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Sustainable aviation fuel production *via* the methanol pathway: a technical review

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Due to the compatibility towards today's aviation infrastructure, sustainable aviation fuels (SAF) are expected to contribute to a significant reduction of this sector's CO_2 emissions. The methanol pathway represents a synthesis-based route for producing SAF that can utilize various feedstocks, including electrolytically produced H_2 and atmospheric CO_2 through a power-to-liquid (PtL) process, which can be implemented at large-scale. The process is considered advantageous compared to other routes, primarily in terms of yield and low levels of byproduct formation, and is projected to efficiently produce jet fuel (C_8–C_{16}). This review analyzes the state of science for the entire process chain consisting of methanol synthesis, methanol-to-olefin conversion, oligomerization, and hydrogenation. Here, special attention is drawn to the respective feedstocks, reaction systems, reactor design and process layouts to highlight technology-specific challenges to be considered. After individually reviewing the sub-processes, their interfaces are analyzed to derive research demands on the process side.

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1 Introduction

With an estimated total emission of 0.8 Gt_{CO_2}, the aviation sector accounted for over 2% of the global anthropogenic carbon dioxide (CO_2) emissions in 2022.[1,2] These emissions are projected to triple by the year 2050, provided that no counter measures are taken.[3,4] The primary source of these emissions is the combustion of fossil-based jet fuel during flight operations accounting to about 2.5 kg of CO_2 per litre of jet fuel.[5] Despite the global decrease of fuel consumption per passenger of 23% between 2005 and 2017, *i.e.* from 4.4 L per 100 km to 3.4 L per 100 km, this efficiency gain is counterbalanced by the projected annual growth in passenger numbers of 4.3%.[6,7] In addition to CO_2, significant emissions from global aviation include nitrogen oxides (NO_x), water vapor, soot, sulfate aerosols, and increased cloudiness due to contrail formation.[8,9] Both CO_2 and non-CO_2 emissions contribute to net surface warming and anthropogenic climate changes,[10] with approximately one-third of the radiative forcing attributed to CO_2 and the other two-thirds caused by particulate emissions and water vapor forming contrail cirrus clouds.[11,12]

The climate impact of aviation could be mitigated by adopting new technologies, such as electric or hydrogen (H_2) fuelled aircrafts.[13] However, electrification of aviation faces significant challenges due to the low energy-density of batteries. Currently, 50 kg of batteries are needed to supply the same amount of energy as 1 kg of jet fuel, complicating their adaption for long-distance flights.[14] Due to its low volumetric energy density and difficult handling, hydrogen fuelled aircrafts also require further research and development to address challenges regarding onboard storage of hydrogen, restricted flight ranges, as well as comprehensive updates to aviation infrastructure and aircraft designs.[15] Given the current state of the aviation industry and the operational fleet, it is hardly possible to find alternatives to liquid jet fuels, possessing high energy densities and a short implementation interval.[16]

Sustainable aviation fuels (SAFs) are commonly referred to as kerosene-type fuels that can be produced from renewable energy sources.[17] SAFs are identified as viable drop-in replacements and blendstocks for fossil-based jet fuel, capable of mitigating the environmental impact by decreasing fossil CO_2 and other GHG emissions. Indeed, the International Air Transport Association (IATA) has recognized SAF production as the most promising short-term strategy to reduce CO_2 emissions in the aviation sector.[18] Additionally, the production of SAF could contribute to meeting the increasing global demand for jet fuel while enhancing energy security and reducing reliance on fossil fuels.[19]

SAF can be categorized based on their production routes and the type of feedstocks with the primary distinction between biological and non-biological origin, as shown in Fig. 1. For SAF to be commercially permitted for usage, it must be certified by the ASTM D7566 Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons, set by the American Society for Testing and Materials (ASTM).[20] The

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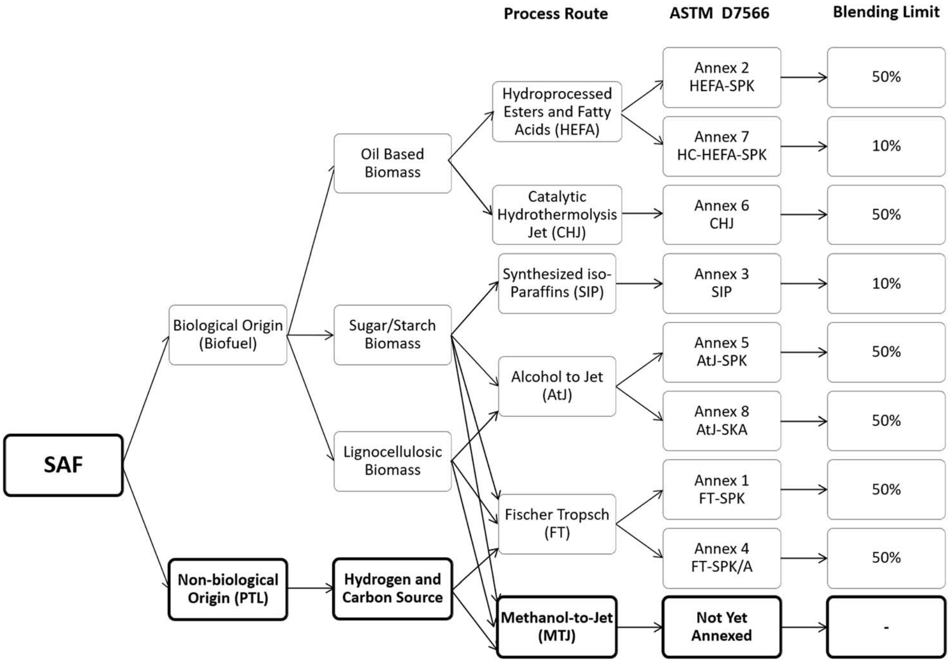

Fig. 1 Main production routes for synthetic jet fuel production.[19]

qualification process for new candidates of non-petroleum alternative jet fuels is specified by ASTM D4054 Standard Practice for Evaluation of New Aviation Turbine Fuels and Fuel Additives.[21,22] Once an alternative jet fuel production route is qualified, the standard specification for that jet fuel would be added as an annex to ASTM D7566. These ASTM standards ensure that the produced SAF possess compatible characteristics with the commercially available fossil-based jet fuels (Jet A/Jet A-1), specified in ASTM D1655 Standard Specification for Aviation Turbine Fuels.[23]

Table 1 compares selected ASTM property requirements for Jet A and a selection of alternative jet fuel routes. Notably, stricter requirements for alternative fuels have been implemented due to various concerns about the specific distinctions between synthetic chemical blends with petroleum distillates.[24] To date, no 100% drop-in SAF process routes have been approved by ASTM and most approved production routes have a 50% maximum blending limit. This can be attributed to the significantly reduced aromatics content in the SAF produced, which could affect the seal compatibility of aircraft engines.[25] The aviation industry aims to progress towards the use of 100% SAF that comply with safety and operability requirements of the ASTM qualification process.[26]

In 2024, SAF represented only 0.3% of global jet fuel produced.[27] Large-scale production of SAF faces significant challenges, primarily due to their production costs which are estimated to be 1.2 to 7 times higher than the market price of conventional fossil jet fuel.[28,29] The EU council recently adopted the RefuelEU aviation initiative designed to stimulate large-scale production of SAF and reduce production costs with increasing technological maturity.[28,29] This initiative includes a new regulation mandating a gradual increase of the minimum SAF share in jet fuel blends at EU airports from 2% in 2025 to 70% by 2050.[30] Moreover, it sets targets for renewable fuels of

Table 1 Selected ASTM properties of Jet A/A-1 and SPK of FT, HEFA and ATJ[20,23]

Property requirement	Jet A	SAF (FT-SPK/HEFA-SPK/ATJ-SPK)
Acidity (total mg KOH per g)	<0.1	<0.015
Distillation, 10% recovered (°C)	<205	<205
Distillation, final boiling point (°C)	<300	<300
Flash point (°C)	>38	>38
Freezing point (°C)	<-40	<-40
Viscosity at -20 °C ($mm^2\ s^{-1}$)	<8	<8
Density at 15 °C ($kg\ m^{-3}$)	775 to 840	730 to 770
Aromatics	8–25 vol%	<0.5 wt%
Sulfur (wt%)	0.3	0.0015
Metals (mg per kg metal)		
(Al, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Pt, Sn, Sr, Ti, V, Zn), mg kg^{-1}	No requirement	0.1

non-biological origin (RFNBO), starting at 0.7% in 2030, with an increase to 35% by 2050. This increase is anticipated to enhance the development of synthetic jet fuels, including e-fuels produced *via* Power-to-Liquid (PTL) processes.

