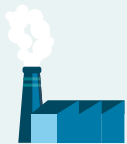


CARBON MANAGEMENT

7 OPPORTUNITIES FOR IMPROVING THE
CARBON FOOTPRINT THROUGH CO₂ UTILIZATION



REVERSE WATER-
GAS SHIFT



DRY REFORMING
OF METHANE

METHANATION
OF CO₂



METHANOL
SYNTHESIS



METHANOL-TO-
HYDROCARBONS



FUELS



DIALKYL
CARBONATES



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INTRO

CARBON MANAGEMENT: THE ROAD TO REDUCING CO₂ EMISSIONS IN THE CHEMICAL INDUSTRY

During the past years, public awareness of climate change has increased as a result of rising CO₂ emissions. Recently, the proportion of CO₂ in the atmosphere exceeded 400 ppm¹ for the first time in history. It is generally agreed that high levels of CO₂ cause global warming and extreme weather conditions. This rising CO₂ concentration is attributed to CO₂ emissions from various industries and the transportation sector. These emissions have dramatically increased since the middle of last century.

Due to regulation and taxation of CO₂ emissions and public pressure, industry and the transportation sector need to diminish their greenhouse gas output significantly and increase the share of renewable energies they use. In recent decades, the global economy has already taken steps to become more sustainable by reducing CO₂ emissions and making use of renewable energies. A shift in the raw material base away from coal and oil towards gas and renewable feedstocks as sources of energy and material plays a major role,

as does increased process efficiency. The ultimate goal is to achieve full carbon neutrality in a way that is acceptable to society. Governmental climate change goals aim for net-zero by 2050. To achieve that, established industry processes need to be improved, new concepts and technologies need to be developed, and the raw material basis needs to be fundamentally changed. The various challenges and opportunities associated with reducing CO₂ emissions along industrial value chains are outlined in "carbon management".

Maintaining an acceptable lifestyle with drastically reduced emissions is challenging. Even more challenging is the situation in emerging countries, where the steep rise in energy demands in the transportation, chemical industry, and energy sectors is met largely by fossil resources. Global CO₂ emissions reached 35 billion tons in 2019. An overview of how worldwide CO₂ emissions have evolved in the past 100 years is given below in figure 1.

¹EPICA DOME C CO₂ record (2015) & NOAA (2018)

ANNUAL TOTAL CO₂ EMISSIONS, BY WORLD REGION

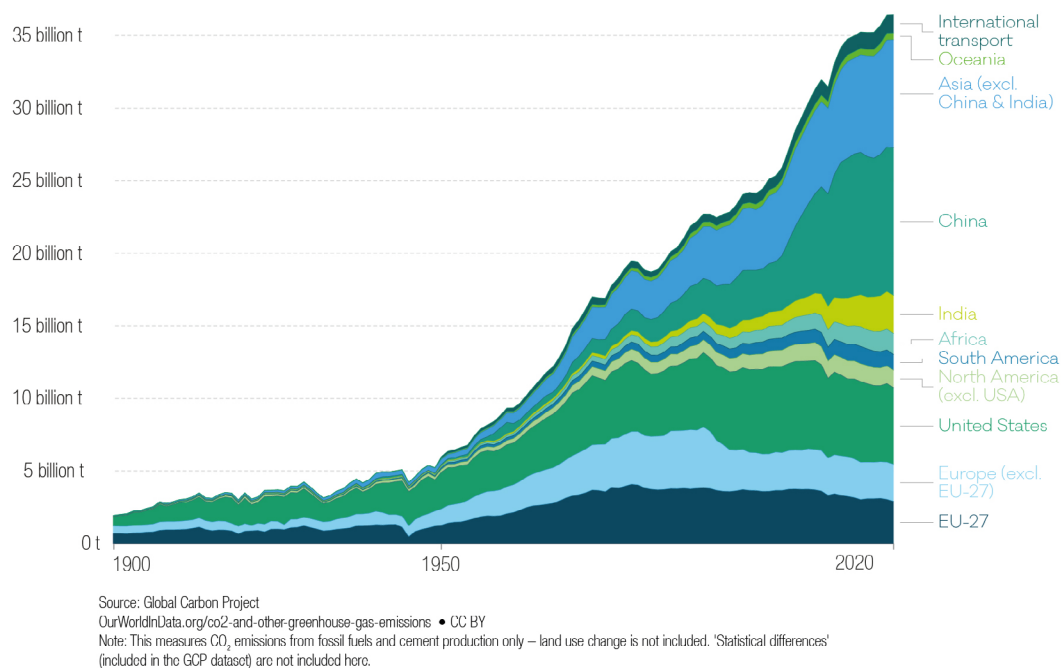


Figure 1: CO₂ emissions from fossil fuels and cement production by world regions & transport

The rate at which carbonaceous raw materials are transformed to ultimately end up as CO₂ or as waste is much higher than the rate at which raw materials are regenerated. In general, there are three pathways:

1. **Reduction of CO₂ generation**, or at least emissions, wherever possible by increasing process efficiency and utilizing renewable energies.
2. **Capture of CO₂** emitted into or already present in the atmosphere for storage or transformation into persistent products that do not interfere with our global climate regulation mechanisms.
3. **Utilization of CO₂** as a feedstock in chemical production processes. The carbon footprint generated from this approach will depend on the nature of the products that are made from CO₂ and on the source of energy driving the process. If persistent products are made using renewable energy sources, a negative carbon footprint is the result, which is, of course, extremely desirable.

A crucial element is the supply of low-carbon energy, which must be competitive with fossil-based energy in terms of price and availability. In the past, the cost of energy was the only KPI, but the economic case is likely to be strongly enhanced when the cost of carbon is considered by taxing CO₂ emissions. The share of renewable energies such as wind and solar power must be increased significantly to replace conventional power plants.

This white paper focuses on the **third pathway, where CO₂ is utilized as a feedstock in chemical processes**. Making use of existing assets and smart integration of CO₂ into the industrial value chain are key strategies for a fast transition.

Consequently, the current value chains will be analyzed and potential starting points for renewable processes will be discussed.

Since the majority of CO₂ emissions come from the combustion of fossil fuels, one key to a decarbonized future is to recycle CO₂ in fuel-producing processes. At the moment, most fuel is produced by oil refining, but alternative processes using the conversion of synthesis gas as a key step are already established.

This paper discusses many different processes in catalytic CO₂ utilization and conversion in terms of their potential and challenges in future industrial applications for achieving a lower carbon footprint.



Figure 2: Overview of the processes covered in this white paper



METHANOL SYNTHESIS

METHANOL SYNTHESIS FROM CO₂ AS A MAJOR OR SOLE FEEDSTOCK IS DISCUSSED AS ONE OPTION FOR OVERCOMING CLIMATE CHANGE

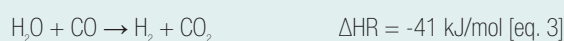
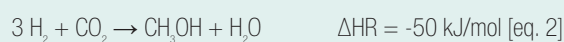
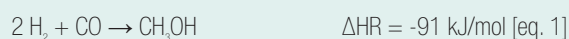
Methanol has one of the highest production capacities among organic base chemicals and is thus of extreme importance for the global chemical industry. One unique feature of MeOH is its versatility. It can be the starting material for other oxygen-con-

taining base chemicals (formaldehyde, acetic acid), it can be used to produce light olefins and fuels via the various methanol-to-hydrocarbons processes, and serve as a drop-in fuel in combustion engines.

METHANOL AS A VERSATILE BASE CHEMICAL

Methanol is available via various large-scale processes starting from synthesis gas. Though the formation from synthesis gas is frequently described by eq. 1, it is well established that MeOH formation proceeds by hydrogenation of CO₂ (eq. 2), and that the CO-consuming step is the water-gas shift re-

action (eq. 3). The synthesis of MeOH from CO₂ alone is discussed as one option for overcoming climate change associated with increasing levels of CO₂ emissions and CO₂ enrichment in the atmosphere.



