Karlsruhe Institute of Technology

refuels – Raw Materials, Processes and Applications for Synthetic Fuels

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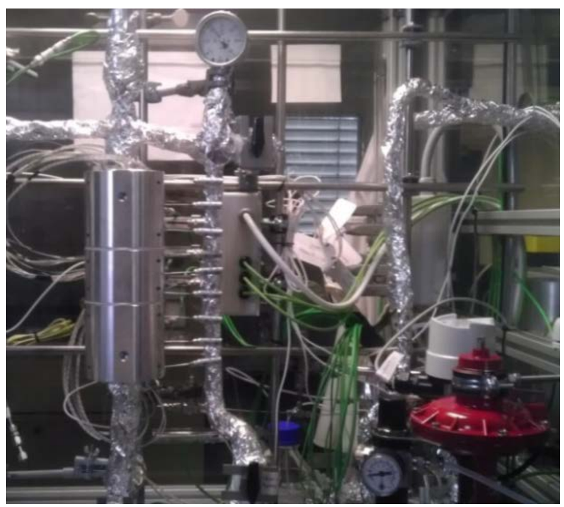
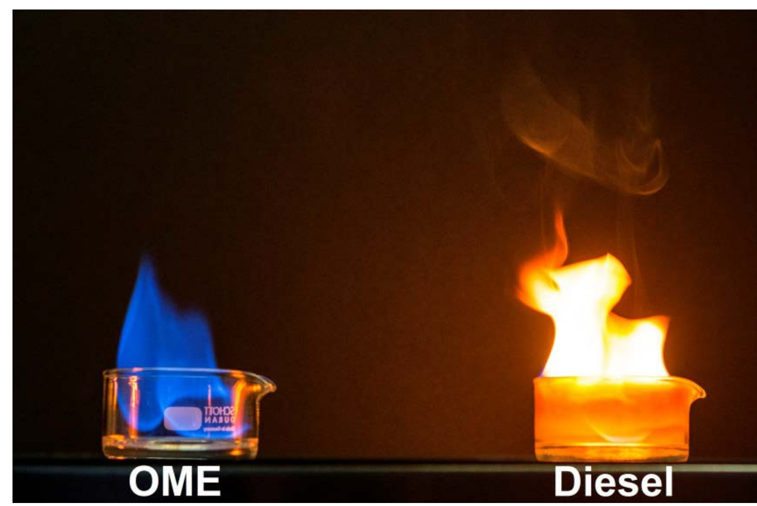
COMSYN European 2nd Generation Biofuels - Opportunities and Applications
1st Workshop of the European Project COMSYN
German Aerospace Center (DLR) Stuttgart - INERATEC GmbH and KIT Karlsruhe, April 18-19, 2018

Institute of Catalysis Research and Technology (IKFT)





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Legislative background

Technological background

OME fuels

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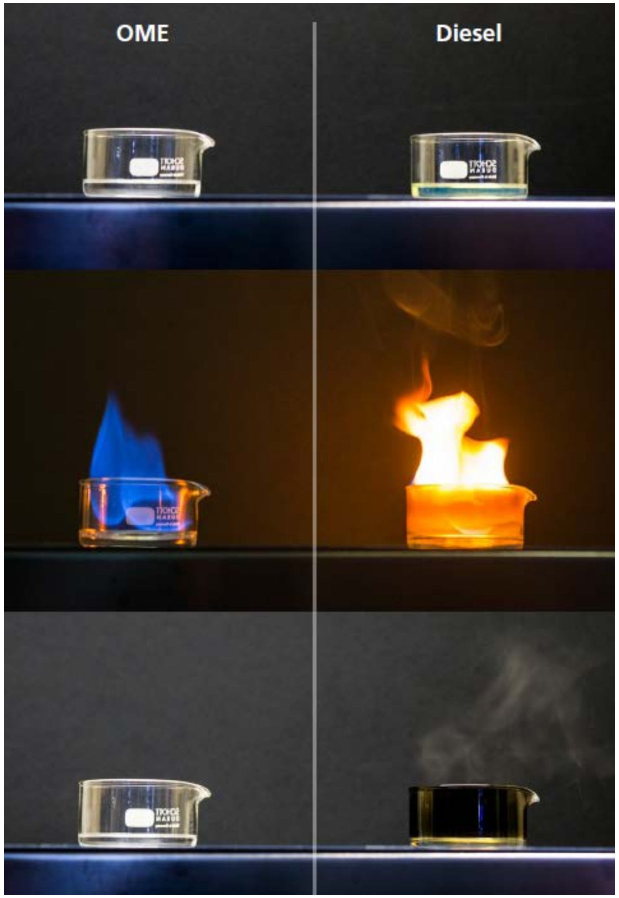
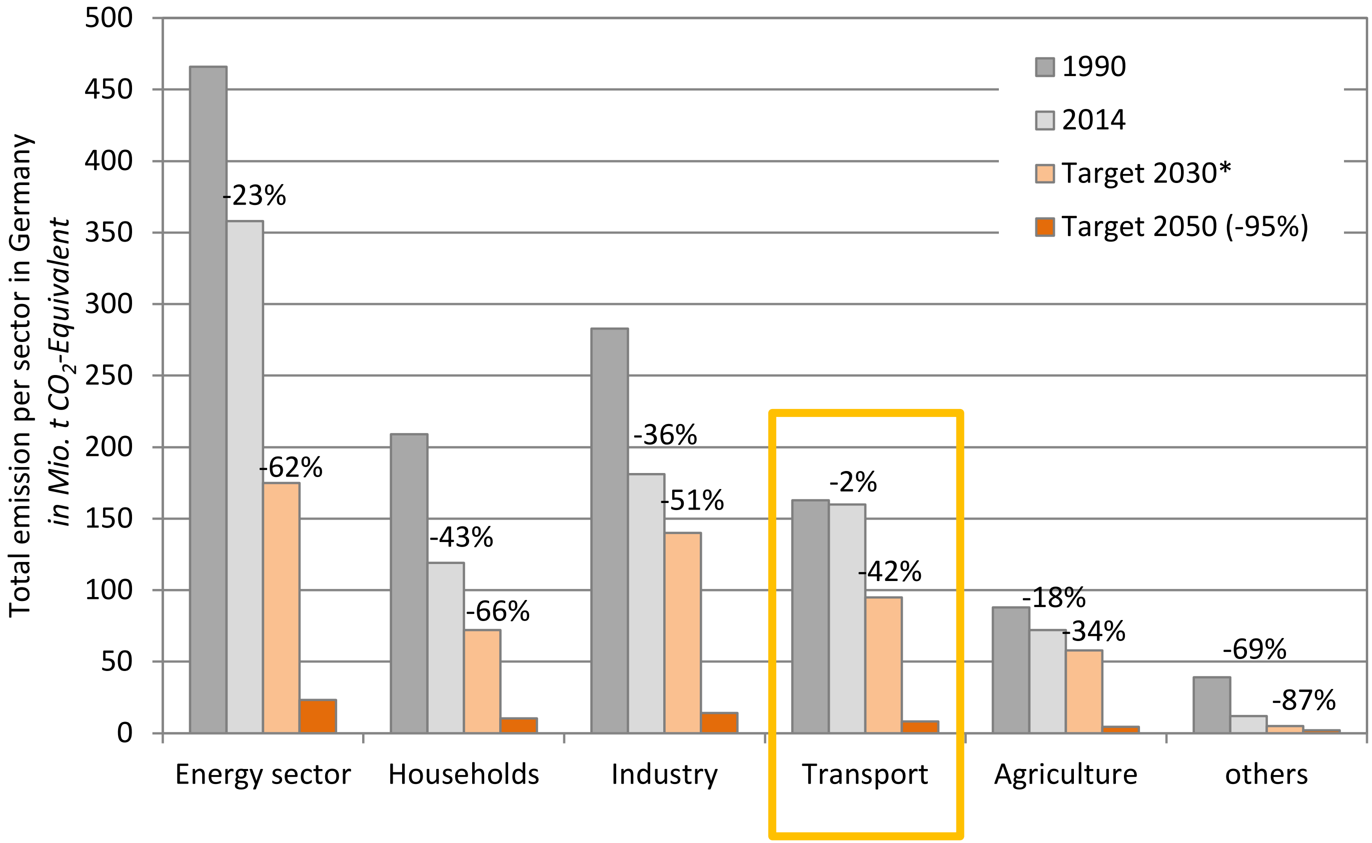


Legislative background (I)

Main driver for biofuel activities in Germany: Climate protection by low-carbon technologies, CO_2 use and efficient renewable fuels and products from biomass and electricity