Projected jet fuel demand at EU airports is anticipated to reach approximately 46 Mt per a by 2030.[31] Currently, the annual production capacity of SAF in the EU stands at just over 1 Mt per a.[32] With the inclusion of facilities currently under construction, the estimated SAF production capacity for 2030 in the EU is projected to be between 3.5 and 3.8 Mt per a,[32,33] potentially aligning with the mandated SAF demand of 6% by that year. However, to meet the more ambitious targets of 34% by 2040 and 70% by 2050, significant increases in production capacity will be necessary.

The major SAF production routes have been analysed in several recent reviews,[6,13,18,29,34–37] evaluating the interaction between policy framework, economic considerations, commercialization status, and technical performance. Reviewing the market for ASTM certified SAF routes of biofuels and e-fuels, Detsios *et al.* concluded that currently feedstocks of biological origins dominate among the various SAF production pathways.[18] A more extensive review by Khanal *et al.* provides a detailed analysis of SAF production *via* various biofuel routes.[36]

Among ASTM approved SAF production routes, the hydroprocessed esters and fatty acids (HEFA) process, currently dominates the SAF market with more than 90% of the total share.[29,38] HEFA jet fuel and HVO diesel are produced *via* hydrotreatment and subsequent isomerization of fats, oils, and greases (FOG), or other bio-oils.[39] Recent commercial developments were made with regard to industrial scale production of bio-jet fuel from the Alcohol-to-Jet fuel (ATJ) route with a wide range of biogenic feedstocks,[40] with a recent demonstration plant by Lanzajet at a production scale of 30 000 t/a.[41] Additionally, the ATJ process has been demonstrated using isobutanol derived from cellulosic non-edible crops biomass.[42] Up to date, the ASTM D7566 refers to ATJ that uses ethanol or isobutanol as feedstock, while methanol as a feedstock is not included in the ATJ classification.[20]

Within Europe, the production of SAF from biological origins is strictly regulated, as the feedstock use of food and food crops in aviation is limited by EU regulation 2023/2405.[6,43] Additionally, the expansion in bio-based jet fuel frequently prompts concerns regarding food *versus* fuel and land-use change.[18] This underscores the need for further development of jet fuel as RFNBO.

PTL routes, which can lead to the production of electro-sustainable aviation fuels (eSAF), a type of synthetic aviation fuel produced using renewable electricity, offer compelling advantages over biofuels due to a greater potential for greenhouse gas reduction, as well as a lower land and water demand.[44–46] Currently, the economic viability of these processes is hindered due to the high production costs of green H_2.[47] However, it is expected that these costs will decrease with the improvement of the major electrolysis technologies.[48] The main PTL routes for jet fuel production being discussed today are the FT pathway as well as the methanol-to-jet fuel (MTJ) pathway.[49,50] While SAF derived from the FT process has already been certified as a drop-in aviation fuel according to ASTM D7566 standards, MTJ-based SAF is currently in the process of obtaining approval through ASTM D4054.[17]

With availability of FOG feedstocks being a limiting factor, the ATJ route and the Fischer–Tropsch (FT) route are expected to produce a significant amount of bio-based jet fuel in the future.[51] The FT process, originally developed in Germany for producing liquid transport fuels from coal, is capable of transforming synthesis gas, *i.e.* here a mixture of carbon monoxide (CO) and H_2, into liquid fuels such as SAF.[52] Synthesis gas can either be produced from biological or non-biological origin.[53,54] The bio-based FT process entails gasification of biomass into synthesis gas before converting it into liquid fuels. Nonetheless, the need for extensive conditioning and cleaning of the synthesis gas from biomass gasification can limit the efficiency and commercial feasibility of bio-based FT synthesis.[55,56]

FT technology can be integrated into PTL production route, where synthesis gas is generated from CO_2, electricity, and water instead of biogenic feedstocks. However, FT synthesis faces some challenges regarding syngas generation due to the high energy intensity of CO_2-to-CO-conversion by reverse water gas shift reaction (rWGS) or the low TRL of co-electrolysis.[57,58] Moreover, its high exothermic heat and complex reaction kinetics present a challenge for direct coupling of the process to fluctuating renewable power.[59,60]

While many review articles dealing with the characteristics of FT synthesis for SAF production are available today,[52,53,61,62] knowledge regarding the MTJ process chain is still limited. This review examines the current state of science across each subprocess of the MTJ process chain, focusing on the reaction systems, the different catalysts used in each synthesis step and the variables that impact the jet fuel yield, emphasizing areas for future research that can be done by the scientific community. It highlights the necessity to develop an integrated process concept that not only achieves high yields of SAF, but also is economically viable. Based on a systematic analysis of various process configurations, concepts for an integrated process are proposed. The review identifies key challenges and poses research questions critical for the future technological development of the MTJ pathway. Finally, challenges in process integration are outlined, offering a perspective for further research and development in this field.

2 SAF production *via* methanol

The production of SAF from H_2 and CO_2 *via* the methanol pathway involves four main subprocesses: methanol synthesis, methanol-to-olefins (MTO) conversion, oligomerization, and hydrogenation.[19,63,64]

A simplified schematic of the MTJ process chain is shown in Fig. 2, together with a rough range of the respective process conditions applied and used catalyst types. In a first step, H_2 and CO_x obtained from carbon neutral sources, such as biomass or air, are converted into methanol and water over Cu-based catalyst in an exothermic reaction in a temperature and

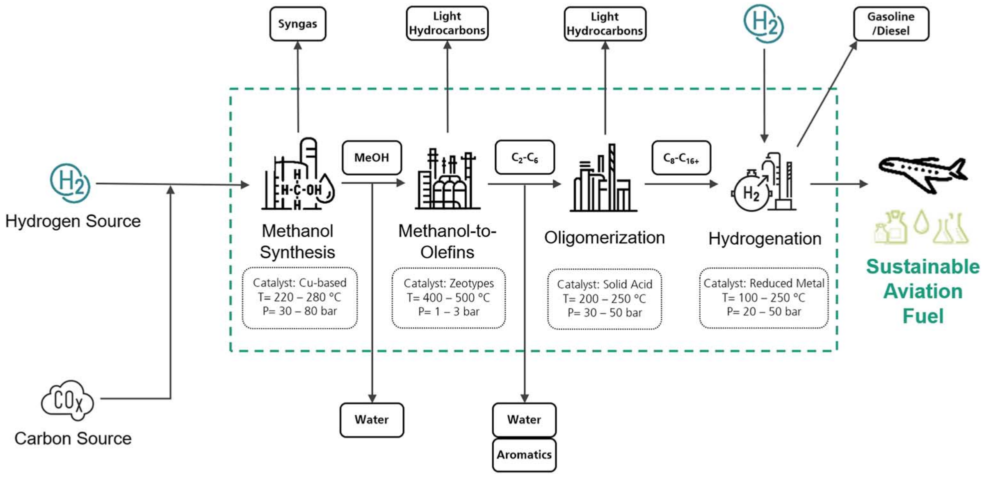

Fig. 2 Sustainable aviation fuel production from hydrogen and carbon source *via* the methanol pathway. The grey streams represent potential by-products that may occur in the process.[18,56,57]