CHALLENGES FROM USING CO₂ AS A FEEDSTOCK

The use of CO₂ as the major or sole feedstock (see also figure 4) for MeOH synthesis poses two major challenges: the reaction rates of the established Cu-based catalysts with pure CO₂ are lower than with CO-rich feed gases; and the selectivity for MeOH can be lower due to formation of CO by the competing reverse water-gas shift reaction (eq. 3 backward). Further development is required in preparing and testing novel material compositions, for example with the goal of improving the reaction rate and selectivity with unconventional feedstocks.

Furthermore, benchmarking of commercial catalysts with regard to activity, selectivity, and stability, including protocols for accelerated thermal aging, is of great importance. The process needs to be optimized under conditions similar to those found in commercial plants, i.e. with separation of the produced MeOH containing liquid inside the reactor system for further analysis and recycling of the gaseous fraction of the effluent back to the reactor inlet.

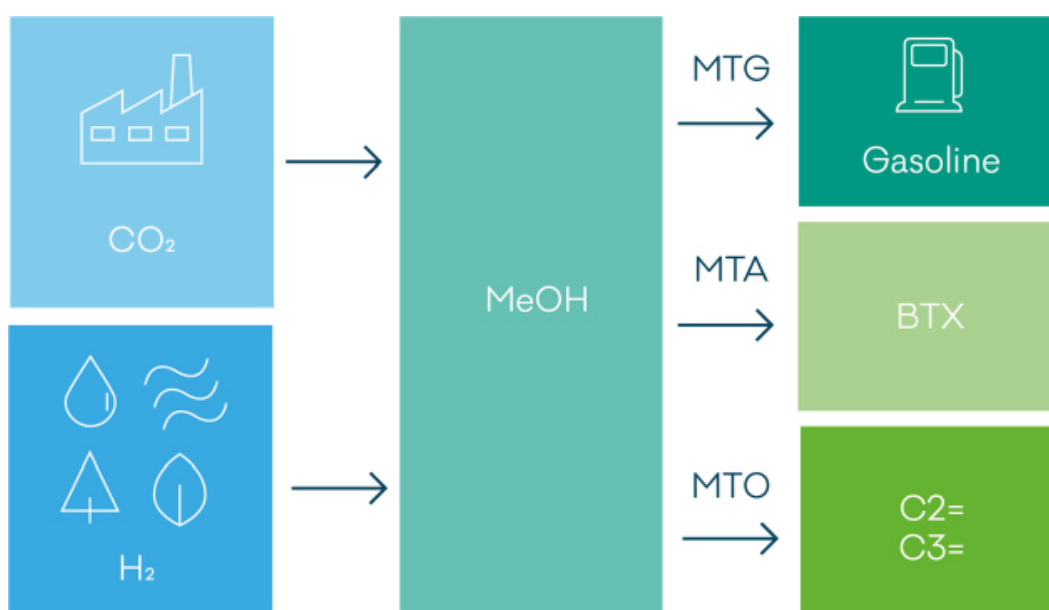


Figure 3: From CO₂ and H₂ via methanol to valuable products

LITERATURE RELATED TO METHANOL SYNTHESIS

BASF,

"BASF develops process for climate-friendly methanol", press release, 2019.

P. Kolb, T. Kaltschmitt,

"Methanol Synthesis in a Fixed Bed Recycle-reactor System: Effect of once-Through and Recycle Operation on Activity and Productivity", DGMK Conference Paper, 2017.

P. Kolb, T. Kaltschmitt,

"Methanol Synthesis: Effects in once-Through and Recycle Operation", DGMK Conference Presentation, 2017.



METHANOL-TO-
HYDROCARBONS

CONVERSION PROCESSES OF GREEN METHANOL: FROM A RENEWABLE FEEDSTOCK TO A BROAD RANGE OF BASE CHEMICALS

METHANOL AS AN IMPORTANT INDUSTRIAL FEEDSTOCK

Methanol can be derived from various feedstocks containing carbon, such as biomass, coal, gas and even CO₂. Considering the current discussion of how to solve the climate crisis, methanol plays a key role in many carbon capture and utilization pathways. Sustainable syngas using green H₂ and CO₂ can further be converted to methanol as a valuable carbon-neutral compound exhibiting increased energy density. Methanol can serve as an intermediate to produce hydrocarbons within a renewable context.

First discovered by Mobil in the 70s, the conversion of MeOH to hydrocarbons (MTH) has attracted significant attention. Starting historically from a flexible carbon feedstock, basic petrochemicals and fuels can be efficiently obtained.

The hydrocarbons can be used for different production routes in the chemical and petrochemical industries. The current discussion about climate change and CO₂ reduction also plays a role in the topic described herein. Reaching net zero by 2050 or "fit for 55" – the European Commission's goal to reduce carbon emissions by 55 % by 2030 – are only achievable with a broad technology portfolio for carbon capture, utilization and storage. Considering new synthesis routes for methanol production by utilizing CO₂, the methanol-to-hydrocarbon reaction will also have a significant impact on lowering the carbon footprint compared to similar products via conventional routes.

CONVERSION PROCESSES OF GREEN METHANOL: FROM A RENEWABLE FEEDSTOCK TO A BROAD RANGE OF BASE CHEMICALS



Figure 4: Different methods of methanol utilization for further usage

ROUTES TO PRODUCE HYDROCARBONS FROM METHANOL

The methanol-to-hydrocarbon reaction is still part of scientific research across the world. The zeolite materials ZSM-5 and SAPO-34 are often mentioned as catalysts for this reaction type. The product spectrum is heavily dependent on several parameters, such as the microstructure of the zeolitic catalyst and its acidity as well as the temperature and pressure of the process, the reactant concentration in the feed, and the contact time. Using zeolites with narrow channels as catalysts (such as SAPO-34), lower olefins are produced with high selectivity, but the lifetime of the catalyst is short because the channels are blocked by the heavier products. On the other hand, ZSM-5 with wider channels has a much longer lifetime but generates a complex mixture of linear and branched olefins and paraffins as well as substituted benzenes. Depending on the desired product spectrum, research activities are dedicated to the formation of aromatics (methanol-to-aromatics = MTA), gasoline (methanol-to-gasoline = MTG), or olefins (methanol-to-olefins = MTO).

The MTG process was scaled up to the pilot stage at the beginning of the 90s. It has recently seen a revival, since it offers a way to monetize natural gas if coupled with established methane reforming and MeOH synthesis processes. The MTO process has been commercialized in Asia, especially in regions that are rich in coal but lack large oil or gas resources. It offers a way to produce lower olefins, crucial starting materials for classical petrochemical processes, by a value chain comprising coal to synthesis gas and synthesis gas to MeOH. Since the MTO catalysts rapidly lose activity due to the accumulation of carbonaceous residues in the catalyst microstructure, the process is run in a fluidized bed with continuous catalyst regeneration. Selectivities to ethene and propene of more than 80 % have been reported. Both the rapid deactivation and the still considerable number of heavier byproducts leave room for further catalyst development and optimization. Testing of MTO catalysts on a lab-scale requires fast online analysis tools based on gas chromatography or spectroscopy and reactor technology for short contact time experiments using fluidized bed or entrained flow concepts.

SCIENTIFIC LITERATURE OVERVIEW

Alfred Haas, Christoph Hauber, Marius Kirchmann,

"Time-Resolved Product Analysis of Dimethyl Ether-to-Olefins Conversion on SAPO-34", *ACS Catal.*, 2019, 9, 5679-5691. [DOI](#).

Jerzy Szczygieł, Marek Kułazynski,

"Thermodynamic limitations of synthetic fuel production using carbon dioxide: A cleaner methanol-to-gasoline process", *Journal of Cleaner Production*, 2021, 276, 122790. [DOI](#).