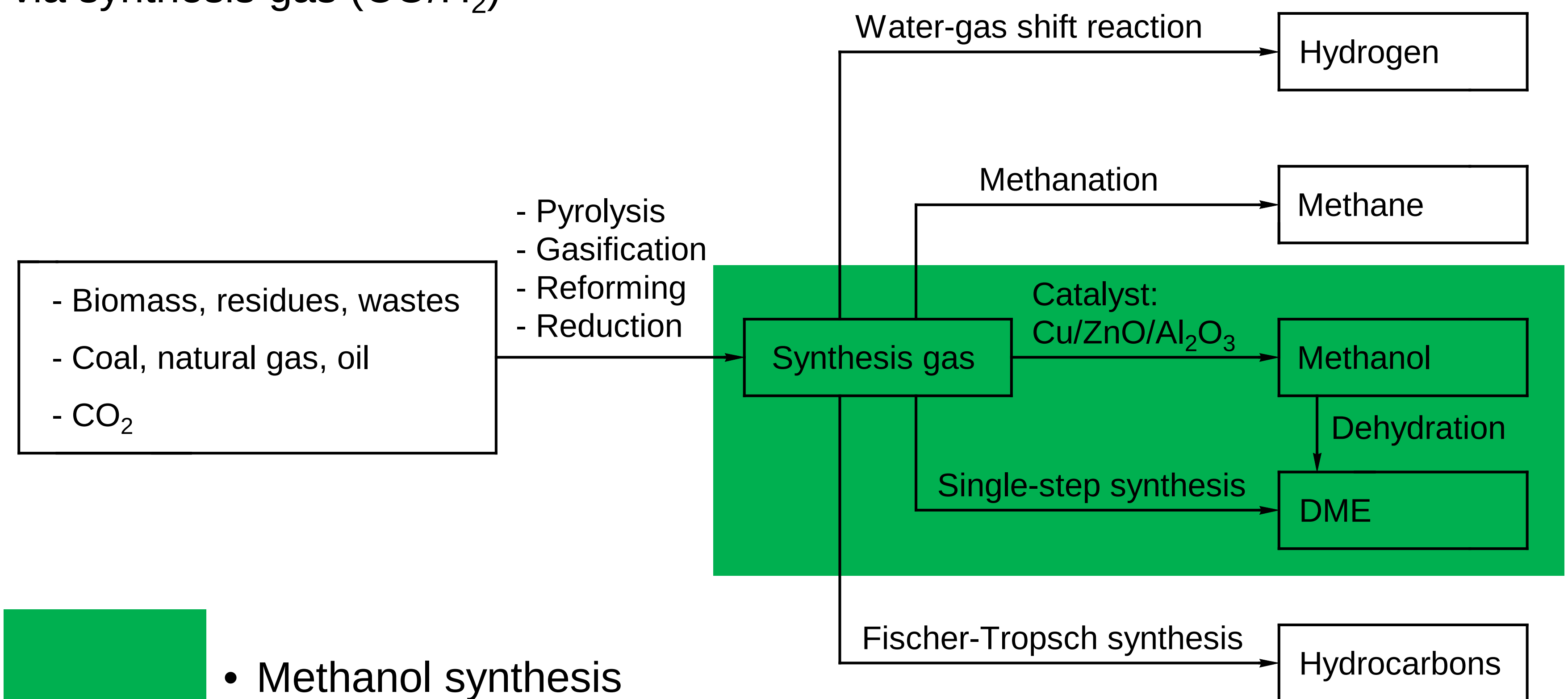
*upper target value

Legislative background (II)

Topic	EU Directives
Energy Carrier • **Renewable energy mandates**	Fixed in RED 2009/28/EG with 10% RE in 2020 and FQD with 6% CO_2-eq reduction by 2020; No sector-related targets for post-2020 (1990-2030: –40% GHG, 27% renewable energies, 27% improvement of energy efficiency)
• **Legislation for renewable fuels**	RED: 7% cap for biofuels based on food crops, i/dLUC, sustainability criteria and methodology for GHG, min. 60% GHG reduction for new plants
• **Taxes for fuels**	Energy Taxation Directive (ETD)
Energy Infrastructure	Clean Power for Transport Directive (CPD) Alternative Fuels Infrastructure Directive (AFID)
Vehicles • **Legislation for vehicle emission standards**	CO_2 regulations 2020 on tank-to-wheel basis, fleet averages for manufacturers: 95 g/km passenger cars / 120 g/km for HDV EURO VI emission regulations for HC, CO, NO_x, PM
• **Incentives for low emission vehicles**	Individual incentives for EU member countries

Technological background (I)

Synthesis of (bio)fuels from various resources via synthesis gas (CO/H_2)

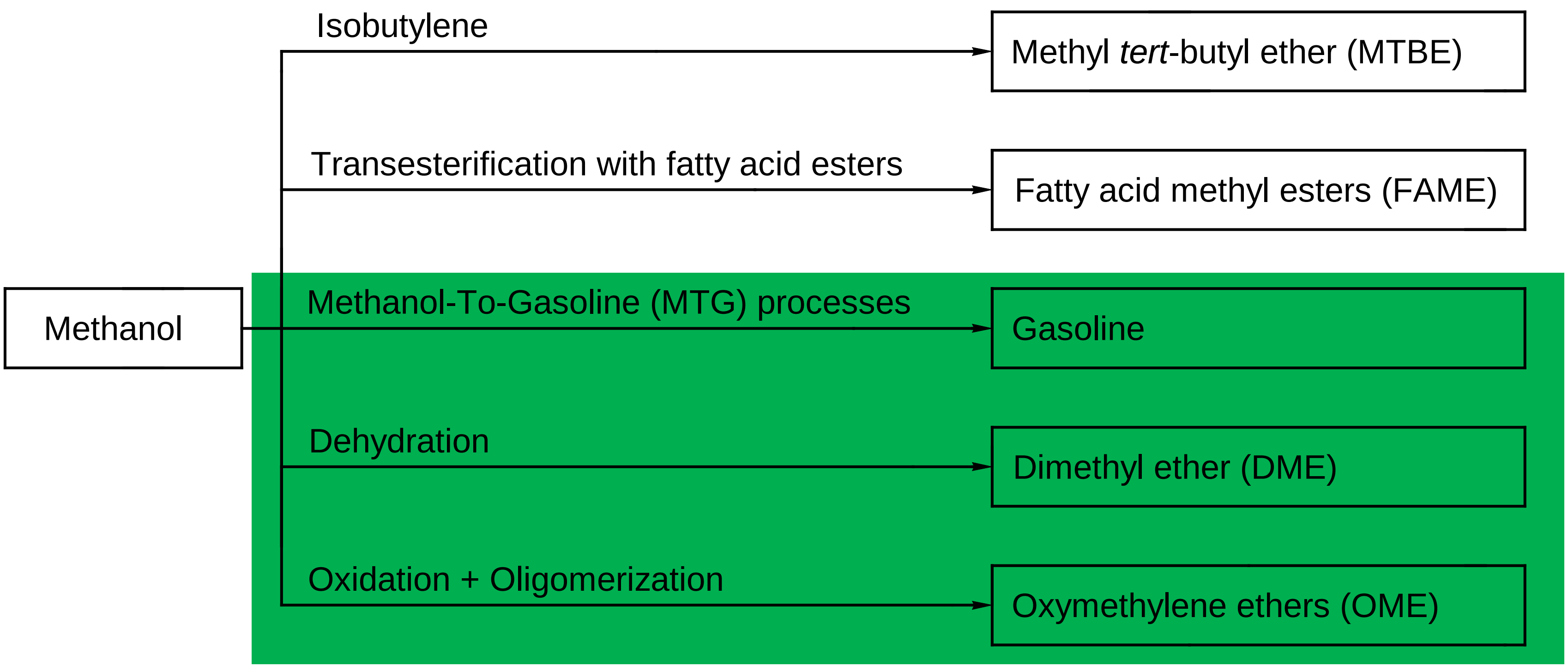


- Methanol synthesis
- Single- and two-step-synthesis of DME

B. Niethammer, S. Wodarz, M. Betz, P. Haltenort, D. Oestreich, K. Hackbarth, U. Arnold, T. Otto, J. Sauer, "Alternative liquid fuels from renewable resources", *Chem. Ing. Tech.* **2018**, *90*, 99-112.

Technological background (II)

Synthesis of fuels and fuel additives from (bio)methanol

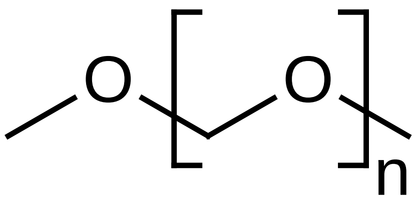


F. Asinger, *Methanol – Chemie- und Energierohstoff*, Springer, Berlin, **1986**.

Why OME fuels?

