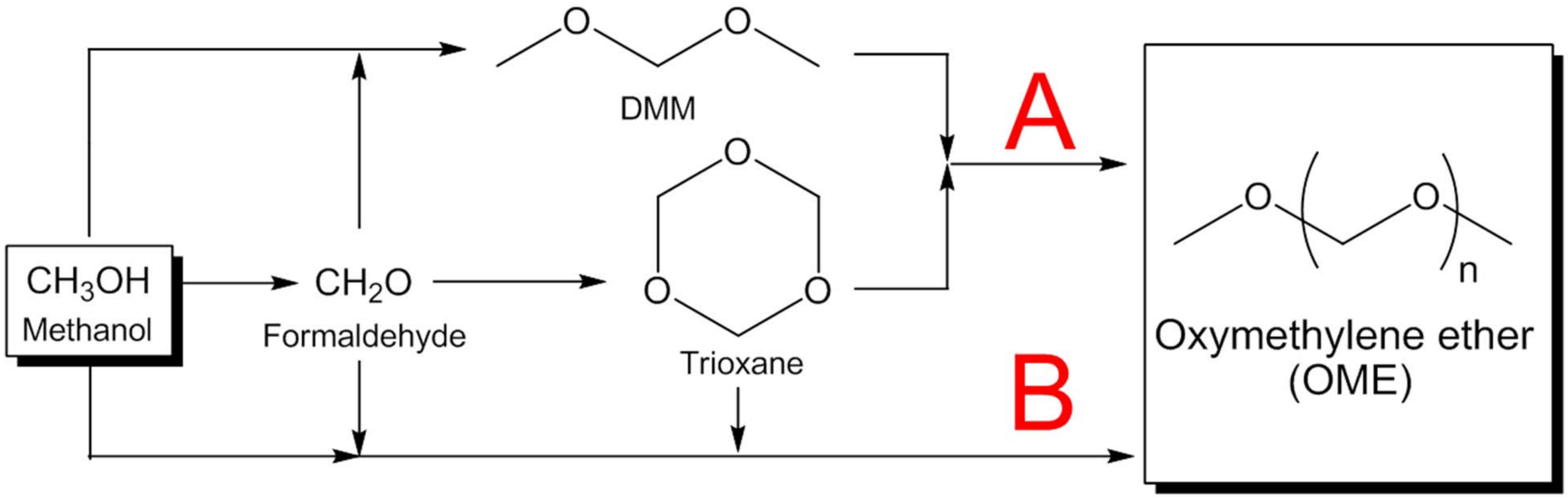
OME:



n = 1-5

- L. Lautenschütz, Dissertation, University of Heidelberg, 2015.
- L. Lautenschütz, D. Oestreich, P. Seidenspinner, U. Arnold, E. Dinjus, J. Sauer, Fuel 2016, 173, 129-137.

Synthesis strategies for OMEs



- Pathway A is on an advanced stage of development
- Pathway B is the most desirable, since it starts directly from the low-cost educts methanol and formaldehyde
- But: a series of byproducts is also formed

- J. Burger, M. Siegert, E. Ströfer, H. Hasse, Fuel 2010, 89, 3315-3319.
- N. Schmitz, F. Homberg, J. Berje, J. Burger, H. Hasse, Ind. Eng. Chem. Res. 2015, 54, 6409-6417.
- N. Schmitz, J. Burger, H. Hasse, Ind. Eng. Chem. Res. 2015, 54, 12553-12560.