U. Olsbye, S. Svelle, M. Bjørgen, P. Beato, T. V.W. Janssens, F. Joensen, S. Bordiga, K. Petter Lillerud,

"Conversion of methanol to hydrocarbons: how zeolite cavity and pore size controls product selectivity", *Angew. Chem. Int. Ed.*, 2012, 51, 5810 – 5831. [DOI](#).

Peng Tian, Yingxu Wei, Mao Ye, Zhongmin Liu,

"Methanol to Olefins (MTO): From Fundamentals to Commercialization", *ACS Catal.*, 2015, 5, 1922–1938. [DOI](#).



REVERSE WATER- GAS SHIFT

REDUCTION OF CO₂ TO CO VIA THE REVERSE WATER-GAS SHIFT REACTION, A SUSTAINABLE ROUTE FOR SYNGAS PRODUCTION

THE ROLE OF CO INSIDE THE INDUSTRIAL VALUE CHAIN

CO is a well-established base chemical in the chemical industry. Typically, it is used in the presence of hydrogen as synthesis gas. Although handling is challenging due to its toxicity, its unique properties make it a versatile feedstock. It can be generated from fossil and renewable resources.

Currently, most syngas is produced via steam methane reforming. Products derived from syngas cover a broad spectrum. Depending on the catalysts, waxes or olefins can be produced

via Fischer Tropsch synthesis, which are utilized as feedstock in the fuel, lubricant, or polymer industry.

Furthermore, syngas can be blended with CO₂ for methanol/DME synthesis. CO can also react with other organic compounds, e.g. the carbonylation of methanol towards acetic acid or the hydroformylation of olefins to oxo-aldehydes and oxo-alcohols.

UTILIZATION OF CO₂ FROM AIR OR FLUE GAS AS A CO FEEDSTOCK

A promising approach to reducing CO₂ emissions is to reduce CO₂ to CO via the reverse water-gas shift reaction and utilize the more sustainable syngas generated in the established syngas conversion processes (see figure 6). To effectively reduce the carbon footprint, H₂ must be produced from renewable sources, such as wind and solar-powered water electrolysis. CO₂ can be supplied from resources like waste disposal or

industrial processes exhibiting large CO₂ emissions, such as steel or cement production, or directly from air. The syngas produced in this way can serve as a renewable alternative to conventional syngas from steam methane reforming, which also makes the products from these syngas conversion processes more sustainable.

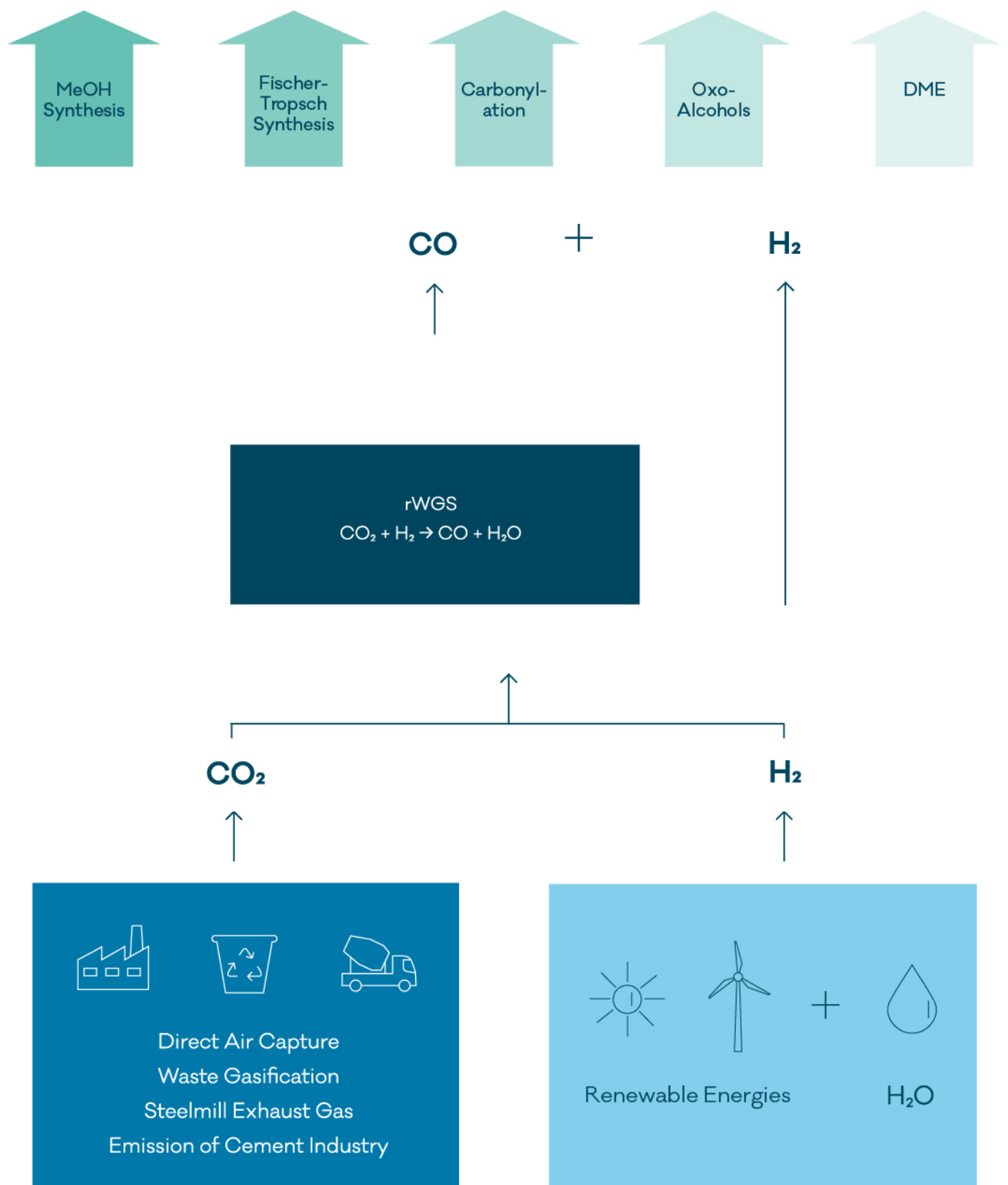


Figure 5: Reverse Water-Gas Shift

WHAT ARE THE CHALLENGES IN THE REVERSE WATER-GAS SHIFT REACTION?

First and foremost, production of green H_2 on a sufficiently large scale is still not established. The cost-efficient supply of hydrogen from low-carbon electricity will play a key role in the successful application of sustainable rWGS in the chemical industry. The CO_2 used is present only in low concentrations in the gaseous feedstocks and contains a range of impurities. This requires gas separation and purification techniques, or

a new generation of catalysts with sufficient activity, selectivity, and stability. So far, catalyst development is still in its early stages. Several catalysts are under discussion, such as $K-Mo_2C$, Ni/SiO_2 or Pt/TiO_2 . The challenges in catalyst development are comparable to those faced by steam methane reforming catalysts, where hydrothermal ageing and coking are important deactivation mechanisms.