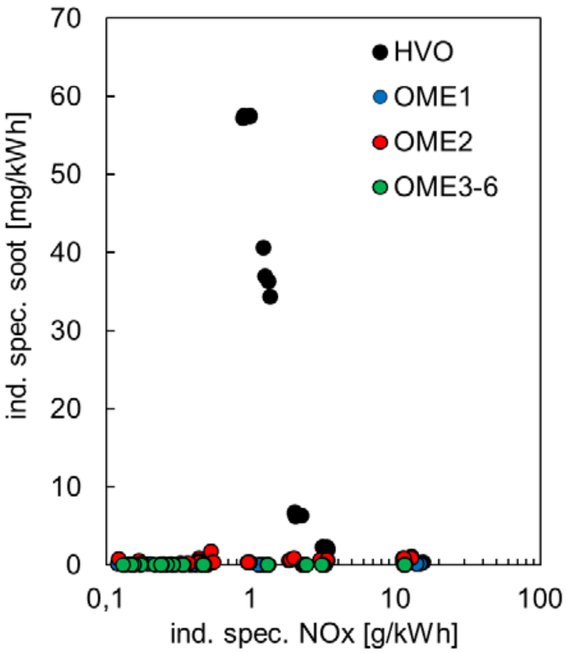
- Absence of carbon-carbon bonds => soot-free combustion
- Non-toxic, non-corrosive => safe handling
- Properties similar to diesel => good miscibility with diesel

Molecular structure of OMEs:



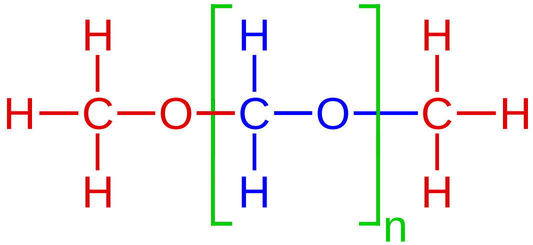
n = 1-5

Elimination of soot-NO_x trade-off:



M. Härtl, K. Gaukel, D. Pélerin, G. Wachtmeister, E. Jacob, "Oxymethylenether als potenziell CO_2-neutraler Kraftstoff für saubere Dieselmotoren Teil 1: Motorenuntersuchungen", *MTZ Motortech. Z.* **2017**, *78(2)*, 52-59.

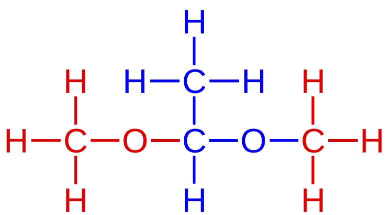
Molecular structure & fuel performance (I)



Variation of aldehyde (formaldehyde → acetaldehyde)
Variation of end group (methyl, ethyl, acetate)
Variation of chain length

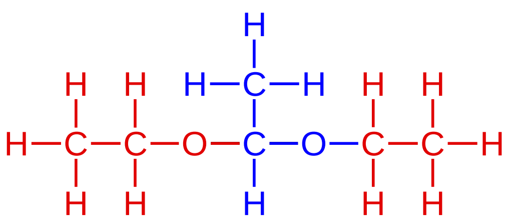
Variation of aldehyde

Acetaldehyde + methanol:



1,1-Dimethoxyethane:
No detailed fuel investigations

Acetaldehyde + ethanol:



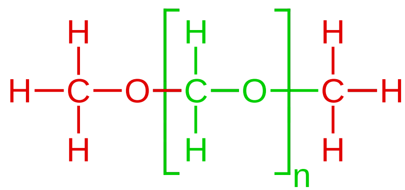
1,1-Diethoxyethane:
- Diesel: Soot reduction only
- Efficient octane enhancer

- F. Frusteri, L. Spadaro, C. Beatrice, C. Guido, “Oxygenated additives production for diesel engine emission improvement“, *Chem. Eng. J.* **2007**, *134*, 239-245.
- M.-Z. Vagabov, R. Vagabov, Z. Mangueva, F. Latypova, E. Rakhmankulov, “Use of 1,1-diethoxyethane for increasing knocking resistance of automotive gasoline“, WO 2012/143465 A1, **2012**.

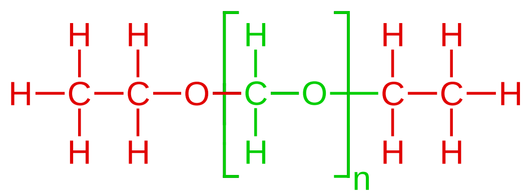
Molecular structure & fuel performance (II)

Variation of end group

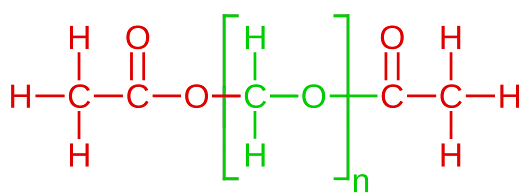
Trioxane
+ methylal

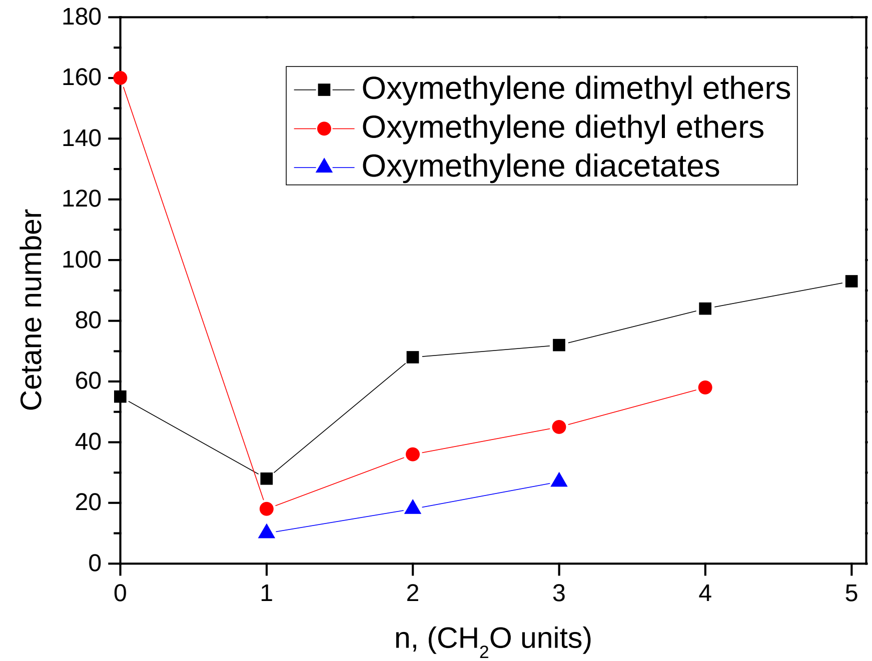


Trioxane
+ ethylal



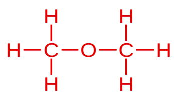
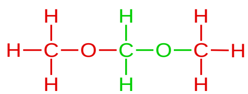
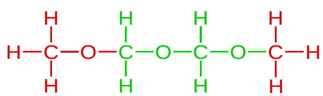
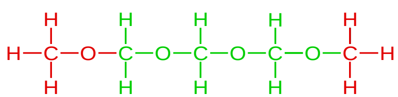
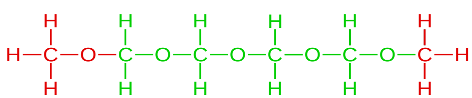
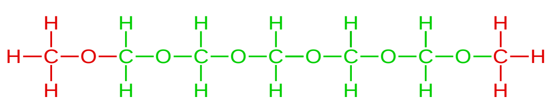
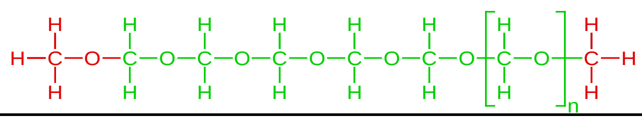
Trioxane
+ acetanhydride



