TNO innovation for life

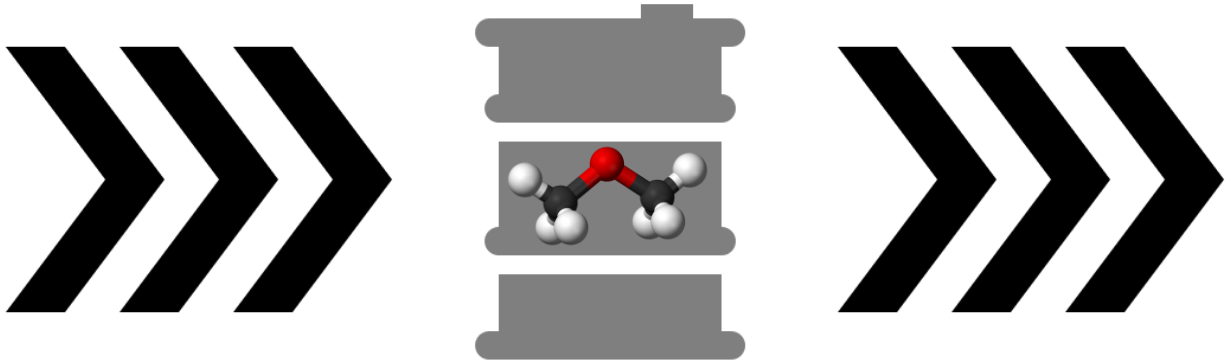
DELIVERING ON A DECADES-OLD PROMISE: RENEWABLE DME

RECENT ADVANCES IN RENEWABLE DME PRODUCTION | DR. IR. J. BOON

DELIVERING ON A DECADES-OLD PROMISE: RENEWABLE DME

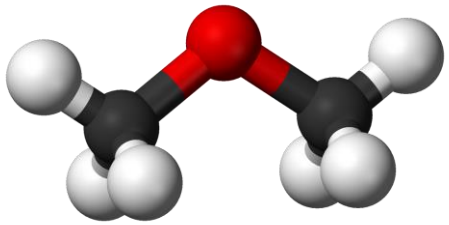
MARKET PULL AND TECHNOLOGY PUSH

- Dimethyl ether, DME
- Market & Market development
- Production
- Renewable DME
  - Technology, separation enhancement
  - Serving the markets



DIMETHYL ETHER
CURRENT MARKET

- DME (CH_3OCH_3): dehydrated methanol ($2\ CH_3OH = CH_3OCH_3 + H_2O$)
- Nontoxic, combusts well (no soot), mild vapour pressure (handles similar to LPG)
- Aerosol propellant, refrigerant, fuel; significant market in China, Japan, Korea (MT+)



- Fuel: Good LPG substitute
  Blends containing up to 20% volume DME generally require no modifications to equipment or distribution networks
  DME_Fact_Sheet_LPG_Blends.pdf (aboutdme.org)

Properties		DME	LPG
Vapor Pressure	*kPA*	530	520
Liquid Density	*kg/m³*	667	540
Heating Value	*MJ/kg*	28.8	46
Bottle Fill	*%*	85	80
Mass per Bottle Unit Vol.	*kg/m³*	567	432
Energy per Bottle Unit Vol.	*GJ/m³*	16.3	19.9

IDA
International DME Association
DME: 21st Century Energy

- Fuel: Good diesel substitute
  No carbon-carbon bonds, thus seriously limiting the possibility of forming carbonaceous particulate emissions
  High enough cetane number to perform well as a compression-ignition fuel
  Dimethyl Ether (dieselnet.com) / Mack Trucks tests alternative fuel DME | Volvo Group / Ford

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DIMETHYL ETHER

FUTURE MARKET: DME AS FEEDSTOCK

- Methanol to olefins
  DME to olefins

$$2CH_3OH \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} CH_3OCH_3 \xrightarrow{-H_2O} \underset{H_2C=CH_2 \,\&\, H_2C=CH-CH_3}{\text{ethylene \& propylene}}$$

Beyond Oil and Gas: The Methanol Economy | Wiley Online Books

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- Methanol to gasoline
  DME to gasoline

$$2CH_3OH \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} CH_3OCH_3 \xrightarrow{-H_2O} \text{light olefins} \rightarrow \begin{matrix}\text{alkanes}\\ \text{higher olefins}\\ \text{aromatics}\end{matrix}$$