SCIENTIFIC LITERATURE OVERVIEW OF ACADEMIC AND INDUSTRIAL RWGS APPLICATIONS

Y. A. Daza, J. N. Kuhn,

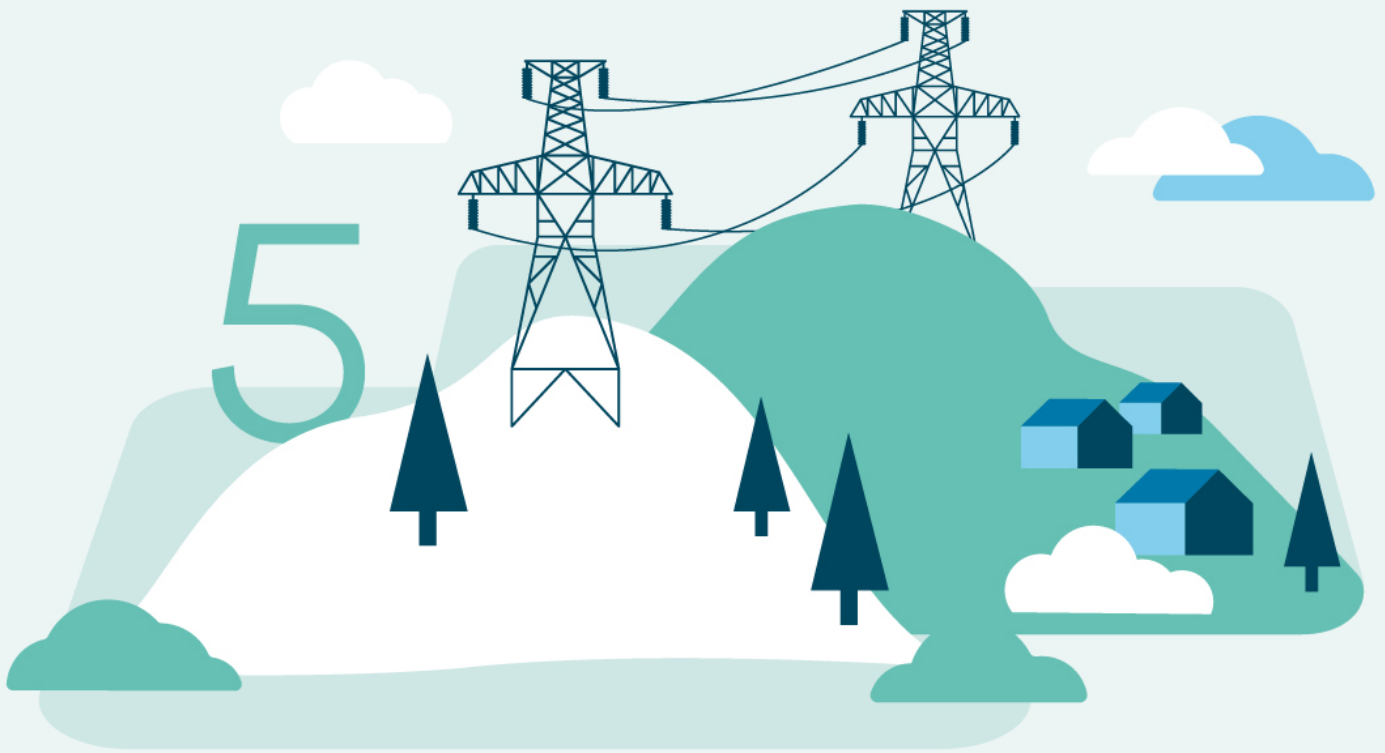
" CO_2 conversion by reverse water-gas shift catalysis: comparison of catalysts, mechanisms and their consequences for CO_2 conversion to liquid fuels", RSC Adv., 2016, 6, 49675-49691. [DOI](#).

Thalita S. Galhardo, Adriano H. Braga, Bruno H. Arpini, János Szanyi, Renato V. Gonçalves, Bruno F. Zornio, Caetano R. Miranda, and Liane M. Rossi,

"Optimizing Active Sites for High CO Selectivity during CO_2 Hydrogenation over Supported Nickel Catalysts", J. Am. Chem. Soc., 2021, 143, 4268–4280. [DOI](#).

M. Juneau, M. Vonglis, J. Hartvigsen, L. Frost, D. Bayerl, M. Dixit, G. Mpourmpakis, J. R. Morse, J. W. Baldwin, H. D. Willauer, M. D. Porosoff,

"Assessing the viability of $K-Mo_2C$ for reverse water–gas shift scale-up: molecular to laboratory to pilot scale", Energy Environ. Sci., 2020, 13, 2524–2539. [DOI](#).



METHANATION OF CO₂

METHANATION AS A TOOL FOR UPGRADING FLUE GAS STREAMS CONTAINING CO/CO₂ TO SYNTHETIC NATURAL GAS

Within the power-to-gas concept, renewable H₂ is produced from wind and solar powered water electrolysis and further utilized for the catalytic methanation of CO and CO₂. Synthetic natural gas (SNG) serves as a long-term energy carrier, e.g. for grid stability in future power systems, where the fluctuating supply of renewable energies has to be matched with power demand temporally and locally by re-converting SNG into

electricity. Furthermore, renewable methane is suitable as a CO₂-neutral fuel for heavy-duty traffic, e.g. LNG-trucks continuing to use well-developed combustion engines. One big advantage is the existing infrastructure, since SNG can be injected, distributed, and stored in the wide-ranging natural gas grid. This also allows the production of SNG in small, decentralized plants.

WHAT ARE THE CHALLENGES IN THE METHANATION OF INDUSTRIAL OFF-GAS?

The hydrogenation of pure CO or CO₂ feeds to SNG is well developed. However, utilizing industrially relevant feedstocks and process conditions to deliver pipeline-quality SNG, as in the methanation of raw biogas, flue, or furnace gas (e.g. from steel or cement production), requires appropriate catalyst and process design. Usually, effluent gas from such applications contains mixtures of CO and CO₂ featuring a wide range of compositions that need to be converted to SNG. Large proportions of CH₄ can already be included in the feed for methanation that needs to be considered.

In addition, trace components are present which can harm the active site of the catalyst through poisoning, oxidation, or coking. The catalysts face various challenging process conditions

in process-integrated methanation reactions. Depending on the process steps upstream or downstream of the methanation reactor, SNG has to be produced in unfavorable parameter ranges for temperature, pressure, and severity that may lead to sintering of the metal nanoparticles and degradation effects in the catalyst. Therefore, it is crucial to test the catalysts under industrially relevant conditions to evaluate their performance and stability. Troubleshooting / tech service support campaigns need to be executed in parallel to industrial methanation plant operation in order to optimize processes. For upcoming catalyst change-out, competitive catalyst testing will help to find the best candidate and ensure the quality of the product.