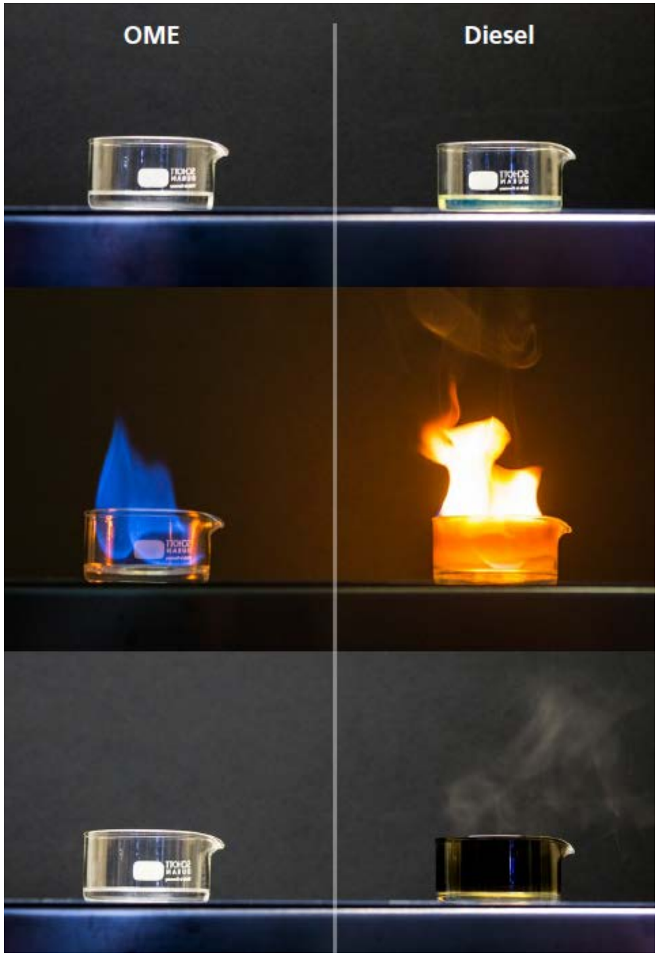


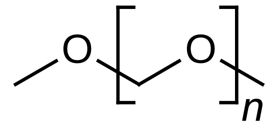
- L. Lautenschütz, “Neue Erkenntnisse in der Syntheseoptimierung oligomerer Oxymethylendimethylether aus Dimethoxymethan und Trioxan“, Dissertation, University of Heidelberg, **2015**.
- L. Lautenschütz, D. Oestreich, P. Seidenspinner, U. Arnold, E. Dinjus, J. Sauer, “Physico-chemical properties and fuel characteristics of oxymethylene dialkyl ethers”, *Fuel* **2016**, *173*, 129-137.

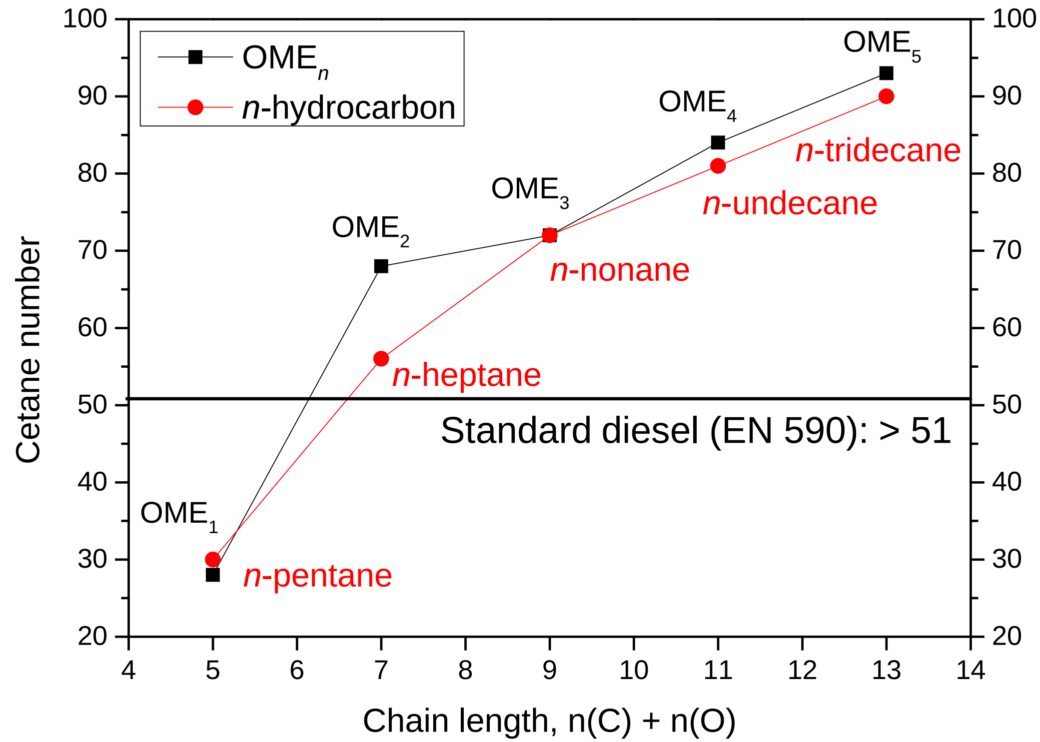
Molecular structure & fuel performance (III)

Variation of chain length		b.p. (°C)	$D_{20°C}$ (kgm^{-3})	CN
	OME_0 Dimethylether (DME)	–24	735 (–25 °C)	55
	OME_1 Dimethoxymethane (DMM) Methylal	42	859	28
	OME_2	105	977	68
	OME_3	156	1030	72
	OME_4	202	1074	84
	OME_5	242	1106	93
	$OME_{>5}$	waxy	not determined	

Cetane numbers of OMEs



OME$_n$  n = 1-5

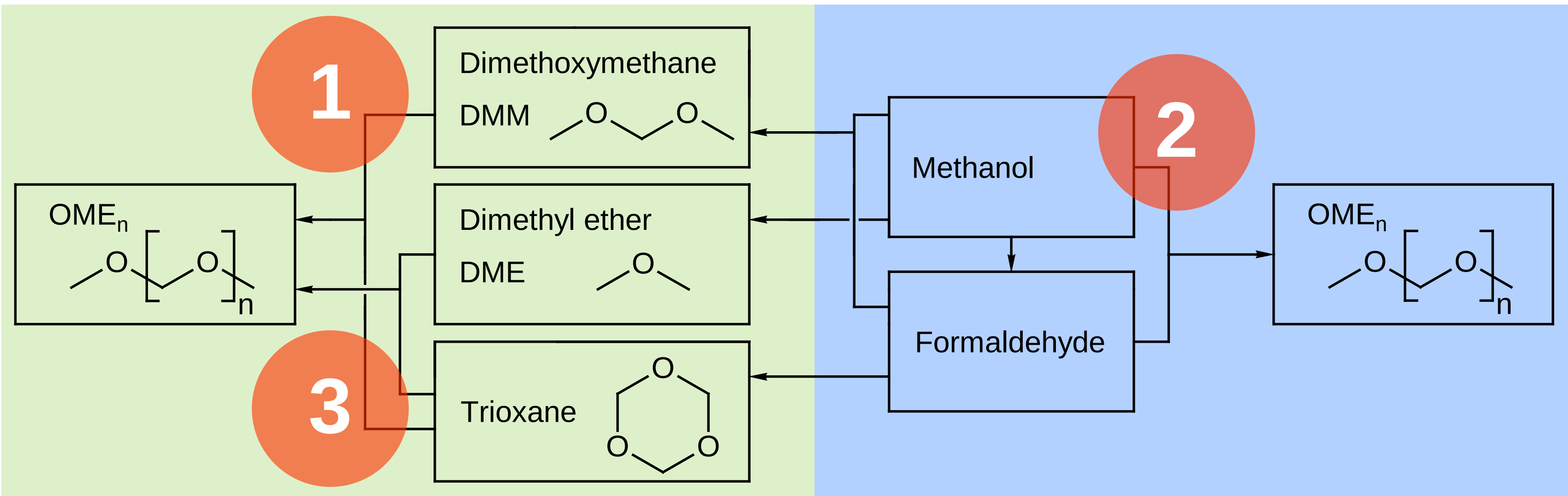


Fuel properties are in good accordance with diesel standards

D. Deutsch, D. Oestreich, L. Lautenschütz, P. Haltenort, U. Arnold, J. Sauer,
"High Purity Oligomeric Oxymethylene Ethers as Diesel Fuels", *Chem. Ing. Tech.* **2017**, *89(4)*, 486-489.