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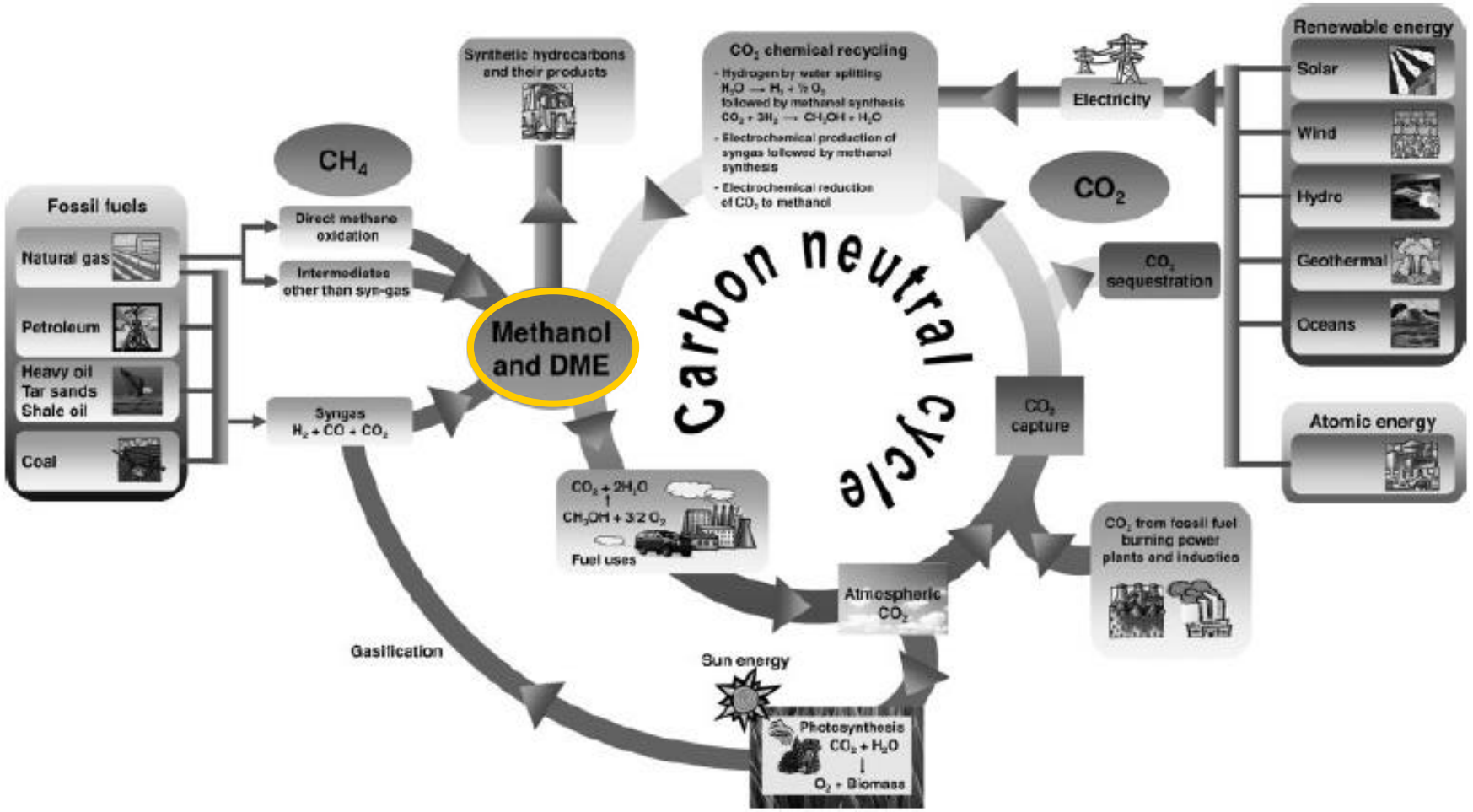
DIMETHYL ETHER

FUTURE MARKET: DME AS FEEDSTOCK

- Methanol to olefins
  DME to olefins
- Methanol to gasoline
  DME to gasoline
- The MeOH *and DME* economy



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DIMETHYL ETHER
PRODUCTION - INDIRECT

$$2CO + 4H_2 \rightarrow 2CH_3OH \qquad \Delta H_{298K} = -43.5\ \text{kcal mol}^{-1}$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H_{298K} = -5.5\ \text{kcal mol}^{-1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H_{298K} = -9.8\ \text{kcal mol}^{-1}$$

COMMERCIAL STANDARD

- First produce methanol
- In a separate process, dehydrate methanol to DME

RENEWABLE DME

- BioDME project (Piteå, Sweden)
  2008 – 2016
  CHEMREC (Topsoe): 4 tpd
- Oberon Fuels (Brawley, California)
  2013/2021
  10,000 gallons rDME per day