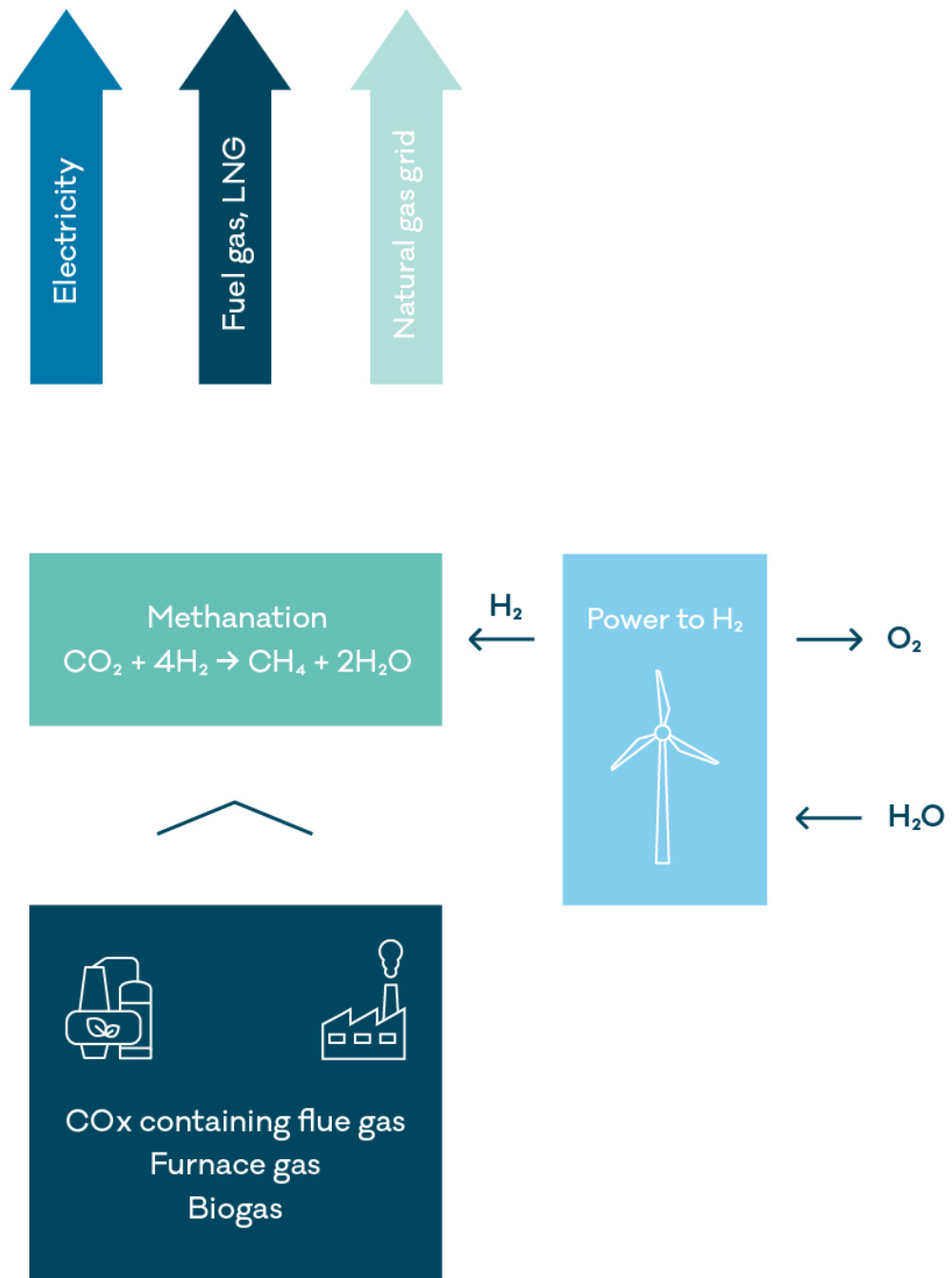


Figure 6: Methanation process

SCIENTIFIC LITERATURE OVERVIEW OF INDUSTRIAL METHANATION APPLICATIONS

1000 h biogas methanation in Denmark has recently been published by Dannesboe et al. The direct catalytic upgrading of biogas was demonstrated to be ready for industrial-scale implementation to deliver pipeline-quality gas. A status review about power-to-gas including electrolysis and methanation was reported by Thema et al. This report summarizes 153

completed, recent, and planned pilot and demonstration projects worldwide since 1988. An overview of developed methanation catalysts and reactor concepts is given by Ashok et al. Development of bimetallic catalysts, benchmarking and kinetic investigations was performed by Mutz et al. for CO₂ methanation within academic research.

C. Dannesboe, J.B. Hansen, I. Johannsen,

"Catalytic methanation of CO₂ in biogas: experimental results from a reactor at full scale", *React. Chem. Eng.*, 2020, 5, 183-189. [DOI](#).

J. Ashok, S. Pati, P. Hongmanorom, Z. Tianxi, C. Junmei, S. Kawi,

"A review of recent catalyst advances in CO₂ methanation processes", *Catal. Today*, 2020, 356, 471–489. [DOI](#).

M. Thema, F. Bauer, M. Sterner,

"Power-to-Gas: Electrolysis and methanation status review", *Renew. Sustain. Energy Rev.*, 2019, 112, 775-787. [DOI](#).

B. Mutz, M. Belimov, W. Wang, P. Sprenger, M.-A. Serrer, D. Wang, P. Pfeifer, W. Kleist, J.-D. Grunwaldt,

"Potential of an Alumina-Supported Ni₃Fe Catalyst in the Methanation of CO₂: Impact of Alloy Formation on Activity and Stability", *ACS Catal.*, 2017, 7, 6802-6814. [DOI](#).



DRY REFORMING OF METHANE

SYNGAS PRODUCTION — A WELL APPLIED AND UNDERSTOOD PART OF THE CHEMICAL INDUSTRY

Syngas generation is currently performed on the basis of fossil resources. The most important process is steam methane reforming, which is a strong endothermic process. The technology is well established and allows cost-efficient production of syngas or H_2 on a large scale. The ratio of $H_2:CO$ is predefined by the feedstock as well as the process.

Other commercialized processes are auto thermal reforming (ATR), where oxygen and steam are introduced, and partial oxidation (POX), where oxygen is also introduced. The difference

between ATR and POX is mainly the oxygen content, which is higher in POX, yielding a lower $H_2:CO$ ratio.

The feedstock also influences the resulting $H_2:CO$ ratio. Due to different natural carbon and hydrogen content, coal yields an $H_2:CO$ ratio of around 1:1, oil has a higher ratio of 2:1, and natural gas has the highest at up to 3:1. Water plays an important role, since it shifts CO to CO_2 , which is another way to produce hydrogen. This is an attractive way of tailoring the syngas composition to the subsequent processes.

REDUCING THE CARBON FOOTPRINT THROUGH SUSTAINABLE SYNGAS PRODUCTION FROM BIOBASED AND FOSSIL CH_4 AND CO_2

CH_4 and CO_2 are both greenhouse gases, which can be converted to CO -rich syngas via dry reforming. Sources of methane can be renewable, e.g. derived from ruminant digestion and manure management associated with domestic livestock, waste, or biomass.

In addition, fossil resources such as natural gas or coal can be applied. Compared to syngas production via steam methane reforming, dry reforming can be operated at a low or even negative carbon footprint, since significant volumes of CO_2 are consumed in the process.

Since fossil and renewable feedstocks can be used, dry reforming might play an important role in the transition of the chemical industry. The produced CO -rich synthesis gas can be used in established syngas conversion processes such as Fischer Tropsch synthesis, the production of methanol, dimethyl ether (DME) as well as the oxo synthesis. Due to the low $H_2:CO$ ratio it might be necessary to increase the $H_2:CO$ ratio in a subsequent process step or to add renewable H_2 to the product stream.