OME synthesis: State of the art

Anhydrous pathways **Aqueous pathways**



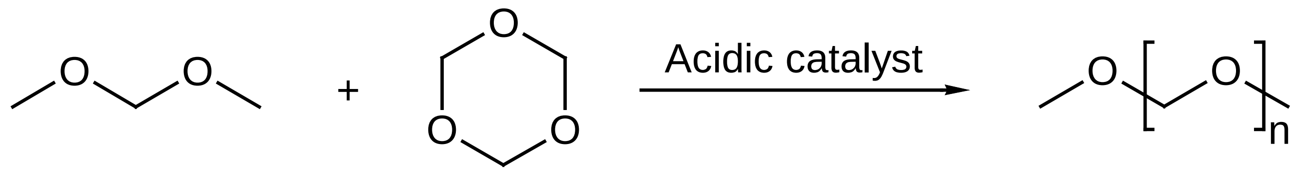
- Reactions starting from DMM
- High OME selectivity
- Low amounts of byproducts
- Comparatively simple product separation
- Costly starting materials

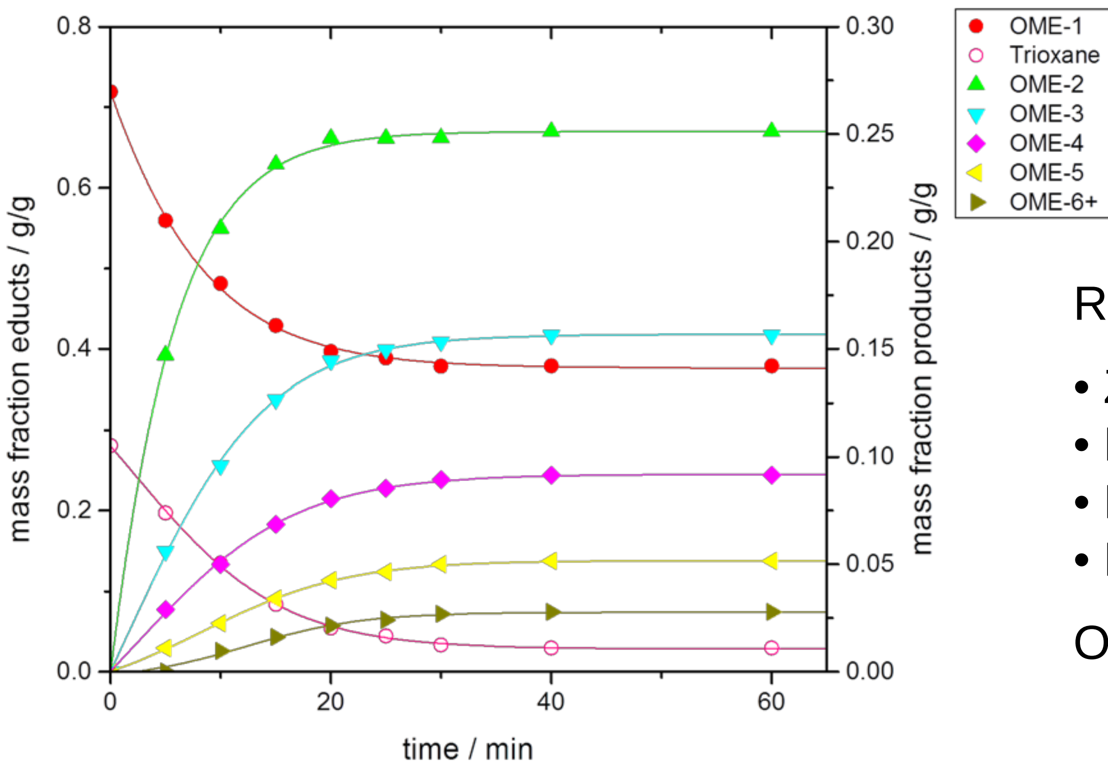
- Reactions starting from methanol
- Low-cost starting materials
- Formation of byproducts (hemiacetals)
- Removal of water

L. Lautenschütz, D. Oestreich, P. Haltenort, U. Arnold, E. Dinjus, J. Sauer, "Efficient synthesis of oxymethylene dimethyl ethers (OME) from dimethoxymethane and trioxane over zeolites", *Fuel Process. Technol.* **2017**, *165*, 27-33.

OME synthesis: DMM + trioxane

1





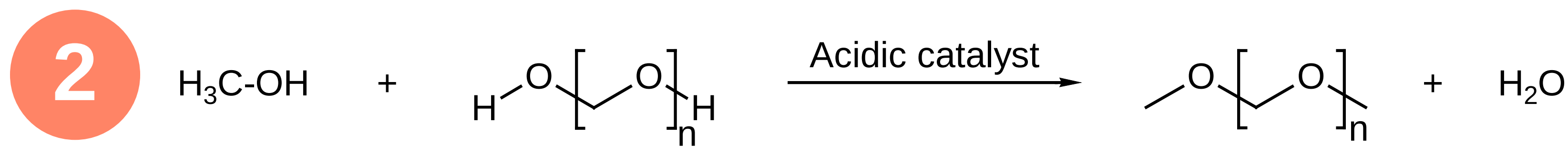
Recent progress:

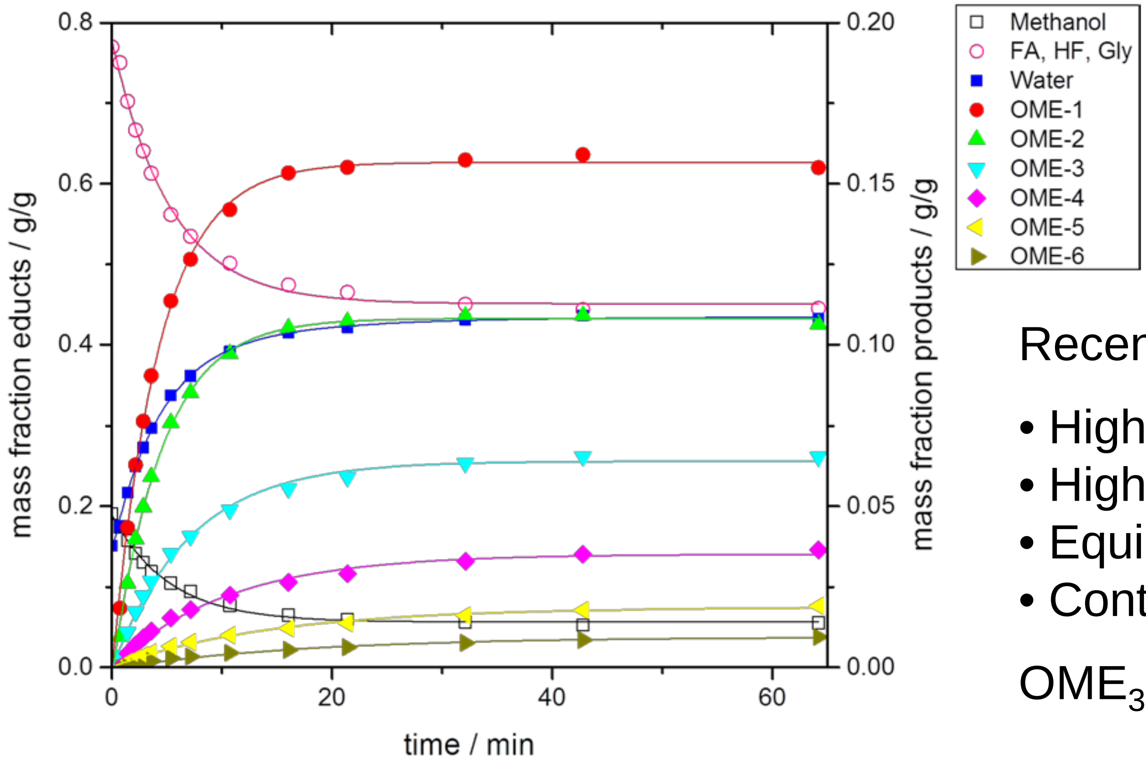
- Zeolite BEA catalyst
- Reaction within minutes at 25 °C
- Reliable separation of catalyst
- Elimination of byproducts

$OME_{3\text{-}5}$ yield: ~30 wt%

Reaction conditions:19 g DMM, 7.5 g trioxane, 0.075 g Amberlyst 36, T = 60 °C

OME synthesis: Methanol + formaldehyde





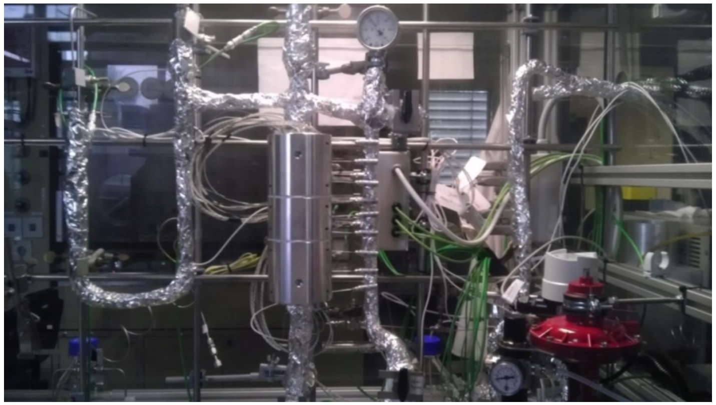
Recent progress:

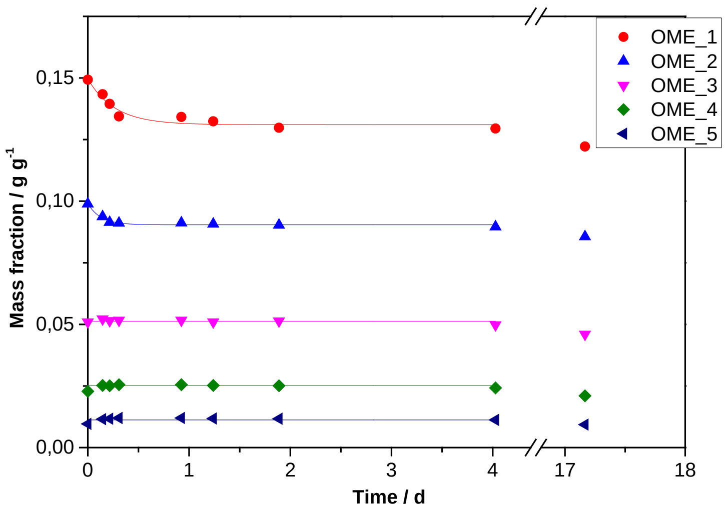
- Highly active Dowex catalysts
- High catalyst stability
- Equilibria and kinetics determined
- Continuous production demonstrated

$OME_{3\text{-}5}$ yield: ~12 wt%

Reaction conditions: 40 g MeOH, 60 g formaldehyde (5% water), 1.0 g Amberlyst 36, T = 80 °C

2 OMEs from methanol + formaldehyde Continuously operating laboratory plant





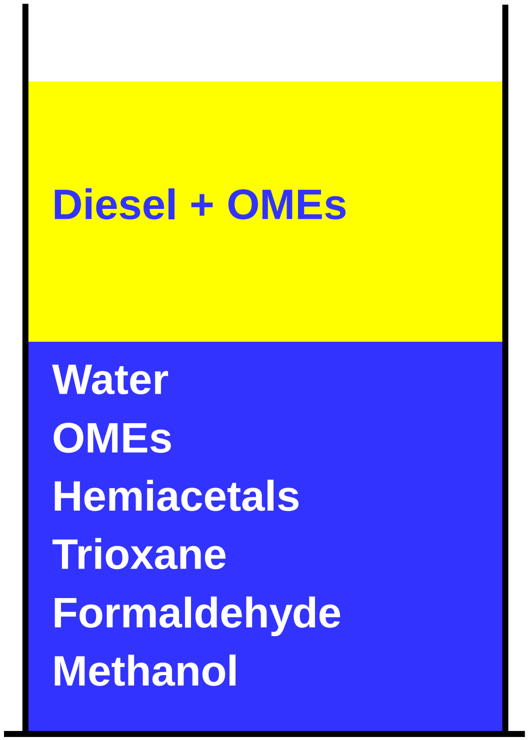
- Continuous long-term operation
- Variable temperatures and pressures
- Defined feed compositions
- Recording of concentration profiles
- Recording of temperature profiles
- Analysis via online-GC/MS
- Catalyst long-term testing
- Kinetic modelling

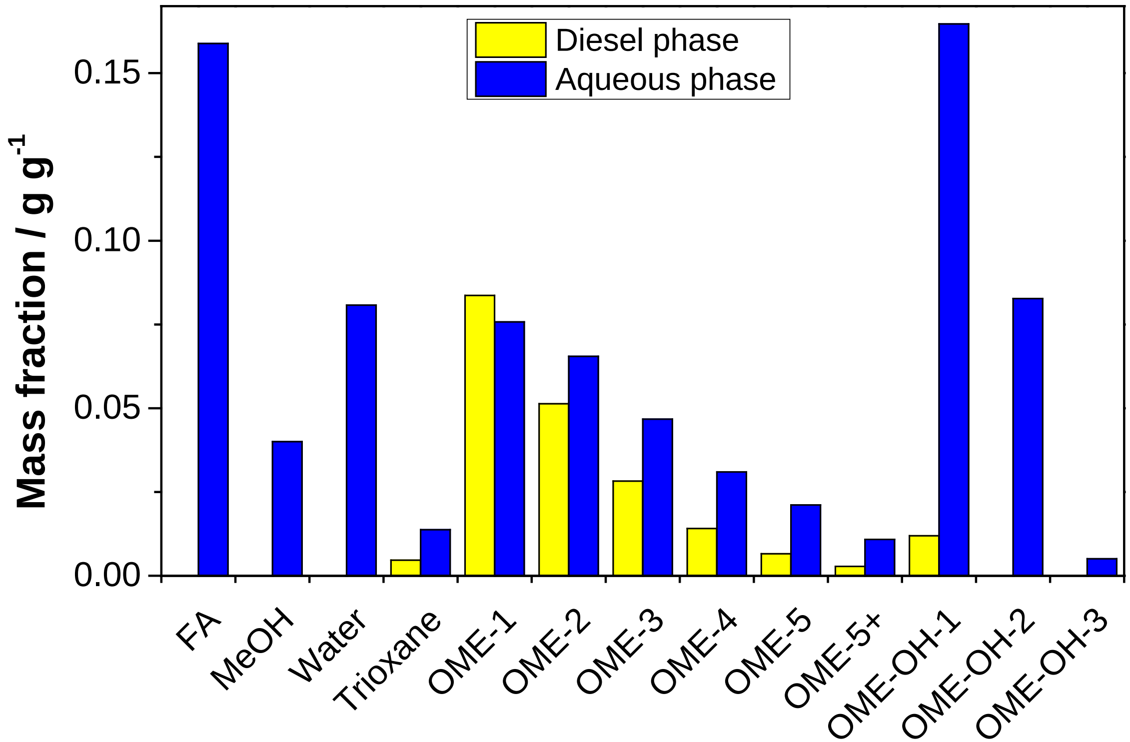
D. Oestreich, L. Lautenschütz, U. Arnold, J. Sauer, “Reaction kinetics and equilibrium parameters for the production of oxymethylene dimethyl ethers (OMEs) from methanol and formaldehyde”, *Chem. Eng. Sci.* **2017**, *163*, 92-104.

Run at 90% of maximum methanol conversion
Reaction conditions: *p*-FA/MeOH = 3:2 g/g, T = 40 °C, p = 0.1 MPa, Dowex50Wx2 (200-400 mesh)