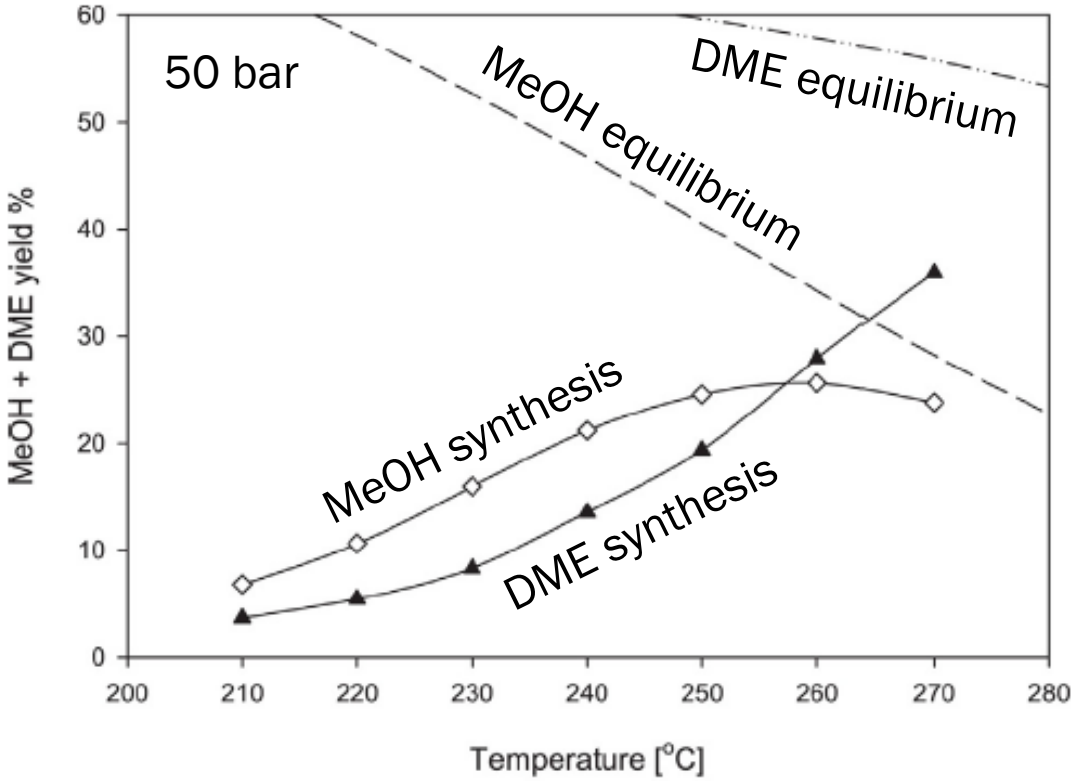
Beyond Oil and Gas: The Methanol Economy | Wiley Online Books
BioDME (etipbioenergy.eu)

DIMETHYL ETHER
PRODUCTION - DIRECT

$$2CO + 4H_2 \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H_{298K} = -49.0\,\text{kcal mol}^{-1}$$

$$3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2 \qquad \Delta H_{298K} = -58.7\,\text{kcal mol}^{-1}$$

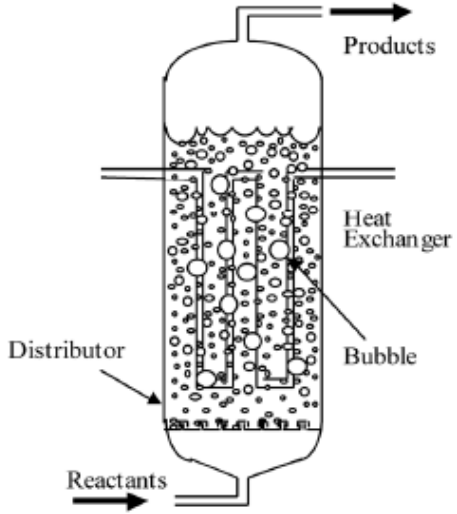
- Direct production from syngas
  - Higher equilibrium yield
  - Less recycles
  - Less unit operations
- Critical points
  - Even more heat production than methanol synthesis
  - Catalyst stability in presence of water

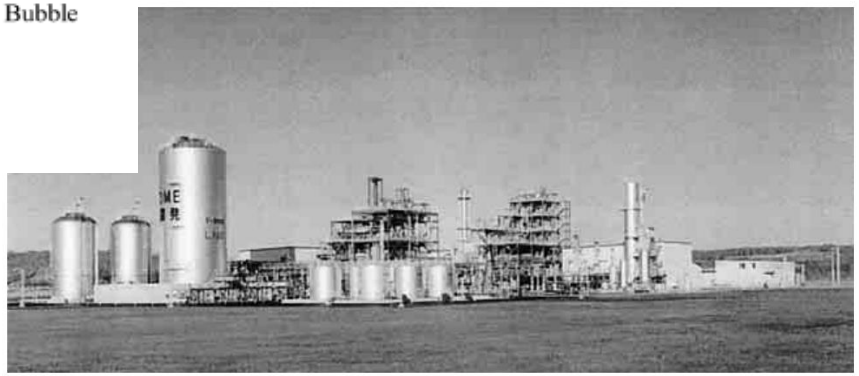


Beyond Oil and Gas: The Methanol Economy | Wiley Online Books
Dadgar, et al. (2016). *Catalysis today*, *270*, 76-84.