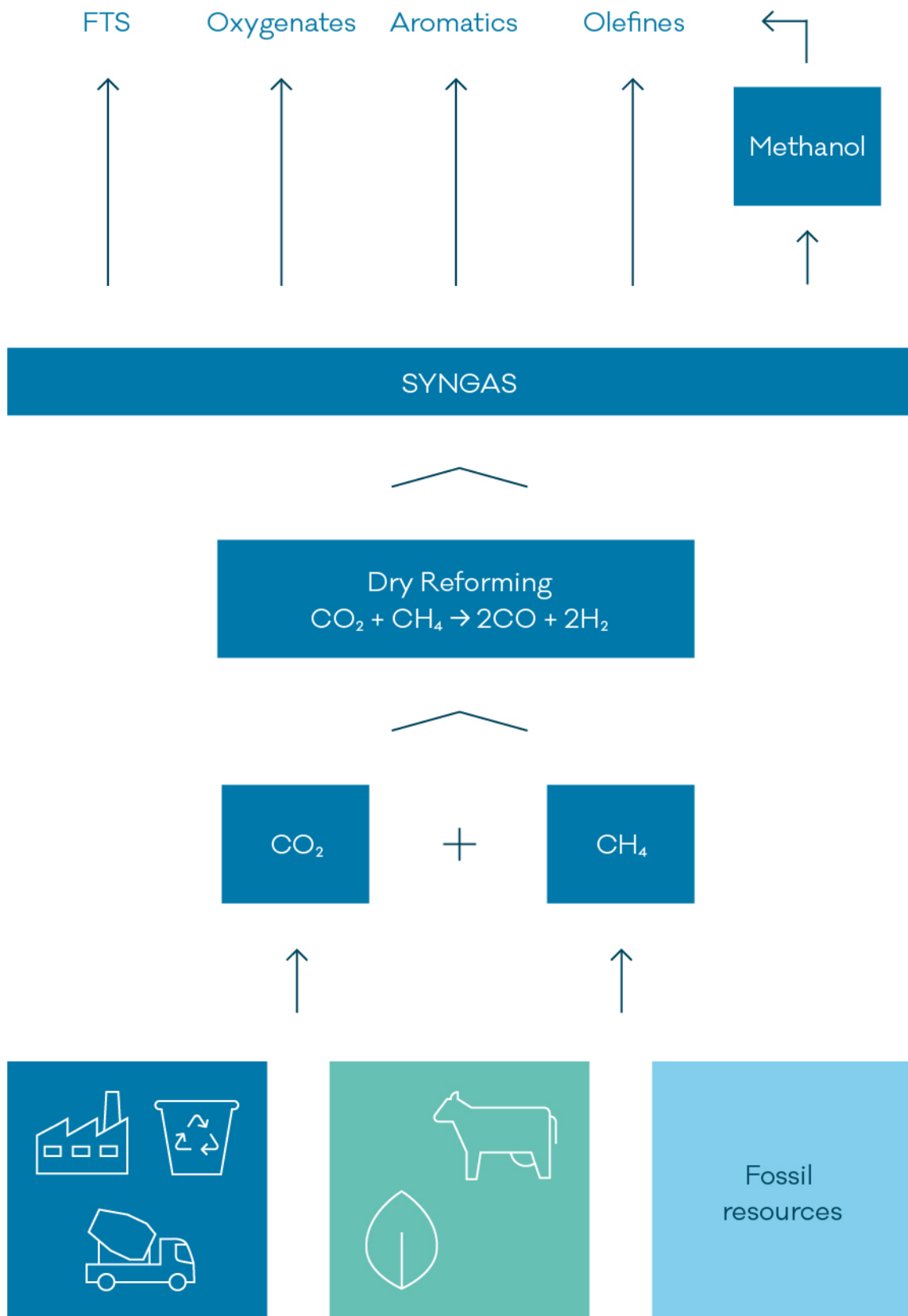


Figure 7: Dry reforming of methane

WHAT ARE THE CHALLENGES IN DRY REFORMING OF METHANE?

First, dry reforming of methane is still at an early-stage compared to well-applied syngas generation technologies like steam reforming of methane, auto thermal reforming, or partial oxidation of methane. The supply and utilization of CO_2 feeds might be decentralized where fossil-derived feed is converted on an industrial scale. Therefore, cost-efficient processes need to be developed on both a small and large scale. The CH_4 and CO_2 supplied will come from manifold sources with a wide ran-

ge of impurities. This requires gas separation and purification techniques, or a new generation of catalysts with sufficient activity, selectivity, and stability. So far, catalyst development is still in its early stages and the challenges in catalyst development are comparable to those faced by steam methane reforming catalysts, where hydrothermal ageing and coking are important deactivation mechanisms.

SCIENTIFIC LITERATURE OVERVIEW OF ACADEMIC AND INDUSTRIAL DRY REFORMING APPLICATIONS

K. Wittich, M. Krämer, N. Bottke, S. A. Schunk,

"Catalytic Dry Reforming of Methane: Insights from Model Systems", ChemCatChem, 2020, 12, 2130-2147. [DOI](#).

A. Giehr, L. Maier, S. A. Schunk, O. Deutschmann,

"Thermodynamic Considerations on the Oxidation State of $\text{Co/Y-Al}_2\text{O}_3$ and $\text{Ni/Y-Al}_2\text{O}_3$ Catalysts under Dry and Steam Reforming Conditions", ChemCatChem, 2017, 10, 751-757. [DOI](#).

M. Usman, W. M. A. Wan Daud, H. F. Abbas,

"Dry reforming of methane: Influence of process parameters - A review", Renew. Sust. Energ. Rev. 2015, 45,710–744. [DOI](#).



E-FUELS

E-FUELS AS ONE POTENTIAL OPTION FOR DECARBONIZING THE TRANSPORTATION SECTOR

The production of renewable fuels from CO₂ and H₂ via power-to-liquid (PtL) technologies is becoming increasingly important. Considering the current climate debate, e-fuels are recognized as one option for decarbonizing the fuels value chain, which is mainly based on fossil resources at the moment. The term e-fuel also implies the use of green energy to produce the raw material hydrogen, e.g. via electrolysis, and to run the whole production process itself. Many activities in this field are ongoing and one promising goal is to reduce

the carbon footprint of the transportation sector. In addition to the discussion on the use of batteries or fuel cells, e-fuels also play an important role. As such, several technologies are being considered in parallel to address solutions for the future. The aviation sector is particularly reliant on e-fuel technology. Several companies around the globe are currently publishing their activities regarding sustainable aviation fuel but there are many remaining obstacles on the pathway to sufficient e-fuels supply, not only for jet fuel.

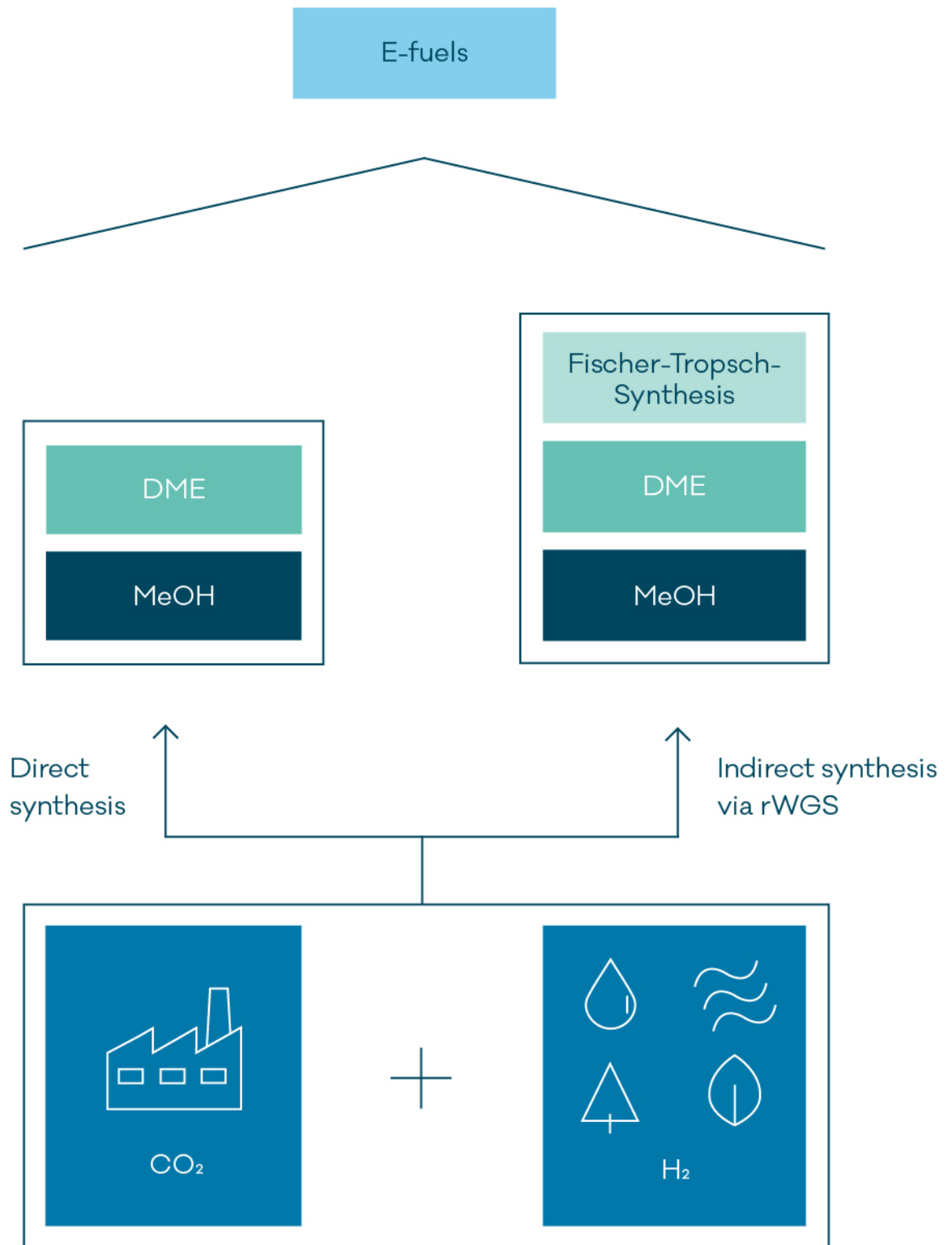


Figure 8: E-fuels

METHODS OF PRODUCING E-FUELS

The most promising methods for producing e-fuels include methanol, DME as C1 building block, and Fischer-Tropsch synthesis. Conventional FT or MeOH production technology can be applied in converting CO₂ and renewable H₂ into synthesis gas, e.g. via upstream rWGS reaction using an additional process step.