pressure range of 220–280 °C and 30–80 bar, respectively.[58] Subsequently, the purified methanol is converted into light olefins during the MTO synthesis step over Zeotype catalyst at process conditions of 400–500 °C and 1–3 bar.[65] The product stream of the MTO synthesis is quenched, and water is separated and partially recycled to the MTO reactor. C_2–C_6 olefins are separated from lighter and heavier components using fractionation columns.[66–68] In the subsequent oligomerization step, the chain length of the olefins (C_2–C_6) is increased over solid acid catalyst at synthesis conditions of 200–250 °C and 30–50 bar.[69] Along the process chain, the olefin oligomerization is a critical step to obtain hydrocarbons with the desirable combustion properties in the synthetic jet fuel-range. The oligomerization mechanism of ethylene and higher olefins differs, which confers complexity to the oligomerization process. This will be discussed further in Section 2.3. The oligomerized product is mixed with H_2 and hydrogenated over a reduced metal catalyst at 100–250 °C and 20–50 bar to saturate the olefinic double bonds.[69] The product is cooled and the excess H_2 is recycled back to the fixed-bed hydrogenation reactor.[70] Finally, the jet fuel product, with a typical carbon range of mainly C_8–C_{16}, is separated from lighter and heavier hydrocarbons using fractionation columns.[71]

Especially in the context of PTL, MTJ shows potential for SAF production regarding the following aspects:

(1) As methanol can be produced from both CO and CO_2, CO_2 can be utilized directly without the need of a reverse water gas shift stage or co-electrolysis.[72]

(2) The possibility of dynamic methanol synthesis operation enables a direct link of renewable energy to jet fuel production.[73–77]

(3) The exothermic heat of jet fuel production can be integrated into the process chain to allow reduced heat demands.

(4) MTJ can produce jet fuel at high yields with low levels of byproduct formation.[17,71] This is an advantage over FT, where the formation of light hydrocarbons, such as, methane can be significant.

(5) By optimizing the synthesis conditions, jet fuel derived from methanol could be produced with low levels of aromatic compounds compared to fossil jet fuel, which contributes to reduced contrail formation and lessens the adverse climate effects of aviation emissions.[78,79]

Each of the individual subprocesses of the MTJ process chain are currently operational on industrial scale in various plants and refineries.[80–82] However, to date, there have been no commercial scale implementations of specific concepts integrating the various subprocesses of the MTJ pathway, reflecting the relatively low TRL of an integrated MTJ process.[17,71]

Various companies and institutions are working on the process development of MTJ, such as ExxonMobil, UOP and Topsoe.[83–85] Several research projects are investigating this topic, such as SAFari and M2SAF.[86,87] Moreover, several techno-economic analyses have investigated the MTJ process, although the optimization towards jet fuel mainly includes strong simplifications.[49,88–91] A detailed process optimization was published by Bube *et al.*, focusing on new modelling approach for the oligomerization of short-chain olefins within the framework of MTJ.[17,90] Scientific studies conducted by Bube *et al.*, Saad *et al.*, and Eyberg *et al.* estimate the production costs of eSAF *via* the MTJ process between 4.2 and 9.45 EUR per kg.[88–90] Eyberg *et al.* compared the levelized cost of production (LCOP) at optimal energy efficiency cases for the FT process and the MTJ process, estimating it to be 8.78 EUR per kg and 9.45 EUR per kg, respectively. However, both estimates corresponds to a value of 0.81 EUR per kWh, reflecting differences in the lower heating value (LHV) associated with the respective jet fuel compositions obtained.[89] The Project SkyPower initiative, representing multiple stakeholders in the eSAF sector, estimates that production costs for eSAF in Europe will range between 5 and 8 EUR per kg by 2030.[92] Overall, the estimated production costs are subjected to varying assumptions regarding feedstock costs, plant capacity and the boundary conditions, with water electrolysis and CO_2 capture accounting to 74–79%.[88–90] Moreover, it is important to note that these studies underly systematic uncertainties caused by technical assumptions, such as conversions, selectivities and chain growth probability.[17,90]

The following sections review the feedstock, catalyst, reaction networks, process layouts and products of each subprocess within the MTJ route, with the objective of enhancing the selectivity towards jet fuel range hydrocarbons.

2.1 Methanol synthesis

With a global production capacity of nearly 140 Mt per a in 2022, thermochemical methanol synthesis, implemented by BASF in 1923, is today one of the most important chemical production processes.[93,94] Methanol is used as a platform molecule to produce fuels and chemicals, with the main consumption driven by China.[95] Besides traditional derivatives like formaldehyde, methyl *tert*-butyl ether (MTBE) or acetic acid, methanol is today widely used for the production of olefins and propylene by MTO or methanol-to-propylene (MTP).[96,97] Due to the fixed demand for RFNBO by the EU, an additional path of utilization for carbon neutrally produced methanol is expected to emerge by the MTJ process.[43] Thus, this technology will be reviewed in the next subsections to point out obstacles to be addressed by the scientific community to ensure a reliable scale up of thermochemical SAF production *via* methanol.

2.1.1 Feedstocks. Methanol can be formed from synthesis gases (syngases) containing H_2, CO and CO_2 covering a wide concentration range.[98] Importantly, the CO/CO_2 ratio in the syngas as one of the most relevant parameters for the description of methanol synthesis is directly related to the feedstock and its processing method.[72,98]

Today, the main feedstocks for methanol production are natural gas and coal, providing a CO-rich synthesis gas for methanol synthesis by either reforming or gasification technologies.[93] Depending on the feedstock applied, these processes generate cradle-to-gate CO_2 emissions between 0.85 $t_{CO_2,eq}/t_{MeOH}$ and 2.97 $t_{CO_2,eq}/t_{MeOH}$ for a basic natural gas or coal based process, respectively.[99,100] Assuming thermal treatment of methanol end-of-life additional 1.38 $t_{CO_2,eq}/t_{MeOH}$ would be emitted through a stoichiometric oxidation. Thus, to decrease the CO_2 emissions caused by methanol production and utilization, carbon neutral production routes including carbon cycles need to be established.[101] Biogenic or atmospheric carbon oxides reacted with carbon-neutrally produced H_2 by water electrolysis is currently seen as a promising pathway to satisfy the methanol world market in the future.[102] Whilst these Power-to-Methanol (PTM) processes offer the potential of carbon neutrally produced methanol, the partial or entire replacement of CO by CO_2 in the syngas entails disadvantages originating from the high chemical stability of CO_2 in comparison to CO and the formation of water as by-product (see Section 2.1.2 for more details).

Due to the high feedstock availability, biomass has a large potential for the production of green fuels and chemicals.[93,103] Depending on the way of processing, biomass can deliver both, pure CO_2, *e.g.* in case of fermentation, or a syngas containing CO_2, CO, H_2 and nitrogen (N_2), *e.g.* in case of gasification. In case of a biomass gasification, the syngas produced can offer a high similarity to conventional syngas with an optional addition of surplus electrolytic H_2.[72,104–106] Thus, this process is advantageous with regard to the supply of existing methanol synthesis plants.[98] When the gasification is performed with pure O_2 instead of air, the N_2 content in the syngas can be reduced, offering an advantageously low inert gas content.[107]

By application of various reforming technologies, a CO and H_2 containing syngas can be produced from biomethane.[103,108–111] Biogenic CO_2 can be captured *via* amine wash from fermentation processes or combustion processes.[112] However, in this case surplus H_2 must be supplied to obtain a syngas suitable for methanol synthesis. In any case, bio-based syngas contains catalyst poisons such as chlorine or sulfur-containing compounds.[72,110,113] Thus, these trace compounds need to be removed from the syngas before entering the synthesis process.