DIMETHYL ETHER
PRODUCTION - DIRECT

- Topsoe (1984 - 1987) Houston, Texas
  - Adiabatic gas-phase 1 t/d gasoline (part of TIGAS process)
  - CO_2 removal before syngas recycle; CO_2 as byproduct
- Air Products & Chemicals (1999) La Porte, Texas
  - Slurry-based pilot plant 10 t/d 'LPDME'
- JFE (2004-2006) Shiranuka-cho, Japan
  - Slurry reactor demonstration plant 100 t/d
  - CO_2 recycle to the autothermal methane reformer
  - H_2O as the byproduct





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JFE Technical Report No.8 (jfe-steel.co.jp)
Madsen. *Process for the preparation of dimethyl ether*. U.S. Patent No 7,652,176, 2010.
Single-Loop Conversion of Synthesis Gas to Gasoline through Methanol & DME (tu-freiberg.de)
Gogate, M. R. (2018). *Prog. Petrochem. Sci.*, *2*.

DIMETHYL ETHER
PRODUCTION - DIRECT

- KOGAS (2008) Incheon, Korea
  - Cooled fixed bed 10 t/d DME
  - CO_2 removal before syngas recycle; CO_2 as byproduct
- KIT Bioliq (2014) Karsruhe, Germany
  - Adiabatic fixed bed, 600 t/a gasoline
- MHI (2020) La Brea, Trinidad and Tobago
  - 20,000 t/a DME
- Linde-BASF (2019, announced)
  - Dry reforming and one-step production of DME

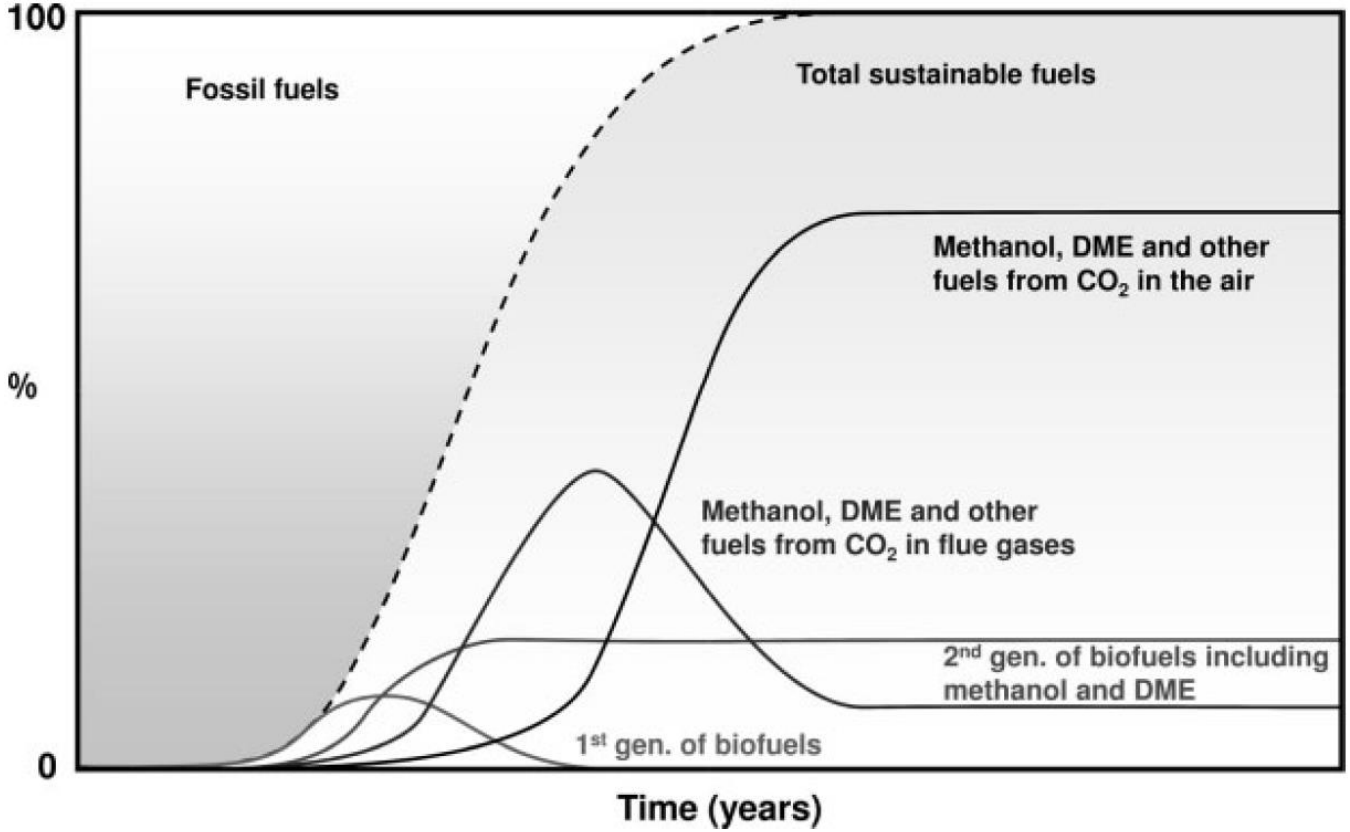
van Kampen, et al. (2020). *Journal of CO_2 Utilization*, *37*, 295-308.
Chung, et al. (2012). *Transactions of the Korean hydrogen and new energy society*, *23*(5), 559-571.
bioliq – Startseite
Stiefel, et al. (2011). *Fuel Processing Technology*, *92*(8), 1466-1474.
Boymans, E. H., & Liakakou, E. T. (2017). Advanced liquid biofuels synthesis.