World-wide activities in the field of OMEs

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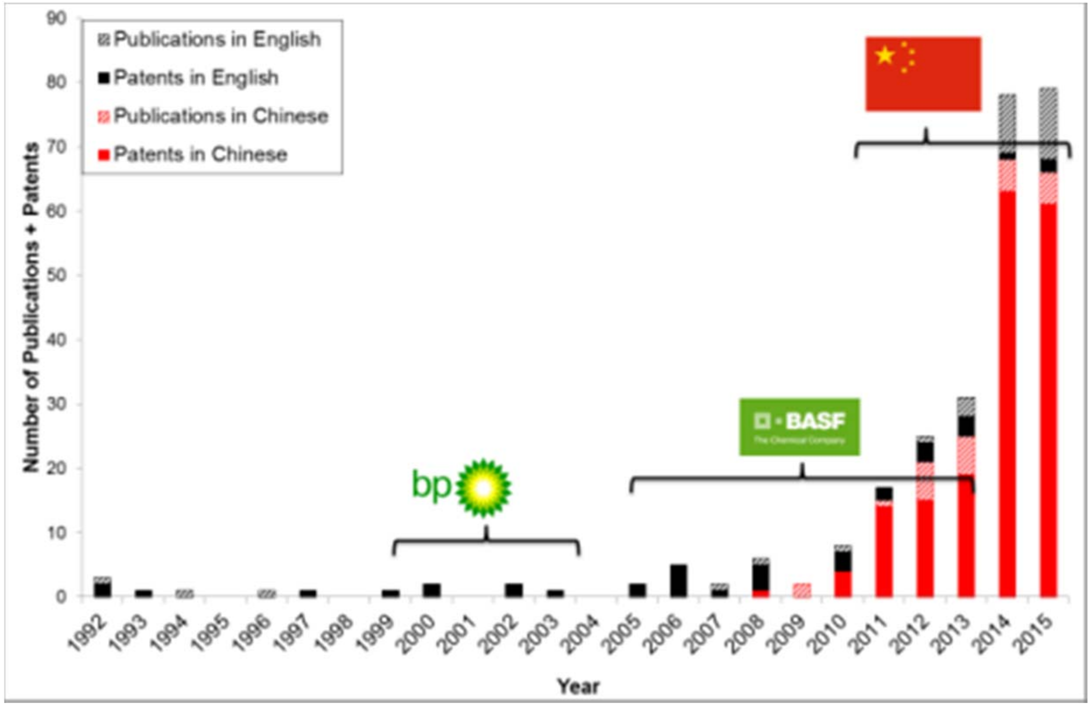
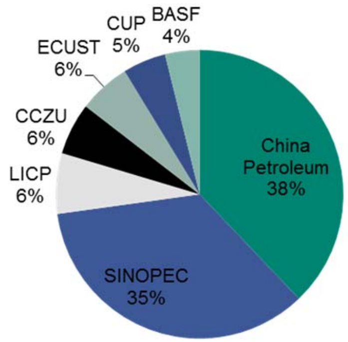


Companies



LICP: Lanzhou Institute of Chemical Physics Chinese Academy of Sciences, China

CCZU: Changzhou University, China

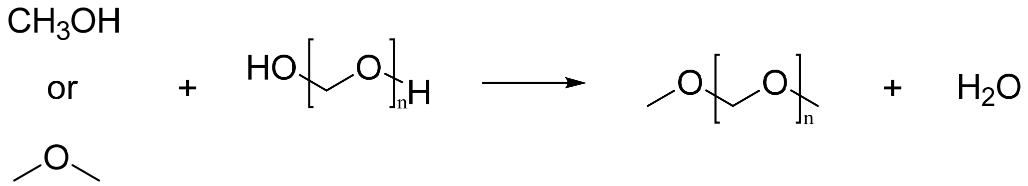
ECUST: East China University of Science and Technology, China

CUP: China University of Petroleum (Huadong)

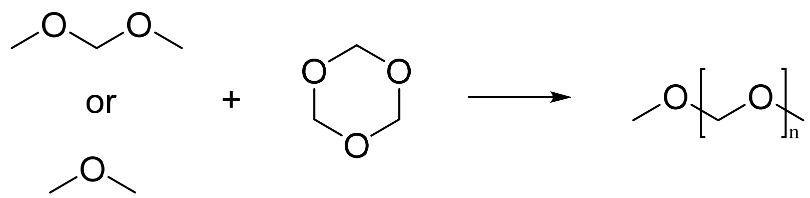
Activities in China are rapidly increasing