Alternatively to biomass, CO_2 can be obtained from the atmosphere or sea water by direct air capture (DAC) or direct ocean capture (DOC), respectively.[114–118] While these technologies still need to be scaled up to reach reasonable costs, they offer the potential of providing CO_2 at any location.[116]

In the context of carbon capture and utilization (CCU), carbon oxides for methanol synthesis can also be obtained from fossil or mineral sources, *e.g.* from cement plants,[119,120] steel mills[121–124] or waste incineration plants.[125,126] While these carbon oxides are comparatively easy to exploit due to their high availability and concentration at the respective point source, their utilization has to be evaluated carefully with regard to international emission reduction targets.[102]

If H_2 cannot be obtained by thermochemical methods, current state of the art involves electrochemical H_2 production by electrolysis with four major technologies being proton exchange membrane electrolysis (PEMEL), anion exchange membrane electrolysis (AEM), alkaline electrolysis (AEL) or high-temperature electrolysis (HTE).[127,128]

2.1.2 Catalyst and reaction network. After advanced gas cleaning techniques for the removal of sulfur species from the syngas were implemented in the 1960s, Cu/ZnO/Al_2O_3 catalysts were enabled for their industrial application.[129] Despite ongoing research for more stable and active catalysts based on different metals such as indium or noble metals,[130–132] this catalyst system remains the industrial standard today.[133,134]

Methanol synthesis on conventional catalysts can be described macroscopically by CO hydrogenation, CO_2 hydrogenation and water–gas-shift reaction (WGS):

$$CO_{2(g)} + 3H_{2(g)} \rightleftarrows CH_3OH_{(g)} + H_2O_{(g)} \quad \Delta H_R^0 = -50\ \text{kJ mol}^{-1}$$

$$CO_{(g)} + H_2O_{(g)} \rightleftarrows CO_{2(g)} + H_{2(g)} \quad \Delta H_R^0 = -41\ \text{kJ mol}^{-1}$$

$$CO_{(g)} + 2H_{2(g)} \rightleftarrows CH_3OH_{(g)} \quad \Delta H_R^0 = -91\ \text{kJ mol}^{-1}$$

In this reaction network, CO hydrogenation can be defined as the combination of CO_2 hydrogenation and WGS. Currently, this combination is considered as the main source of methanol over conventional Cu/ZnO/Al_2O_3 methanol synthesis catalysts by various studies,[135–138] while the actual mechanistic nature of methanol synthesis is still debated.[139–141] Due the equimolar formation of water, equilibrium conversion of CO_2 hydrogenation is lower compared to CO hydrogenation.[142,143] Moreover, water was shown to be responsible for inhibited methanol reaction kinetics[144] and accelerated deactivation of the catalyst.[145–147] As increased CO_2 contents in the synthesis gas enhance water formation along the reactor by both CO_2 hydrogenation and reverse WGS (rWGS), many studies have dealt with enhancement of the catalyst for CO_2-based methanol synthesis.[148–151] Switching from the Al_2O_3-support towards ZrO_2 or Ga_2O_3 is most widely applied to stabilize the Cu species on the catalytic surface.[152–154]

For the kinetic description of methanol synthesis, plenty different kinetic models have been proposed in scientific literature[155–161] among which the model by Vanden Bussche *et al.*[155] and Graaf *et al.*[156] have gained most popularity in the scientific community. However, due to different reaction conditions, catalysts and mechanistic assumptions which these models are based on, they were proven to show strong deviations with regard to product formation and the axial temperature profile inside the reactor.[162–166]

2.1.3 Process layout and reactors. Regarding reactor design for conventional methanol synthesis, multiple approaches are known in literature.[58,167–169] Among the common reactor types, the adiabatic multi bed reactor with intercooler or quench injection of fresh syngas as well as the steam cooled tubular reactor and the gas-gas-cooled reactor are most widely applied.[143] Fig. 3 shows a simplified process flow diagram of methanol synthesis process including a single stage crude methanol distillation and a light gas recovery to decrease losses of dissolved gases.[170]

Depending on plant size, syngas composition and economical aspects, many combinations of different reactor types were studied in both, scientific and patent literature.[171–174] To overcome the thermodynamic limitation of CO_2 hydrogenation, removal of water and/or methanol from the reaction mixture either by interstage absorption,[175] adsorption[176,177] or condensation[122,178–183] were identified as promising pathways. Recently, *in situ* removal of the products inside the reactor by sorption or membrane separation has gained attention in this context.[184–189] However, these technologies have not yet been demonstrated on a larger scale. Another way to tackle the thermodynamic and catalytic challenges of CO_2-based methanol synthesis is the so-called CAMERE process coupling an upstream rWGS stage with subsequent methanol synthesis from CO enriched syngas as proposed by Joo and coworkers in 1999.[190,191] Similar approaches were considered as an option within patent literature.[192,193] However, when stable catalysts for CO_2-based methanol synthesis become industrially available, these concepts could become obsolete.

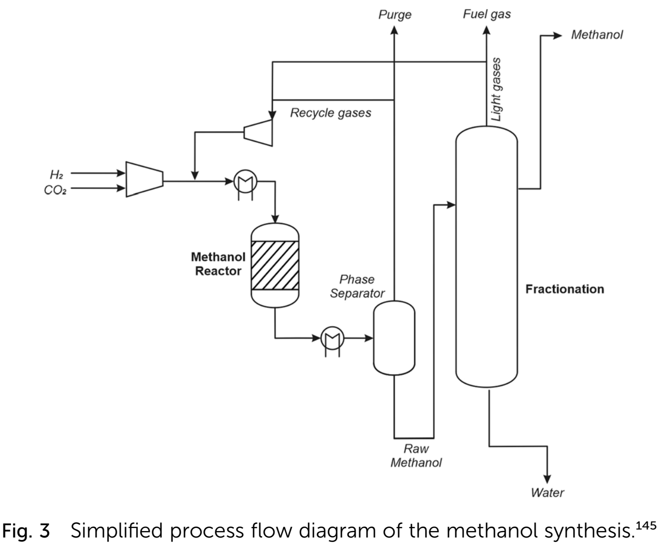

Fig. 3 Simplified process flow diagram of the methanol synthesis.[145]

Another important point differing between fossil and "green" methanol synthesis relates to the process dynamics. While a fossil-based synthesis is usually operated at steady state,[111,194–196] coupling of fluctuating renewable energy sources to methanol synthesis can lead to the demand for dynamic process operation. Here, one main challenge lies in balancing the increased equipment cost and possible difficulties regarding heat integration for the dynamic methanol plant with the advantages of decreased H_2 buffers and an improved utilization of renewable power.[58,73–76,113]

2.1.4 Products. With the effects of WGS and rWGS, *i.e.* CO_2 and CO formation, respectively, excluded, commercial Cu/ZnO/Al_2O_3 catalysts show a carbon selectivity towards methanol >99%.[72,197,198] Industrially, methanol purity is classified by chemical grades[199,200] usually achieved by distillation of raw methanol.[58,113,201] However, in case of directly linked downstream processes utilizing methanol, the degree of necessary purification needs to be defined individually since the removal of water might not be necessary or can be implemented more efficiently in downstream process equipment.[202]

The main side products documented in literature are dimethyl ether (DME), formic acid, methyl formate, methyl acetate, higher alcohols (predominantly ethanol), ketones and paraffins.[171,201,203,204] In a recent study, Nestler *et al.* analysed the side products present in liquid crude methanol samples produced from a variety of different process conditions, and compared those to literature data.[204] In this work, the CO/CO_2 ratio in the reactor feed was identified as the main parameter determining side product formation, with an overall tendency to decrease as CO_2 content increases. From the experimental data obtained, a simplified correlation was derived between the CO/CO_2 ratio and the amount of side products. However, the authors indicated further research demand in this field to obtain a better understanding of the formation mechanisms for different side products, as these could affect the downstream process.