Mitsubishi Heavy Industries, Ltd. Global Website | Commercial Operations Commence at Methanol / Dimethyl Ether Plant in Trinidad and Tobago (mhi.com)
News | 2019-01-10 | BASF Linde CO2-to-DME process (aboutdme.org)

RENEWABLE DME

RENEWABLE DME

- New opportunities
  - DME as 2nd generation biofuel
  - DME from flue gases
  - DME from CO_2 from the air
- Existing challenges remain
  - Efficiency (indirect synthesis)
  - Heat management (direct synthesis)
  - Catalyst deactivation by water (direct synthesis)
  - Energy-intensive purification (CO_2-DME separation)



Technology development

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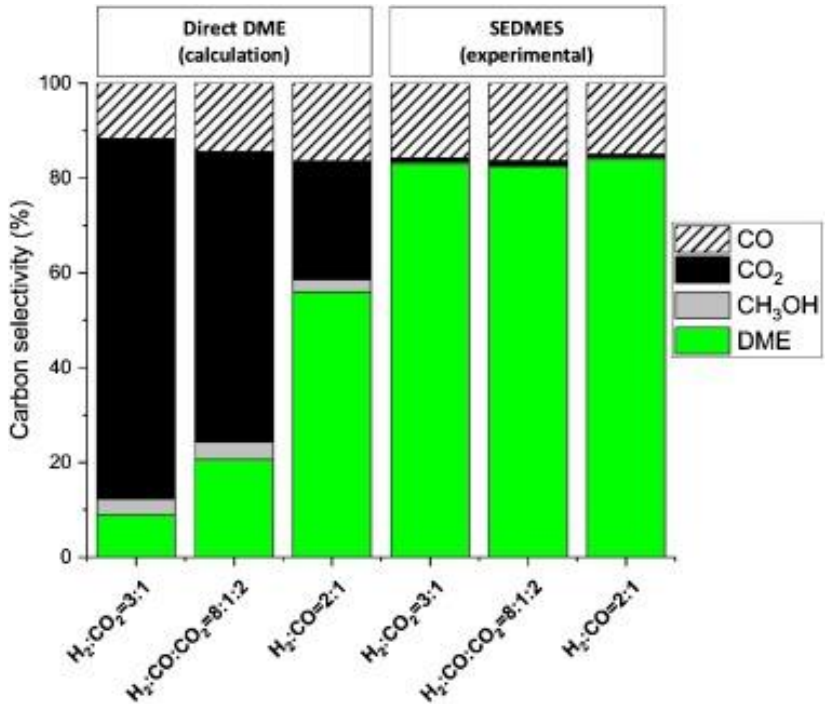
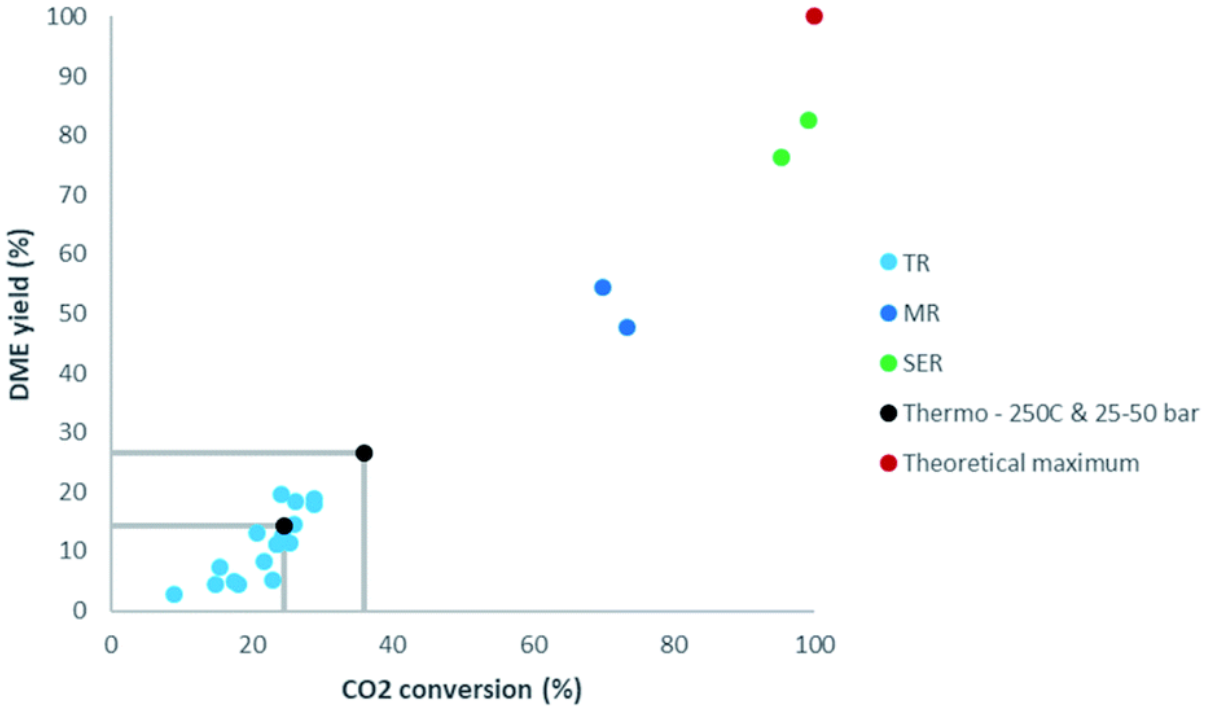
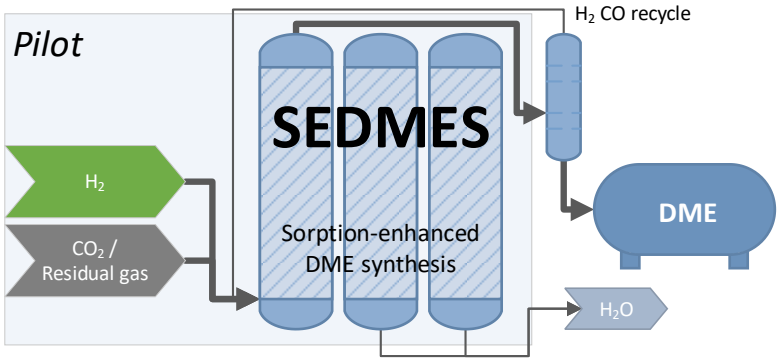
RENEWABLE DME