Synthesis routes at KIT-IKFT

- **Aqueous route:**



- **Anhydrous route:**

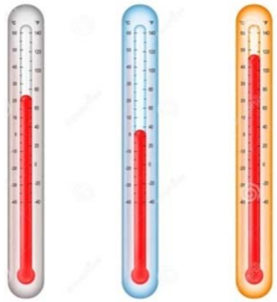


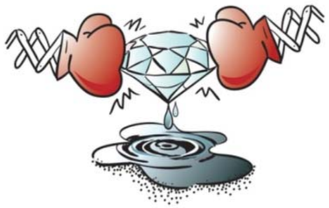
- **Lab-scale catalyst and parameter screening**
  - Batchwise reactions in autoclaves
  - Continuously operating lab plants

Scope of the work

- Catalyst screening

- Parameter study: Variation of temperature, pressure, space velocity, feed ratio





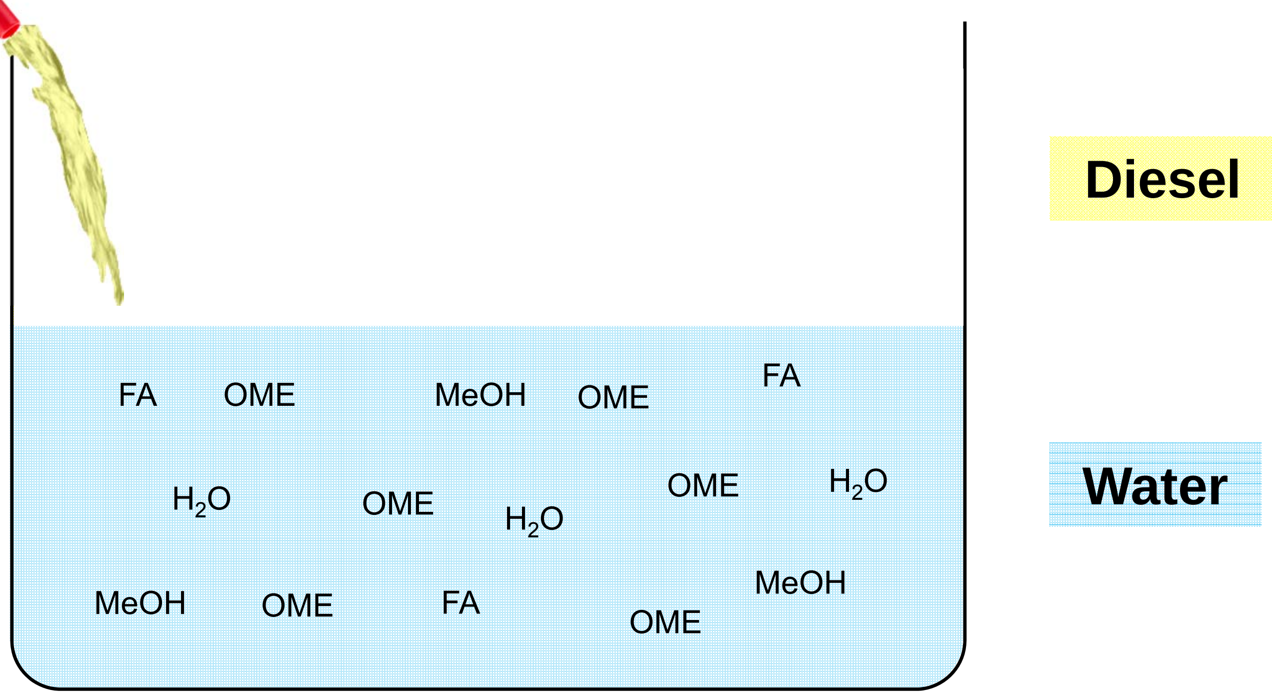
- Educts: Methanol, dimethoxymethane, dimethyl ether, p-formaldehyde, formalin*, trioxane