Methanol and DME can be used directly as drop-in fuels or be converted into kerosene or gasoline using different technologies. Hydrocarbons and waxes from FT synthesis can be upgraded via hydrocracking and isomerization to obtain synthetic fuels. With regard to FT synthesis, this known technology produces different types of fuel such as gasoline, kerosene, or diesel, and therefore offers a higher degree of flexibility.

Other R&D activities address MeOH/DME or FT synthesis directly from CO₂ and H₂. However, this requires in-depth investigation and research efforts into catalyst development and process optimization. Fischer-Tropsch synthesis from CO₂ requires catalyst systems with shift activity as well as tests in industrial-scale reactors.

Mitigating climate change can only be addressed by using a variety of technologies to reduce the carbon footprint, and e-fuels could be a part of the technology pool. Despite all the possibilities mentioned above, the use of e-fuels is still under debate. There will be several challenges for R&D as well as in building up the technology that will need to be overcome in the next decade.

SCIENTIFIC LITERATURE OVERVIEW OF ACADEMIC AND INDUSTRIAL APPLICATIONS

V. Dieterich, A. Buttler, A. Hanel, H. Spliethoff, S. Fendt,

"Power-to-liquid via synthesis of methanol, DME or Fischer-Tropsch-fuels: a review", Energy & Environmental Science Royal Society of Chemistry, 2020, 3207-3252. [DOI](#).

C. Schulz, P. Kolb, D. Krupp, L. Ritter, A. Haas, M. Soorholtz, T.E. Maldonado, T.B. Thiede, C. Knobloch,

"Preparation and High-Throughput Testing of TiO₂-Supported Co Catalysts for Fischer-Tropsch Synthesis", Catalysts, 2021, 11, (3), 352. [DOI](#).

D. Wang, Z. Xie, M.D. Porosoff, J.G. Chen,

"Recent advances in carbon dioxide hydrogenation to produce olefins and aromatics", Chem. 2021, 7, 1-35. [DOI](#).



DIALKYL CARBONATES

GREEN CHEMICALS AND SOLVENTS WITH POTENTIAL FOR SUSTAINABLE SYNTHESIS ROUTES

Dialkyl carbonates are considered to be green chemicals due to their biodegradability and low toxicity. In addition, they can benefit from sustainable synthesis routes by utilizing CO₂ and renewable alcohols (e.g. synthesis of green methanol).

Dialkyl carbonates act as excellent reagents and solvents in chemical applications such as pharmaceuticals, fine chemicals and pesticides. In particular, dimethyl carbonate (DMC) is used as a carbonylation and alkylation agent in organic synthesis. Dialkyl carbonate mixtures are used as a co-solvent in electrolytes for lithium ion batteries. They are used as solvents in adhesives, coatings, paints, and ink formulations. DMC is used in polycarbonate production. Diethyl carbonate (DEC) and DMC are under discussion as fuel additives (e.g. as particulate reducing agents for emissions control). The demand for dialkyl

carbonates is expected to grow further over the coming years. For instance, DMC demand has doubled (from 396 kton to 786 kton) from 2010 to 2018 with an average annual growth rate of 7.8 %, according to Nexant.

In their early days, symmetrical dialkyl carbonates were produced by phosgene alcoholysis. This method was finally banned for safety and environmental reasons. Alternative methods are oxidative carbonylation of the respective alcohols with carbon monoxide in gas or liquid phase, or the conversion of CO₂:

- Direct conversion of CO₂ and alcohols
- Alcoholysis of urea
- Transesterification of cyclic carbonates obtained from CO₂ and epoxides

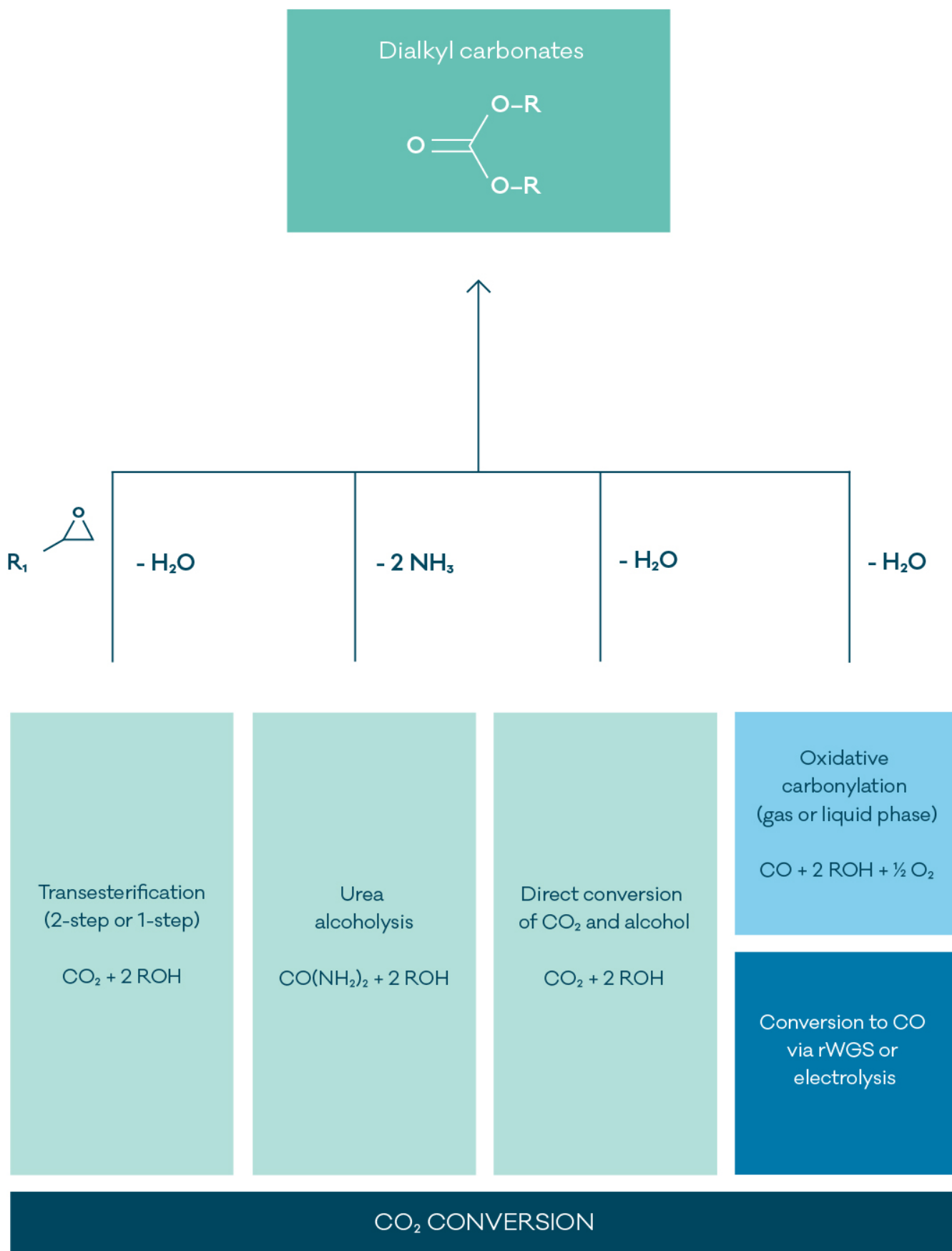


Figure 9: Dialkyl carbonates

WHAT ARE THE CHALLENGES IN THE SYNTHESIS OF DIALKYL CARBONATES?