RENEWABLE DME - TECHNOLOGY

- Separation-enhanced reactors
  - Membrane-enhanced
  - Sorption enhanced (‘SEDMES’)







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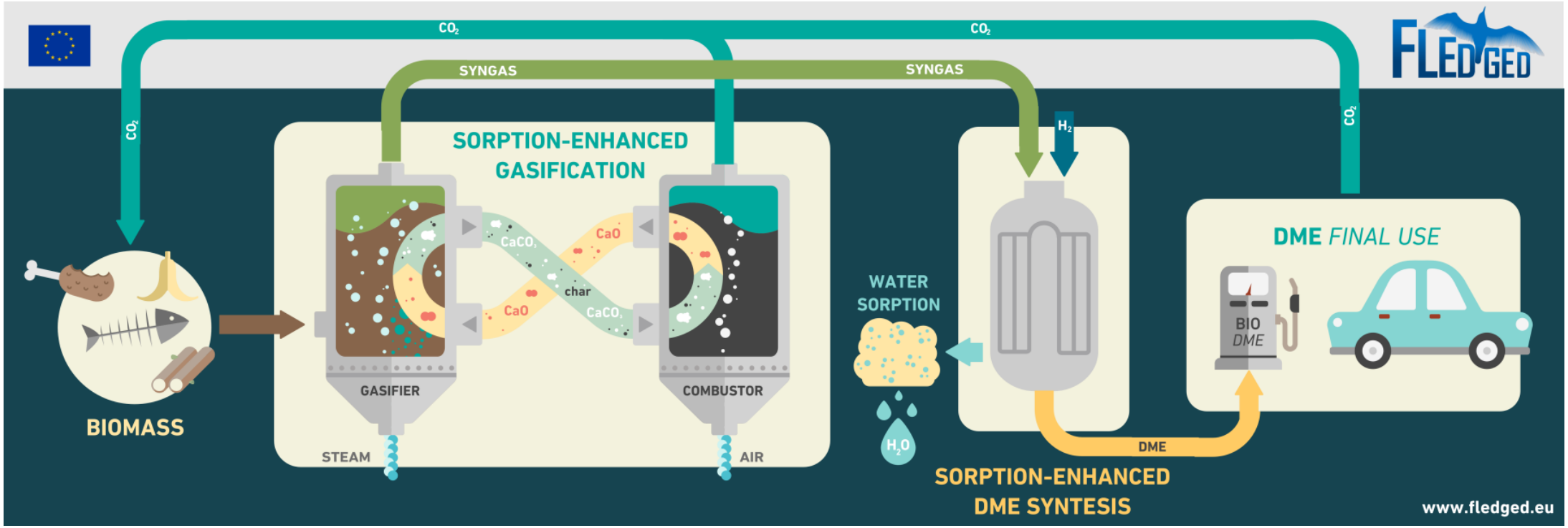
van Kampen, et al. (2020). *Journal of CO_2 Utilization*, *37*, 295-308.