- Development of an economic synthesis process

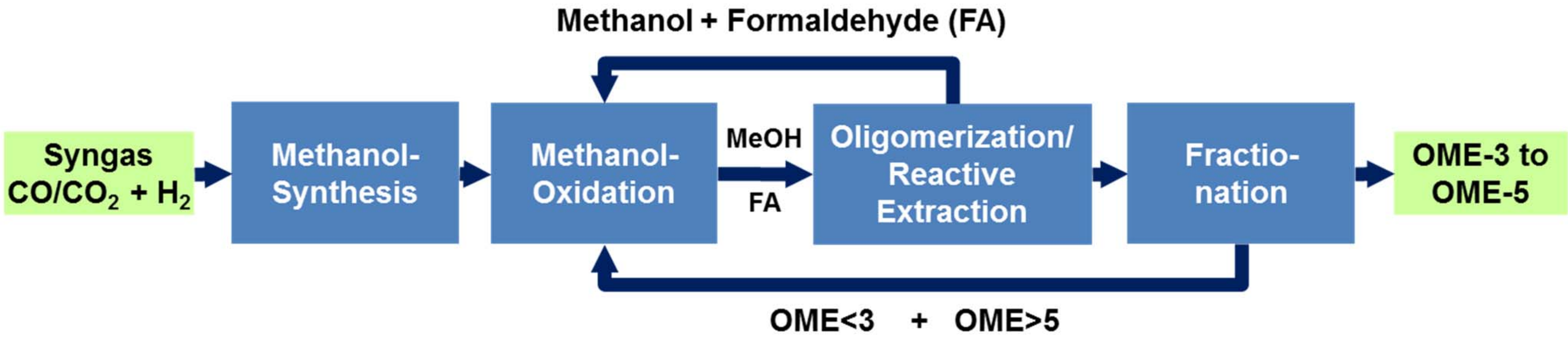
*Formalin: mixture of 37 wt% formaldehyde, 10 wt% methanol, 53 wt% water.