In the context of the MTJ route, the degree of purity necessary for a stable operation of the downstream process, *i.e.* MTO synthesis, should be investigated further, as a simplification in methanol purification can decrease the energy demand of the process chain and offer the potential to for new integrated process schemes.[205]

2.2 Methanol-to-olefins conversion

The methanol-to-hydrocarbons (MTH) process was first developed by Mobil Oil Corporation (today ExxonMobil) in the 1970s.[206] They claimed that a feed of lower alcohol and/or ether, such as methanol, dimethyl ether, or an equilibrium mixture of both, can be converted into a mixture of C_2–C_5 light olefins when contacted over a shape selective aluminosilicate ZSM-5 zeolite catalyst in a fixed-bed reactor. These light olefins can further react to produce paraffins, aromatics, naphthenes and higher olefins, as illustrated in Fig. 4.[207]

This discovery opened the possibility to produce a range of synthetic hydrocarbons through various processes classified by their targeted product. Thus, MTH process can be subdivided into methanol-to-gasoline (MTG),[208] methanol-to-aromatics (MTA),[209] MTP,[210] and MTO processes.[211] Reviewing the MTO synthesis within the MTJ route is crucial for optimal coupling of the subprocess for a maximized jet fuel yield. By examining the state-of-science of the MTO process, opportunities for innovation and efficiency improvements in SAF production can be identified.

2.2.1 Feedstock. Coupled with state of the art upstream processes, MTH processes offer a versatile method to produce hydrocarbons from a wide range of carbon sources, *e.g.* natural gas, coal, or biomass.[82] Thus, the MTH synthesis can also be applied to produce renewable synthetic fuel when "green" methanol is used as a feedstock.[80] Aside from methanol, water can be fed into the reactor to reduce the temperature increase caused by the exothermic MTO synthesis, which in turn influences product selectivity and catalyst activity.[212] High water contents of *e.g.* 74–80 mol% in the feed are known to increase olefin selectivity, decrease formation of aromatics and paraffins, as well as reduce coke formation on the catalyst surface.[213–215] Thus, these results indicate that the utilization of crude methanol could be a promising option to decrease the aromatic content in SAF produced *via* the MTJ pathway.

DME formed as an intermediate product in the MTO synthesis can be converted to hydrocarbons in the DME-to-Olefins (DTO) process.[216,217] Martinez-Espin *et al.* compared pure methanol and DME as feedstocks, and concluded that DME feed results in a higher catalytic activity as well as lower selectivity for aromatic products and ethylene.[218] Additionally, Cordero-Lanzac and co-workers found that the DTO process produces less water and is less exothermic compared to the MTO process.[219] Due to these promising findings, the kinetic and technical impacts of DME cofeeding to olefin synthesis should be evaluated in the context of SAF production in future work.

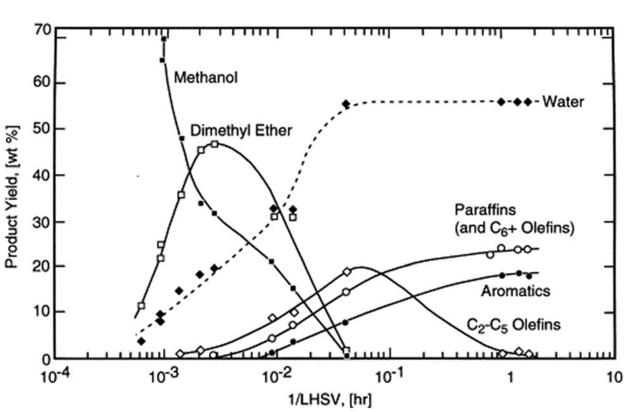

Fig. 4 Formation and consumption of the species involved into MTO synthesis over residence time (reproduced from ref. 181 with permission from Elsevier, copyright 1999).

2.2.2 Catalyst and reaction network. Microporous zeolites or zeotype catalysts containing Brønsted acidic sites are used in the MTO synthesis with H-ZSM-5 and the SAPO-34 being the two most prominent catalysts due to their light olefin selectivity.[220] The topology and acidity of the zeolite catalyst significantly influence the selectivity of MTO synthesis.[221–223] Besides H-ZSM-5 and SAPO-34, other catalysts that have been studied for MTO synthesis include H-ZSM-11, H-ZSM-22 and H-ZSM-48.[224] Notably, a high selectivity to C_{3+} olefins has been reported in MTO over 1-D framework zeolites, such as H-ZSM-48 and H-ZSM-22.[223,225] High C_{3+} olefin yields are particularly advantageous for maximizing the jet fuel selectivity within the MTJ route. For further details on each zeolite topology, readers can refer to the International Zeolite Association (IZA) database.[226]

Along with topology, the product selectivity of the zeolite catalyst in MTO is influenced by concentration, distribution and strength of both Brønsted acid sites (BAS) and Lewis acid sites (LAS).[227] BAS density affects the catalytic activity and catalyst lifetime.[228] It is determined by the framework aluminium content of the zeolite and can, thus, be increased by decreasing the Si/Al ratio. A high BAS density confers a high activity, but facilitates successive reactions along the diffusion pathway, promoting aromatization and coking, whereas lower BAS densities favour methylation and cracking reactions.[229] In addition to BAS density, the distribution of the BAS within the framework influences the reaction pathway and the deactivation by coke formation, thereby affecting olefin selectivity and catalyst lifetime.[230] Hydrogen transfer reactions can be suppressed by reducing the Brønsted acidity of the ZSM-5 zeolite, *e.g.*, by incorporating a Ca promoter.[231] Alkaline earth metal-promoted ZSM-5 zeolites, such as Ca-ZSM-5, can exhibit a lower activity, but a considerably enhanced catalyst lifetime, increased propylene selectivity and decreased aromatics selectivity in MTO, compared to unpromoted zeolites.[221,227,231–233] The promotion with alkaline earth metals decreases the BAS concentration and results in the formation of LAS, which can explain the difference in activity and selectivity. With LAS impacting the reactant adsorption and the stability of transition states on vicinal BAS, the decreased aromatics selectivity can be attributed to a difference in the reactivity of the BAS, in addition to a decreased BAS concentration.[221] As described by Bailleul *et al.*,[221] the LAS strength is decisive for the reactivity of the neighbouring BAS, with Ca and Mg promoted zeolites offering a compromise between activity and selectivity. In addition to modifying the acid properties of the zeolite, Ca promotion alters the effective pore geometry and decreases the micropore volume, which has been suggested to contribute to the composition of the hydrocarbon pool.[232,233] In conclusion, selection of a zeolite with an appropriate topology and tuning the ratio, strength, concentration, and distribution of BAS and LAS in the MTO catalyst is crucial to maximize the desired light olefin yield (C_3–C_6) and catalyst lifetime.

Despite more than 40 years of research on MTO synthesis, more than 20 different models for the reaction mechanism have been proposed.[207,234–241] Modelling of the MTO reaction mechanism remains challenging due to the complex stoichiometry and the large number of elementary reactions. Reaction conditions significantly influence the product distribution and catalyst lifetime in MTO synthesis, as each elementary reaction may have varying orders and activation energies.[242–244] Today, the dual-cycle mechanism (DCM) is the most widely accepted for the mechanistic description of the MTH reaction.[245,246] As schematically shown in Fig. 5, it suggests an autocatalytic olefinic and aromatic cycle to run in parallel.[247] The DCM involves six key categories of chemical reactions, *i.e.*, methylation and cracking of olefins, methylation and dealkylation of aromatics, cyclization and hydrogen transfer, with their respective rates determining the product distribution of the overall synthesis.[247,248] It has been demonstrated that one of the two cycles can be promoted while suppressing the other one by co-feeding species participating in the respective autocatalytic cycle. According to Sun *et al.*, co-feeding of olefins (such as propylene, butylene, pentene and hexene) or aromatics (such as benzene, toluene and xylenes) promotes either the olefinic or aromatic cycle.[249,250] A small olefin recycle to the MTO unit could therefore be beneficial within the MTJ process chain.