2a

OMEs from methanol + formaldehyde Reaction & Extraction

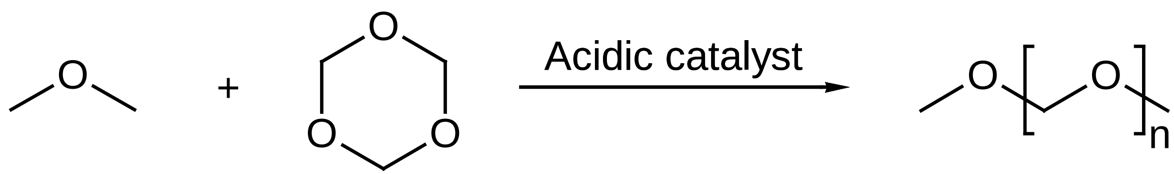


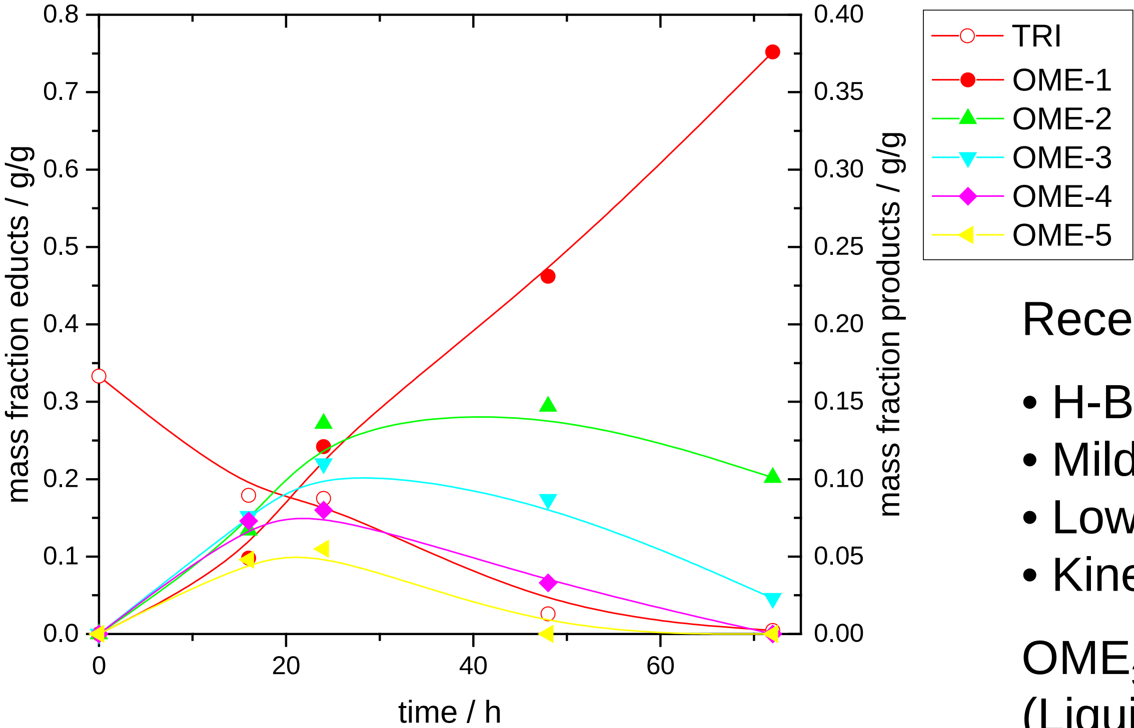


- U. Arnold, L. Lautenschütz, D. Oestreich, J. Sauer, EP 2 987 781 A1, **2016**.
- D. Oestreich, L. Lautenschütz, U. Arnold, J. Sauer, "Production of oxymethylene dimethyl ether (OME)-hydrocarbon fuel blends in a one-step synthesis/extraction procedure", *Fuel* **2018**, *214*, 39-44.

OME synthesis: DME + trioxane

3





Recent progress:

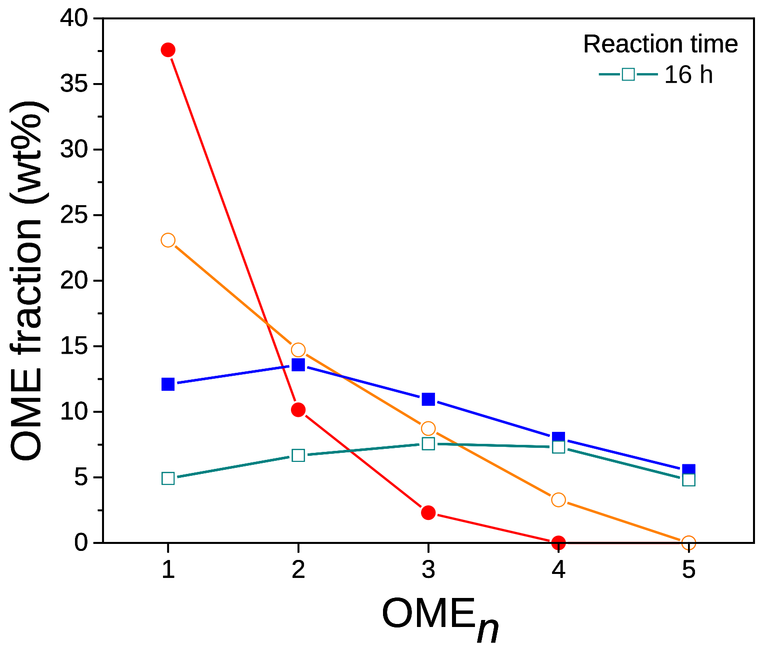
- H-BEA25 catalyst
- Mild reaction conditions (80 °C)
- Low reaction rate
- Kinetic control of selectivity possible

$OME_{3\text{-}5}$ yield: ~20 wt%
(Liquid product phase, 16 h)

Reaction conditions: $n_{trioxane}/n_{DME}$ = 0.25, 0.4 wt% H-BEA 25, 80 °C

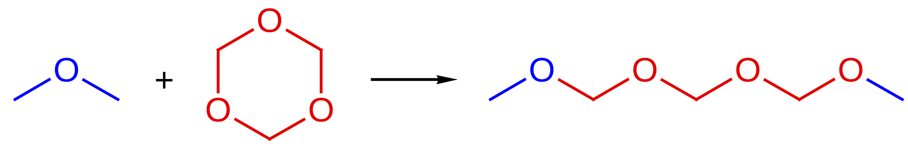
3 OME synthesis: DME + trioxane

Mass fractions of $OME_{1\text{-}5}$ vs. time

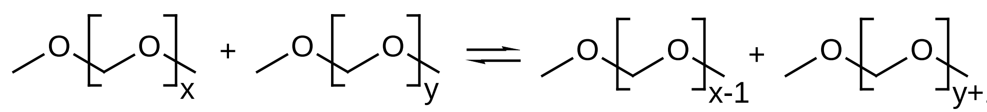


80 °C, 18 bar, $n_{trioxane}/n_{DME}$ = 0.25, 0.4 wt% catalyst

Direct insertion of trioxane into DME



Formation of OME_n mixtures in secondary reactions (transacetalization)

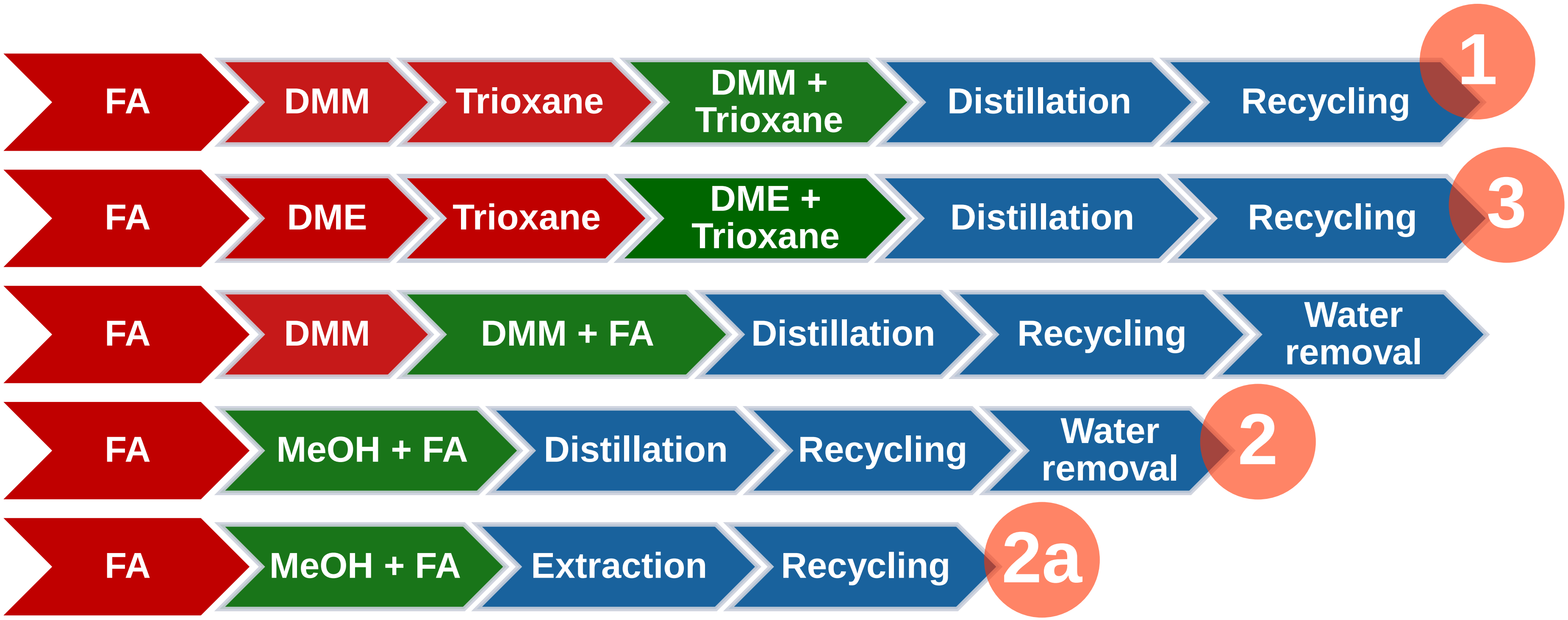


- Efficient OME synthesis from DME with zeolite H-BEA as catalyst
- Accordance with other experimental and theoretical findings for DMM + trioxane

- P. Haltenort, K. Hackbarth, D. Oestreich, L. Lautenschütz, U. Arnold, J. Sauer, “Heterogeneously catalyzed synthesis of oxymethylene dimethyl ethers (OME) from dimethyl ether and trioxane”, *Catal. Commun.* **2018**, *109*, 80-84.
- T.J. Goncalves, U. Arnold, P.N. Plessow, F. Studt, “Theoretical Investigation of the Acid Catalyzed Formation of Oxymethylene Dimethyl Ethers from Trioxane and Dimethoxymethane”, *ACS Catal.* **2017**, *7*, 3615-3621.