OME separation from aqueous reaction solutions by extraction with diesel

⇒ **Direct additivation of diesel possible**

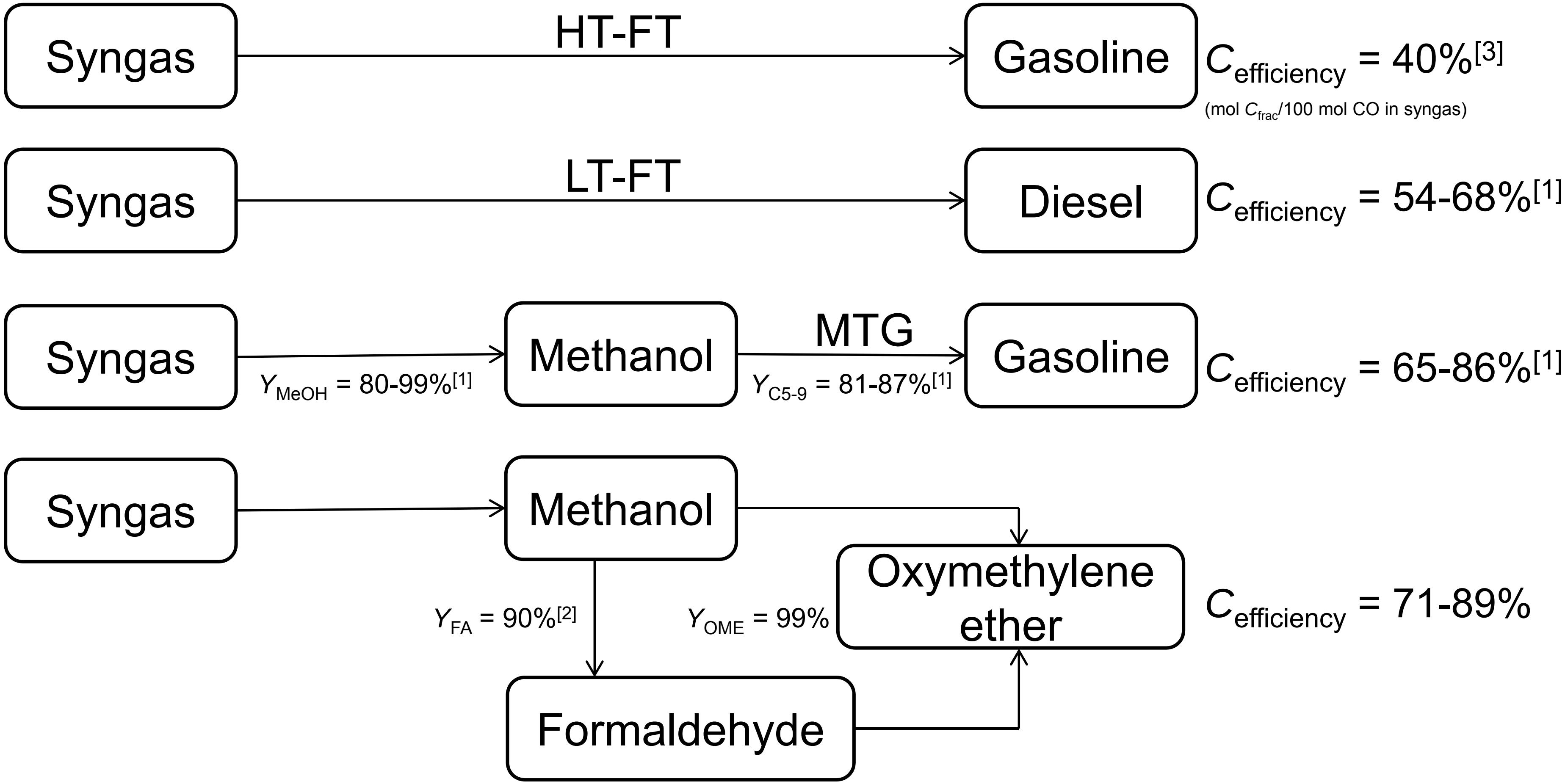


OME synthesis from methanol and formaldehyde: Process development



Challenges:
- Separation of water
- Recycling of educts and byproducts
- Optimization of extraction step

Carbon efficiency in Fischer-Tropsch reactions and methanol-based processes



[1] M.I. Gonzalez, B. Kraushaar-Czarnetzki, G. Schaub, Biomass Convers. Biorefin. 2011, 1, 229-243.
[2] G. Reuss, W. Disteldorf, A.O. Gamer, A. Hilt, "Formaldehyde", Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2000.
[3] M. Crocker, Thermochemical conversion of biomass to liquid fuels and chemicals: Royal Society of Chemistry, 2010.

Content

Commercialization (1)

- DME:
  - Different technologies, eg. Air Liquide, Haldor Topsøe,…
- Fischer-Tropsch:
  - Sasol: South Africa, Qatar
  - Shell: Malaysia, Qatar
  - China Synfuels: China
  - Velocys: USA
- MTG
  - Licensee of Exxon Mobile: China
  - Licensee of Haldor Topsøe: Turkmenistan
  - GTI / Haldor Topsøe: USA
- OME:
  - Chinese Technologies

Commercialization (2)

- Feedstocks:
  - Biomass (Sweden, USA)
  - Coal (China, South Africa)
  - Natural Gas (Malaysia, Qatar)

Potentials and benefits of synthetic fuels

- ☺ Utilize a multitude of feedstocks including feedstocks with low CO_2 footprint
- ☺ "Near-drop-in" fuels compatible with existing car fleet
- ☺ Higher efficiency application in internal combustion engines
- ☺ Low emissions
- ☺ Better handling of fuels compared to existing fuels

Challenges

- 😐 Economics are difficult especially in times with low crude oil price
- 😐 Processes for especially interesting products are not state-of-the-art yet
- 😐 Market introduction may be difficult especially in (over-) saturated markets like Europe
- 😐 Uncertainty of markets which are created and/or highly controlled by government regulations
- 😐 Europe and especially Germany lose competitiveness compared to USA and China

Acknowledgements

- Sponsors and funding agencies
- Partners from industry and academia
- The teams from KIT
- You for your kind attention

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HELMHOLTZ
GEMEINSCHAFT

GEFÖRDERT VOM
Bundesministerium
für Bildung
und Forschung

Gefördert durch:
Bundesministerium
für Ernährung
und Landwirtschaft
aufgrund eines Beschlusses
des Deutschen Bundestages

FNR
Fachagentur Nachwachsende Rohstoffe e.V.