Catalyst coking is a key challenge in MTO synthesis, as coke deposition on the outer surface and internal channels of the zeolite is the primary cause for deactivation in MTO synthesis.[251,252] Moreover, coke formation can consume up to 8% of the methanol feed, reduces the turnover capacity of the catalyst, and necessitates high-temperature regeneration, leading to a permanent structural degradation of the catalyst.[253–256] H-ZSM-5 demonstrates a higher resistance to coking compared to SAPO-34.[245] Unlike deactivation caused by zeolite material degradation or dealumination, deactivation due to coke deposits can be reversed by subjecting the catalyst to a thermal treatment at temperatures between 500 °C and 600 °C and an atmosphere with a low oxygen concentration, to restore the accessibility of the active sites.[257] The deactivation model by Janssens *et al.* assumes that the deactivation rate is directly proportional to methanol conversion and that the reaction between methanol and aromatic species results in coke formation.[257] The model demonstrates that the catalyst's active sites gradually become covered with hydrocarbon pool species, leading to subsequent coke deposition. According to Paunović *et al.*, the rate of coke formation also depends on the concentration and nature of Brønsted acid sites (BAS), as well as the presence of Lewis acid sites (LAS) and framework defects.[253]

Despite being present in low concentrations during MTO synthesis, formaldehyde contributes to the coke-induced deactivation of the zeolite catalyst.[218] Liu *et al.* showed that formaldehyde is predominantly formed at the induction period and exerts a detrimental influence on the catalyst lifetime, by facilitating the formation of non-olefinic products as dienes, polyenes and aromatics, which act as coke precursors.[258] To extend catalyst lifetime, it is relevant to develop strategies to effectively reduce the concentration of formaldehyde by inhibiting its formation or facilitating its rapid decomposition. Such strategies include MeOH dilution,[259] olefin co-feeding,[250] products back-mixing,[256] and substituting MeOH feedstock by DME.[218]

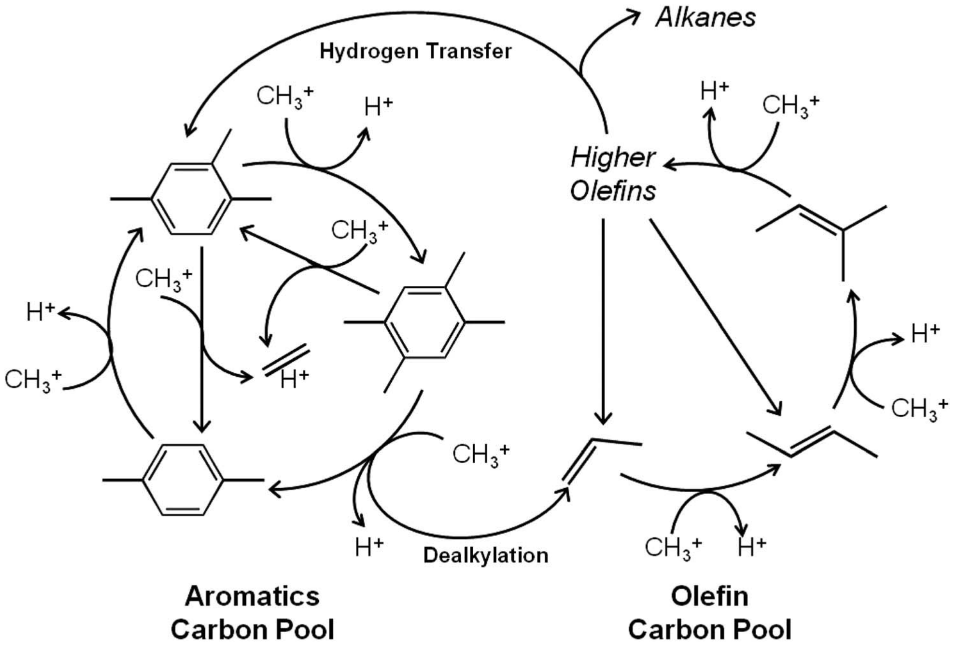

Fig. 5 Dual cycle mechanism of the MTO synthesis (reproduced from ref. 244 with permission from American Chemical Society, copyright 2013).

Kinetic modelling of MTO synthesis is challenging due to the complex reaction network involved. Several studies have investigated MTO synthesis and kinetic modelling using different feedstocks, such as pure methanol or methanol co-fed with olefins, over different catalysts and process conditions.[64,79,218,247–264]

Table 2 summarizes the parameter ranges related to feed composition, synthesis conditions, and catalysts in selected experimental and kinetic investigations. Quantitative data on selectivity and yield are excluded, as these studies were not conducted within the framework of the MTJ process, thus avoiding misinterpretation. Most published kinetic models on MTO synthesis are based on simplified assumptions or are targeting selective propylene production, which is not the primary focus of the MTO synthesis within the MTJ route. A significant shortfall of several kinetic models is the lumping of lower olefins into one lump or lumping methanol and DME together, which affects the robustness of the models due to the different formation mechanisms and reactivities of each component. Another challenge is understanding the interaction between water and zeolite and its effect on the kinetics, as water acts both as diluent and a competing adsorptive. Moreover, the catalytic activity decreases due to deactivation by coke deposition, which should be considered within the MTO kinetics. Additional research is necessary to develop kinetic models optimized for the MTO process conditions relevant to MTJ applications, as extrapolating beyond experimentally investigated conditions could result in unrealistic model predictions.

2.2.3 Process layout and reactors.

ExxonMobil combined the MTO process with Mobil's Olefins to Gasoline and Distillate (MOGD) process. Both processes use the medium pore zeolite H-ZSM-5 catalyst, to convert methanol into gasoline and other distillate fuels, including jet fuel and diesel.[270] Commissioning of a plant in New Zealand with an annual production capacity of 600 000 tons of gasoline utilizing this process marked the beginning of the commercial use of methanol for fuel production in 1985.[81] Topsoe (previously Haldor Topsøe) developed a process integrating gasoline production with the synthesis of methanol and DME from a feedstock of syngas within a single synthesis loop, in a process called Topsøe Integrated Gasoline Synthesis (TIGAS Process).[271] These two processes focus on a high yield of gasoline, while for the MTJ process, a high yield of light olefins is desired in the MTO subprocess.

Today, the UOP/INEOS MTO process and the Lurgi MTP process are two major technologies dominating the MTO market, demonstrating a high TRL for the production of light olefins from methanol. A comparison between available data of the Lurgi MTP and UOP/INEOS MTO processes is shown in Table 3, as they show suitable olefin target product for the MTJ process.[251]

The UOP/INEOS MTO process, developed in the 1990s by UOP and Norsk Hydro (now INEOS) and depicted in Fig. 6 uses the SAPO-34 catalyst in a fluidized bed reactor coupled with a fluidized-bed regenerator. The process is capable of using crude methanol, grade AA methanol or DME as a feed.[272] The feed is evaporated and introduced into the MTO reactor, operating in the vapor phase at temperatures between 340 °C and

Table 2 Summary of selected MTO experimental and kinetic investigations in literature at reaction pressure of 1 bar