BIOMASS TO DME
EU H2020 PROJECT - FLEDGED

- The *FLEDGED* project will deliver a process for *Bio-based Dimethyl Ether (DME)* production from **biomass** gasification, validated in ***industrially relevant*** environment (TRL5).



www.fledged.eu

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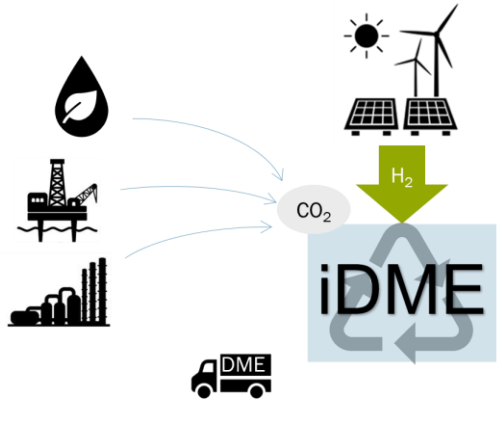
OUTLOOK

International DME Association
DME: 21st Century Energy
aboutdme.org

- New alliances, initiatives
  - Nordic Green, Denmark (2011): Renewable methanol, DME
  - BASF – Linde (2019): Direct DME
  - Nouryon – Enerkem – Air Liquide – Shell – PoRotterdam (2019): W2C, non-recyclable wastes to chemicals (MeOH-DME)
  - Oberon Fuels – SHV Energy (2020): accelerate the use of renewable DME
  - SHV Energy – KEW Technology (2021): Circular Fuels, Advanced thermal conversion technology for renewable DME
  - SHV Energy – UGI International (2021): Dimeta, advancing the production and use of renewable and recycled carbon Dimethyl Ether
  - DME Sweden
- Fuel standards developing
  - 2020 California Governor Gavin Newsom defines the tax rate for DME used as either a diesel replacement or blended with propane, and how it would be sold at retail to consumers.
  - European Committee for Standardization (CEN)
- Novel use cases
  - PtX, grid balancing
  - H_2 carrier, DME fuel cells
  - Industrial circularity: **iDME**

TechnipFMC
TNO
TATA STEEL



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THE ECONOMIST

MARCH 11TH, 1995

New fuel

The lawnmower's tale

COPENHAGEN

HALDOR TOPSOE is a happy man. A sprightly 82-year-old, he is renowned in Denmark for his outspoken views on industry, research, and how to combine the two. He learnt them from the great Dane of the century, Niels Bohr, and has kept alive the belief in far-sighted, open-minded research that the atomic theorist sought to foster when he guided Denmark's research after the second world war. The catalyst company that bears Mr Topsoe's name tries to live up to these ideals, and the new substitute for diesel fuel which it has recently developed may provide a successful example of the strategy; hence the happiness.

At present, dimethyl ether (DME) is mostly used as a propellant in aerosol sprays, a replacement for ozone-eating chlorofluorocarbons. In a previous life it was best known as a chemical step on the road to the production of synthetic fuels, an area that Topsoe was keen on. Low petrol prices in the 1980s made synthetic fuels unattractive, but the company kept up an interest in the stuff.

In 1991, an inspired Topsoe laboratory assistant named Svend-Erik Mikkelsen decided to take some DME home and try it in his lawnmower. After cutting the grass, he tried the fuel out in a diesel fork-lift at the factory. This experiment worked so well that the motor refused to stop, even when the ignition was switched off and the starter cables removed. Impressed, Mr Mikkelsen's managers let him pursue his experiments with researchers at the nearby Technical University of Denmark.

A year later, armed with hard data, Topsoe approached Amoco, an American oil company. This led to a collaboration between Topsoe, Amoco, an American diesel-engine manufacturer called Navistar and a diesel-engine research institute in Austria called AVL. This convinced the diesel engineers that DME is more than just a flash in the cylinder. The results were made public last week at the annual congress of the Society of Automotive Engineers in Detroit.

That DME is environmentally benign is no surprise, given its use in spray cans. The surprise is that is it still green after it has been burnt. Exhaust from a DME-driven diesel engine contains no sulphur, almost no soot (all that can be measured comes from the motor oil), and only about 20% of the nitrogen oxides that diesel produces.