Comparison of OME production processes

Main process steps starting from methanol



■ Synthesis of educts; ■ OME forming reaction; ■ Work-up

FA = formaldehyde, DMM = dimethoxymethane

Current work

Karlsruhe Institute of Technology

OME synthesis

- Optimization of OME synthesis from DME
- Theoretical investigations on catalysts for OME synthesis

Fuel applications

- Combination of OMEs with other fuels
- Investigations on (storage) stability

Chemical modification of OMEs

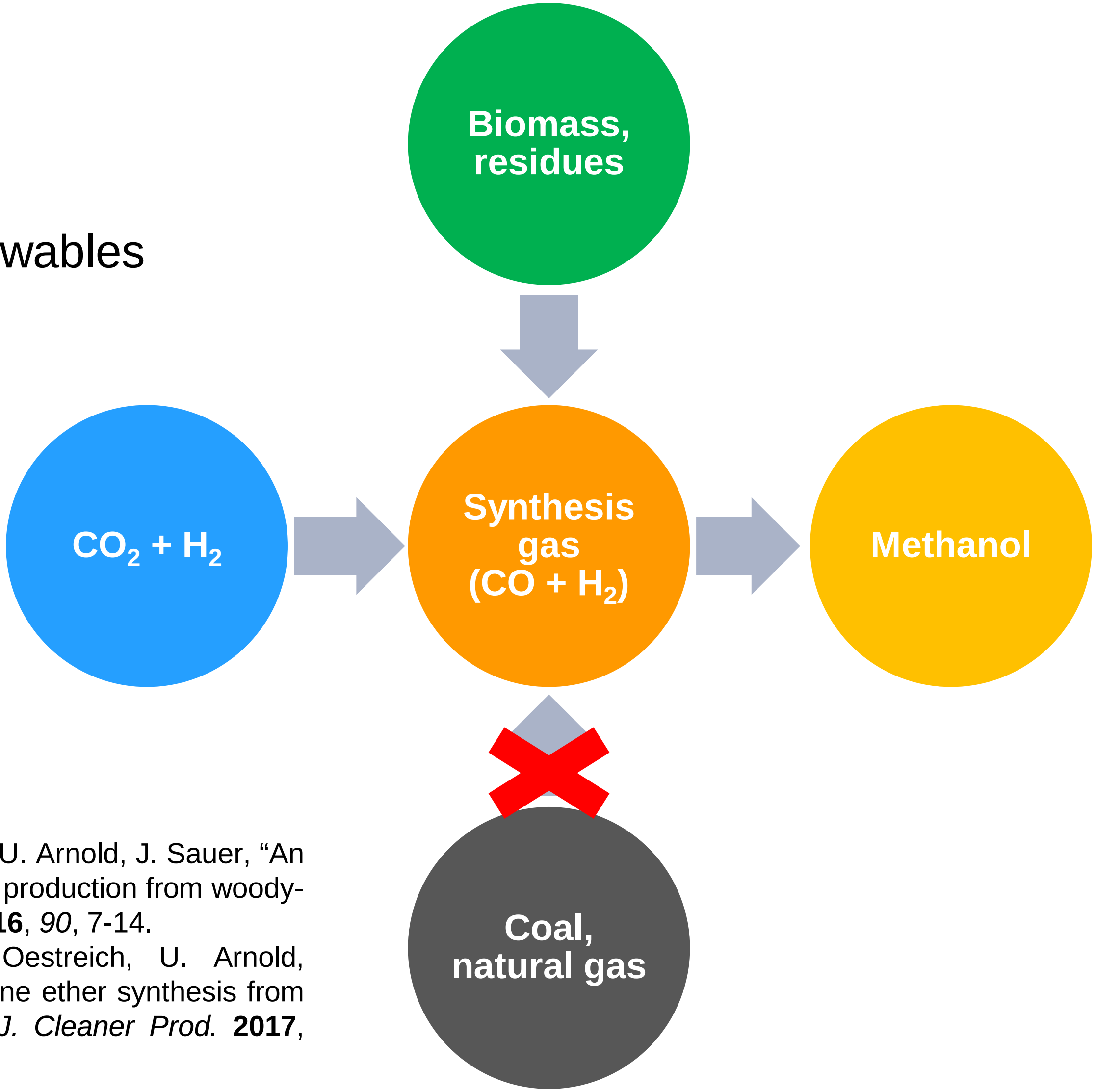
- Variation of end groups
- Modification for non-fuel applications

Life cycle assessment with updated technological data

- In the Power-to-X context
- Entire process chain starting from renewable resources (e.g. woody biomass)

Challenges

Synthesis of OMEs from renewables via “Green Methanol“

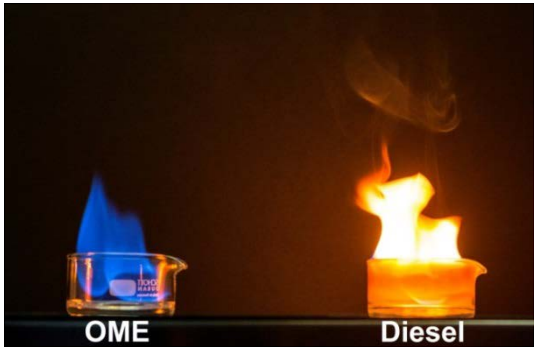


- X. Zhang, A.O. Oyedun, A. Kumar, D. Oestreich, U. Arnold, J. Sauer, “An optimized process design for oxymethylene ether production from woody-biomass-derived syngas”, *Biomass Bioenergy* **2016**, *90*, 7-14.
- N. Mahbub, A.O. Oyedun, A. Kumar, D. Oestreich, U. Arnold, J. Sauer, “A life cycle assessment of oxymethylene ether synthesis from biomass-derived syngas as a diesel additive”, *J. Cleaner Prod.* **2017**, *165*, 1249-1262.

Summary & Outlook

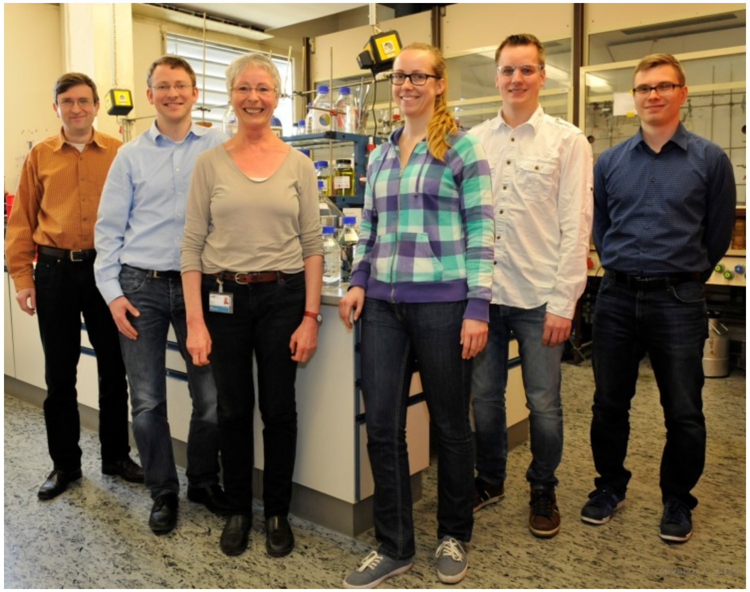
- Soot + NO_x + CO_2 reduction possible
- Comprehensive data on high-purity OMEs are available yet
- OME synthesis from DMM and trioxane is highly developed
- Recent progress in OME synthesis from methanol or DME
- Data for process design available to a large extent
- Up-scaling feasible in the near future
- There is still a large potential for optimization

  - Separation of OMEs
  - Recycling of byproducts
  - Removal of water



Acknowledgements

P. Haltenort
K. Hackbarth
D. Oestreich
L. Lautenschütz
J. Sauer
D. Deutsch
S. Silbernagel-Donath



Fachagentur Nachwachsende Rohstoffe / BMEL
Joint research project (FKZ 22403814):
Oxymethylene ethers (OME): Eco-friendly diesel additives from renewables

FNR
Fachagentur Nachwachsende Rohstoffe e.V.

Bundesministerium für Ernährung und Landwirtschaft