Feed	Temperature (°C)	Catalyst	Si/Al	WHSV (h^{-1})	Olefins yield	Objective of study	Reference
MeOH	500	Ca-modified ZSM-5	40	8	C_2 olefins = 14% C_3 + C_4 olefins = 82%	Aromatic cycle suppression in MTO reaction	231
MeOH	520	Ca-modified ZSM-5	89.8	4.2	C_3 olefins = 49%	Enhance catalytic stability & propylene selectivity	260
DME	400	ZSM-5 ZSM-48 ZSM-22	40.2 73.5 50.4	6 1.5 0.3	$C_2 - C_{11}$ olefins = 26% $C_2 - C_{11}$ olefins = 90% $C_2 - C_{11}$ olefins = 50%	Aromatic cycle suppression in DME to hydrocarbons reaction	261
MeOH	400–550	ZSM-5	25.4	5.8	C_2–C_4 olefins	Kinetic modelling (seven lumps)	262
MeOH	300–450	ZSM-5	24	2.7–25	C_2–C_3 olefins	Role of water on MTO kinetic modelling	263
MeOH	360–480	ZSM-5	200	—	C_2–C_8 olefins	Single event kinetic modelling	264 and 265
MeOH MeOH + C_4H_8	480	ZSM-5	200	5.3	C_3 olefins = 81.6%	MTP monolithic catalyst investigation/kinetic modelling	266
MeOH MeOH + C_4H_8 C_5H_{10}/C_6H_{12}	420–500	B-modified ZSM-5	180	2.0–9.4	C_3 olefins	Methanol and olefins co-feeding investigation/kinetic modelling	267
MeOH + C_3H_6 MeOH + C_4H_8 MeOH + C_5H_{10} MeOH + C_6H_{12}	400–490	ZSM-5	200	—	C_2–C_7 olefins	Methanol and olefins co-conversion/kinetic modelling	268
MeOH + C_3H_6 MeOH + C_4H_8 MeOH + C_5H_{10} MeOH + C_6H_{12}	400–490	ZSM-5	200	—	—	Paraffins and aromatics side reactions/kinetic modelling	269

Table 3 Comparison aspects between the industrial process of Lurgi MTP and UOP/INEOS MTO[251]

	MTP (Lurgi)	MTO (UOP/INEOS)
Catalyst	H-ZSM-5	H-SAPO-34
Temperature, °C	450	350
Pressure, bar	1.5	2
Reactor	Fixed bed	Fluidized bed
Recycle	Water, olefins C_{4+}, C_2	DME
Products[a], wt%		
Propylene	72	42
Ethylene	—	39
C_{5+}	23	5

[a] Composition can vary.

540 °C and pressure between 1 bar and 3 bar.[273] SAPO-34 exhibits high selectivity towards ethylene, with the main products of the process being ethylene and propylene at a selectivity up to 80% and nearly complete methanol conversion.[274–277] A portion of the catalyst from the fluidized-bed reactor is continuously regenerated in the regenerator, allowing the flexibility to adjust the operating temperature by recovering heat from the exothermic MTO reactor.[275] The reactor temperature is crucial to adjust the propylene-to-ethylene ratio, as elevated temperatures favour higher propylene yields and coke formation.[272] The heat of the exothermic synthesis is removed by steam generation and cooling coils in the fluidized bed reactor. Effluent of the reactor is condensed to separate water. The dried gases are subsequently compressed and processed in a downstream fractionation.[274] Similar technologies have been developed in China by Dalian and Sinopec using catalysts containing SAPO-34 in a fluidized bed reactor.[272,273,278]

Lurgi GmbH developed an MTP process where methanol feedstock first is converted into DME and water in an adiabatic pre-reactor, as shown in Fig. 7.[210,279] The resulting mixture of methanol, water, and DME is then sent to the MTP reactor premixed with steam and recycled olefins. The process uses fixed-bed reactors loaded with a H-ZSM-5 catalyst, offering lower investment costs compared to processes using fluidized-bed reactors.[280] However, the fixed-bed reactors are less effective in managing the heat generated by the highly exothermic reaction compared to the fluidized-bed reactor.[281,282] The MTP process produces propylene, and gasoline as a by-product, with a methanol + DME conversion of more than 99%.[210] The reaction section consists of three parallel adiabatic quench bed reactors to facilitate intermittent catalyst regeneration after 500–600 h of time on stream (TOS), with one reactor on standby for coke removal by introducing air.[279] Each reactor is equipped with five or six catalyst beds with feed injection between beds to control reaction temperature.[279,283] The process runs slightly above atmospheric pressure (1.3 to 1.6 bar), with steam added to the feed (0.5–1.0 $\mathrm{kg_{steam}\ kg_{methanol}}^{-1}$), and at reactor inlet temperature between 400 °C and 470 °C.[65,273] Olefins such as C_2 and C_4–C_6 are recycled to the reactor to maximize the propylene yield.[284] Solutions for further increasing the propylene selectivity and prolonging the catalyst lifetime in MTP were proposed by UOP in their MTP patent family centred on moving bed reactor technology.[285–287]

In the context of the MTJ process, MTO aims to produce a mixture of C_{2+} olefins,[17,71,91] in contrast to Fig. 6 and 7, which reduces purification requirements and simplifies the separation process.

Topsoe filed four patents related to MTJ in 2021,[83,288–290] out of which three directly focus on the MTO subprocess. Separate applications were filed for MTO synthesis catalysed by zeolites with 1-D 10-ring pore structures, such as the *MRE, MTT and TON families,[289] and by zeolites with 3-D 10-ring pore structures, such as the MFI family.[288] The MTO subprocess outlined

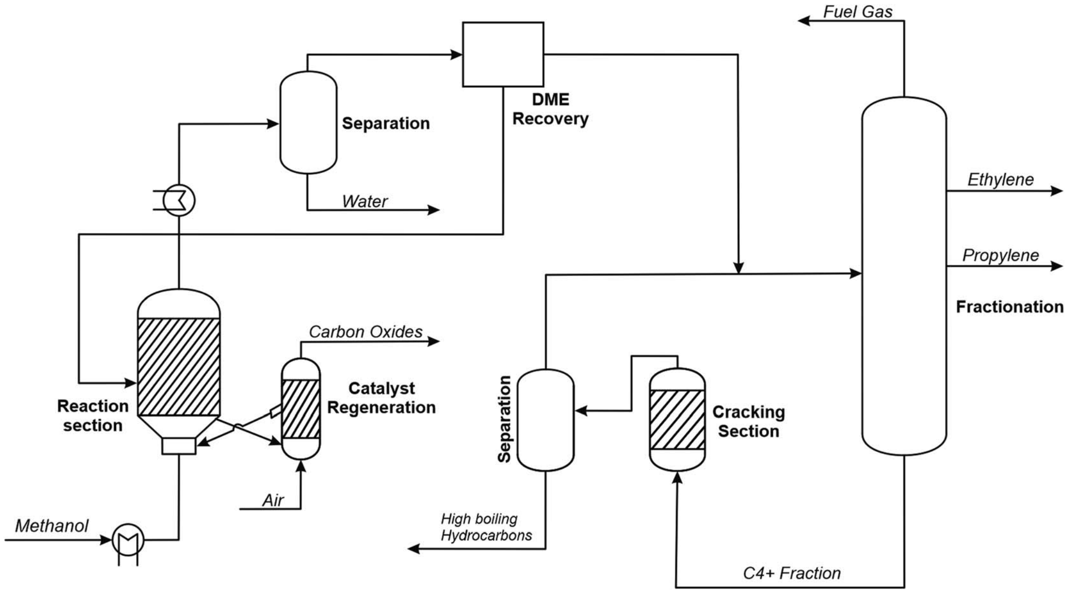

Fig. 6 Simplified process flow diagram of the UOP/INEOS MTO process.[243,258]