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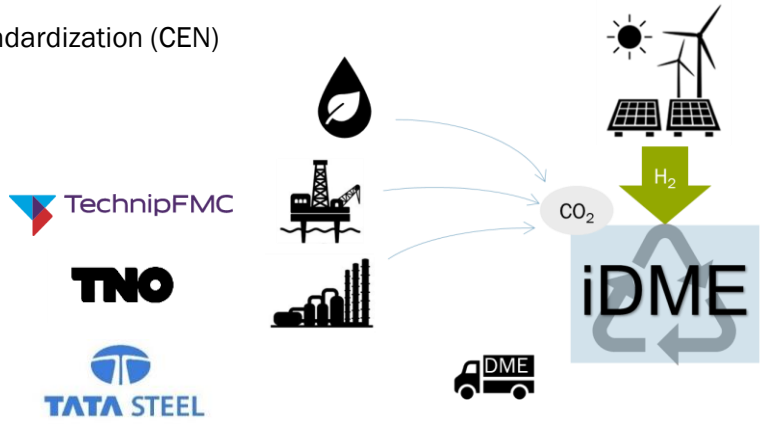

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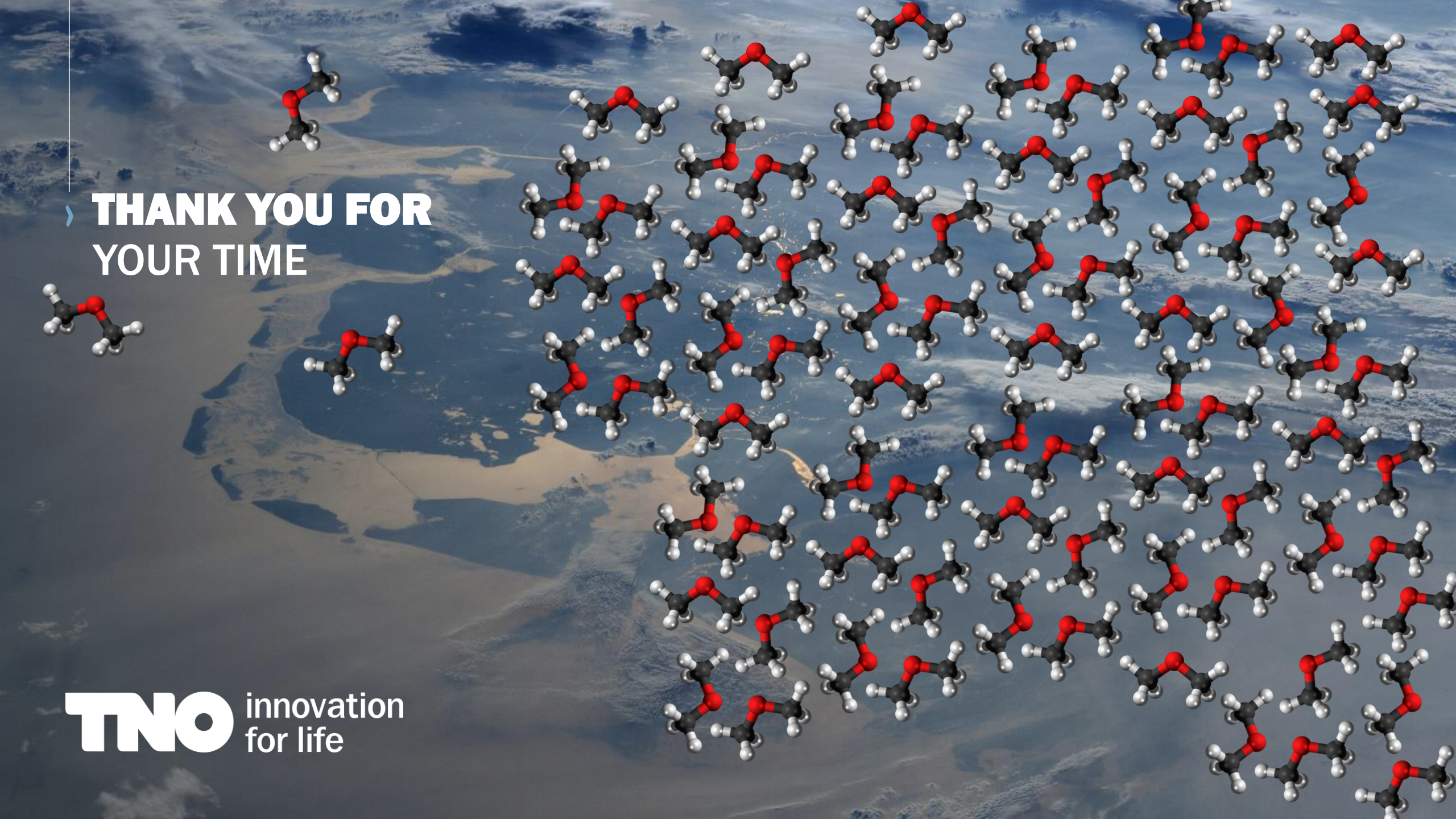
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TNO innovation for life