Direct synthesis from CO₂ and alcohols would be the ideal and most sustainable production route. However, this route suffers from the low reactivity of CO₂ and thermodynamic limitations, and has not left the lab phase so far.

Oxidative carbonylation and the two-step transesterification process (with an intermediate cyclic carbonate) are the current industrial processes. The development and optimization of active and stable catalysts without major separation efforts is of great importance for these commercial processes. With the trend towards larger electrolyzers, oxidative carbonylation could profit from renewable energy and as yet unused sources of industrial CO₂. In this way, CO can be considered the electrochemically activated form of CO₂. In addition, CO can be obtained from CO₂ by reverse water-gas shift.

Converting CO₂ into urea is another way of capturing and activating CO₂. Ammonia is not consumed in this process and can be recycled via urea production (ideally based on renewable energy sources). Active and stable catalysts for substitution of the second amine group as well as removal of excess ammonia are key factors.

In the transesterification process, the epoxide acts as an activator for CO₂. The challenge in two-step transesterification is to improve conversion of the cyclic carbonates as well as selectivity towards the dialkyl carbonates by avoiding unwanted alcoholysis. Transforming the transesterification process into a single-step process would reduce investment, production costs, and energy demand.

Investigations are required in the field of fundamental thermodynamic and kinetic studies as well as proof of concept studies for new process developments in batch, CSTR, fixed, or fluidized bed reactors. Furthermore, it is important to find the optimal reactor system to transfer the batch to continuous operation. Screening, optimization, and up-scaling of new catalyst formulations will help to investigate catalyst activity, selectivity, and stability. Investigating catalyst lifetime as well as the root cause of deactivation under industrially relevant process conditions and feedstocks is of great importance for commercialization.

LEARN MORE ABOUT DIALKYL CARBONATES SYNTHESIS AND APPLICATIONS

Shouying Huang, Bing Yan, Shengping Wang, Xinbin Ma,

"Recent advances in dialkyl carbonates synthesis and applications", Chem. Soc. Rev., 2015, 44, 3079-3116. [DOI](#).

Benjamin Schöffner, Friederike Schöffner, Sergey P. Verevkin, Armin Börner,

"Organic Carbonates as solvents in synthesis and catalysis", Chem. Rev., 2010, 110, 4554-4581. [DOI](#).

Kartikeya Shukla, Vimal Chandra Srivastava,

"Synthesis of organic carbonates from alcoholysis of urea: A review", Catalysis Reviews, 2017, 59 (1), 1-43. [DOI](#).

Marisabel Dolan,

"Technoeconomics – Energy & Chemicals, Dimethyl Carbonate", Nexant Report, Technology and Costs, TECH 2019S8, July 2019, [DOI](#).



CONCLUSION

USING HIGH THROUGHPUT EXPERIMENTATION TO SPEED UP R&D IN CO₂ UTILIZATION

IN SHORT: CARBON MANAGEMENT IS A KEY TOPIC IN REDUCING CO₂ EMISSIONS

With rapidly rising CO₂ emissions over the past years, increasing public awareness of climate change, and due to regulation and taxing of CO₂ emissions, the chemical industry is facing challenges to achieve the aim of net-zero in 2050. Carbon management is a key topic that is attracting growing interest for transforming the chemical industry and transportation sector towards greater sustainability. This white paper has attempted to discuss a broad field for two processes that utilize CO₂ and produce carbon-neutral chemicals and fuels.

One key step involves the production of sustainable syngas from CO₂ used as a building block for hydrocarbons, e.g. via conventional Fischer-Tropsch synthesis. Dry reforming of methane with CO₂ or reverse water-gas shift reaction using green H₂ are valuable and more sustainable extensions to the portfolio of syngas-producing reactions that make use of CO₂ from industrial exhaust streams, biogas, or direct air capture. Methanol is a key intermediate and product in the chemical in-

dustry that is conventionally produced from syngas containing CO₂ or via direct CO₂ hydrogenation. Methanol can be further converted into a broad range of hydrocarbons via methanol-to-hydrocarbons processes. The resulting synthetic fuels exhibit a smaller carbon footprint than conventional synfuels or oil-based fuels.

Synthetic natural gas from direct CO₂ hydrogenation can serve as a chemical energy carrier for grid stability in a future energy system based on renewable energies such as wind and solar power, or used as a drop-in replacement for fossil-based natural gas in the energy sector. The direct hydrogenation of CO₂ towards hydrocarbons without syngas production in a separate reactor is the subject of recent research and is addressed in new power-to-liquid concepts. Finally, CO₂ can be used as a building block for chemicals such as dialkyl carbonates, which are attracting growing interest as solvent, polymer, or methylating agents.



WEBINAR ON-DEMAND

CARBON MANAGEMENT: CO₂ UTILIZATION AND OPPORTUNITIES TO IMPROVE CARBON FOOTPRINT.

Find out how CO₂ can be utilized as a carbon building block. In our free webinar, you will learn why high throughput experimentation is the perfect tool to overcome the challenges in catalyst R&D and process development and move towards a smaller CO₂ footprint. **Register now:** www.hte-company.com/co2

HTE – LEADING SOLUTION PROVIDER FOR FAST AND COST-EFFECTIVE CATALYSIS R&D

At hte – the high throughput experimentation company, we make R&D in the field of catalysis faster and more productive.

We enable cost-effective innovations and reduced time-to-market for new products. Our customers benefit from broad technical and scientific expertise, exceptional customer orientation,

complete end-to-end solutions, and outstanding data quality. Our technology and services comprise contract research programs at our laboratories as well as integrated hardware and software solutions, enabling our customers to establish high throughput workflows in their own laboratories.



HOW HTE IS USING HIGH THROUGHPUT TECHNOLOGIES TO OBTAIN A SMALLER CARBON FOOTPRINT MORE QUICKLY

hte provides extensive expertise in synthesis gas conversion chemistry (Fischer-Tropsch, methanol, DME, higher alcohols) to help you find tailor-made solutions. By challenging existing processes or creating new production routes including CO₂ as a feedstock, hte supports various lab services in catalyst development and process optimization, such as:

- Preparation, screening and up-scaling of new catalyst formulations with respect to catalyst activity, selectivity, and stability
- Detailed analysis of complex hydrocarbon product mixtures, supported by our in-house data management workflows
- Fundamental thermodynamic and kinetic studies
- Proof-of-concept studies for new process developments in batch, CSTR, fixed, or fluidized bed reactors
- Optimizing process conditions in gas or liquid phase operation with the optimal process window (temperature, pressure, flow rate, concentration)
- Investigating catalyst lifetime as well as the root-cause of deactivation under industrially relevant process conditions with conventional or unconventional feedstocks
- Characterization of fast-deactivating catalyst systems, including the study of catalyst regeneration protocols
- Evaluation of short-lived catalysts using fluidized bed experimentation
- Commercial catalyst benchmarking, quality control, and stability testing, including protocols for accelerated thermal aging

hte's extensive toolbox and multi-fold reactor systems allow parallel and fast material testing with excellent comparability that outperforms single testing units and enables rapid, cost-effective innovations to allow our customers to stay ahead of the competition.

CONTACT US

Would you like to hear more about the advantages of high throughput technology? Please do not hesitate to contact us – we very much look forward to hearing from you.

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OUR TEAM

Currently, a team of over 300 people works at hte, each with their own expert skills. We provide access to some of the most experienced and highly skilled chemists, engineers, and software specialists within the field of high throughput experimentation. Our success greatly depends on our innovation pool of experts from different fields who combine knowledge and experience with great passion and enthusiasm.

For this white paper, we built a cross-departmental team to combine our scientific expertise in R&D projects with a customer-oriented perspective. Meet the team of hte scientists, business development managers, and marketing specialists.

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