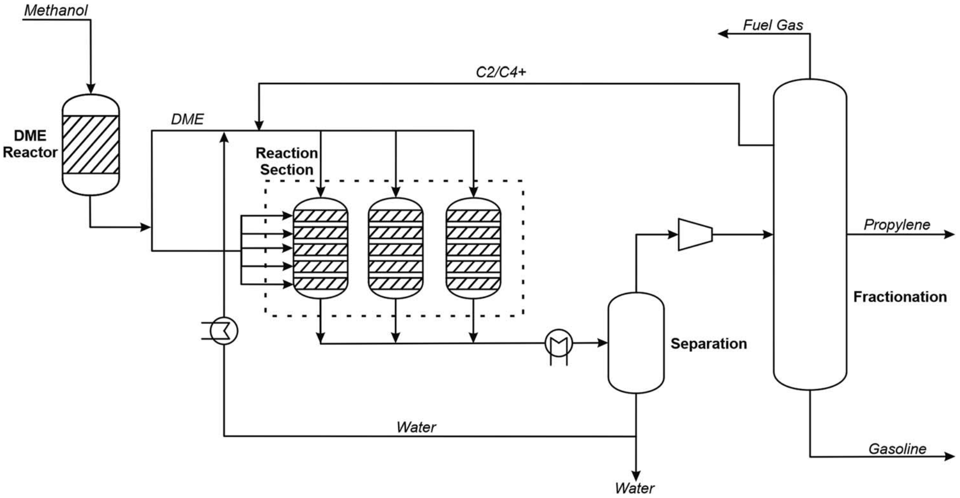

Fig. 7 Simplified process flow diagram of the Lurgi MTP Process.[184,243]

by Topsoe is claimed to produce predominantly C_{4+} olefins. The C_{4+} olefin selectivity, which may exceed 80 wt%, can be attributed to the combination of the catalyst, reactor configuration, and reaction conditions.[288]

Topsoe's MTO synthesis is preferentially carried out in two sets of parallel fixed bed reactors, operated at reaction temperatures below 400 °C and pressures up to 25 bar.[83,288–290] Hydrogen transfer reactions, typically promoted at elevated pressures, may be mitigated by operating temperatures below 400 °C and by limiting the methanol partial pressure by feed dilution to, *e.g.* 5 or 10 vol%.[83,288–290] Furthermore, the relatively mild reaction temperature may suppress monomolecular cracking of higher olefins.[291] Additional factors suggested to contribute to the C_{4+} olefin selectivity include the recycle of C_{3-} olefins, and operating the two reactor sets at a WHSV of 6–10 h^{-1}.[83,288–290] The patents claim that the high-pressure operation of MTO bridges the pressure gap between the MTO and oligomerization subprocess (Fig. 2), reducing the intermediate compression demand and results in energy savings and a simplified process.[83,288–290]

2.2.4 Products. In the context of the MTJ route, the MTO synthesis targets to produce a distribution of C_3–C_6 olefins. Alongside the C_3–C_6 olefins, the ethylene fraction produced could be either partially recycled back to the MTO reactor or directed to the subsequent oligomerization subprocess. The differences between ethylene oligomerization and C_3–C_6 olefins oligomerization will be addressed in the following section. The usage of an H-ZSM-5 catalyst in a fixed bed reactor is expected to yield a more favourable distribution of C_3–C_6 olefins compared to the SAPO-34 catalyst in a fluidized-bed reactor. To enhance the jet fuel yield from the MTJ route, it is essential to minimize the formation of aromatic and paraffinic byproducts during the MTO synthesis. Investigation on the impact of oxygenates, water and aromatics on the oligomerization is still scarce. This should be addressed by further research. Co-feeding a portion of the light olefins product as a recycle stream into the MTO reactor could suppress the aromatic cycle.[249,250]

2.3 Oligomerization

The oligomerization process involves increasing the olefin chain length by coupling of light olefin monomers.[292] Within the MTJ process, the light olefins produced in the MTO unit, predominantly ethylene, propylene, and butylene, are converted into longer-chain hydrocarbon (C_8–C_{16}) suited for jet fuel production.[293–295] On the industrial scale, oligomerization of light olefins is already established for the production of petrochemicals and various fuels, including polymeric gasoline (C_5–C_{10}) and diesel (C_{10}–C_{20}).[296,297] Despite being a mature technology, oligomerization processes are constantly advancing through ongoing research aimed at enhancing catalyst selectivity and lifetime, investigating new feedstocks, and improving both material and energetic efficiency.[294] However, research targeting to improve the selectivity of the oligomerization of mixed light olefins towards jet fuel is still scarce.

Product distribution and selectivity of the oligomerization process are significantly influenced by the feed composition. Oligomerization of various olefinic feedstocks has been investigated in literature, each exhibiting distinct oligomerization pathways and selectivity.[293,298–301] This section focuses on the oligomerization of olefin fractions ranging from C_2 to C_6, which are relevant to the MTJ pathway due to their prevalence in the MTO product.

2.3.1 Catalyst and reaction network. Table 4 provides an overview of different experimental oligomerization studies, including their respective feedstocks, product distributions, catalysts, and synthesis conditions.[19,297,302–309] Quantitative data on selectivity and yield are excluded, as these studies were not conducted within the framework of the MTJ process, thus avoiding misinterpretation.

Advances in the oligomerization of light olefins for synthetic fuel production have been made since UOP developed the first industrial catalyst in 1935, *i.e.* silica-supported solid phosphoric acid (SPA).[297] However, SPA catalyst faced challenges such as limited water tolerance, a short catalyst lifetime, and environmental concerns for its disposal, in addition to a low

Table 4 Summary of selected oligomerization experimental investigations in literature

Olefin feed	Temperature (°C)	Pressure (bar)	Catalyst	Si/Al	WHSV (h^{-1})	Target olefins products	Reference
C_2H_4	120	50	Ni/SiO_2–Al_2O_3	0.6	8	C_6–C_{12}	302
C_3H_6	270	40	Ni/H-ZSM-5	25	4.03	C_6–C_{18+}	303
C_3H_6	200–274	1	H-ZSM-5	12–140	—	C_6–C_{12+}	304
C_3H_6	210–250	2.2	H-ZSM-5	13	—	C_4–C_{9+}	305
C_4H_8	175–325	1.5	H-ZSM-5	30–180	5.6–112	C_8–C_{12}	306
C_2H_4 C_3H_6 C_4H_8	200–450	1	H-ZSM-5 H–Na-ZSM-5	30	—	C_2–C_8	307
C_2H_4 C_3H_6 C_4H_8	120	16–32	Ni/SiO_2–Al_2O_3	—	4	C_6–C_{13+}	308
C_3H_6 C_6H_{12}	200–250	40	Pristine ZSM-5 Meso-ZSM-5	18 12.8	1–8	C_3–C_{12+}	309
C_3H_6/C_3H_8	100–200	20–40	Meso-SiO_2–Al_2O_3	—	1–20	—	297
C_3H_6/C_4H_8	140–260	13.8	H-ZSM-5 H–Y H-beta Amberlyst-36 Purolite-CT275	23 5.2 20 — —	1.1	C_6–C_{12+}	19

productivity and corrosion issues.[310] Regarding current catalyst research, it is observed that studies can be categorized into two main categories:

(1) Ethylene oligomerization over transition metal catalysts.[293,311]

(2) Oligomerization of higher olefins such as propylene and butylene over acidic catalysts.[294,312,313]

The difference is attributed to the distinct oligomerization mechanism operative over the catalyst, namely metal-catalysed 1,2-insertion and Brønsted acid-catalysed oligomerization involving carbenium intermediates.[294] Ethylene oligomerization is not favourable over solid acid catalysts due to an unstable primary carbenium intermediate.[69] Obtaining jet fuel range olefins *via* a single-stage oligomerization of ethylene-containing olefin feedstocks derived from MTO, is therefore challenging.

Ethylene oligomerization has been investigated over a range of homogenous and heterogenous transition metal catalysts.[295,314–318] Among catalysts for ethylene oligomerization, nickel-based catalysts have received the most attention in both academic and industrial applications, due to their activity, selectivity, stability, and low cost.[295] The performance of nickel-based catalysts is largely determined by the number of accessible active sites. With the co-existence of several Ni species in heterogeneous Ni-based catalysts, the exact chemical nature of the active site is debated in the scientific community.[293,317] As discussed by Olivier-Bourbigou *et al.*,[293] experimental evidence has been presented both for Ni(I) species, (coordinatively unsaturated) Ni(II) species, as well as Ni(I)/Ni(II) redox shuttles.

The acid properties and morphology of the catalyst support is likewise of importance, with factors such as the prevalence, density and strength of Brønsted acid sites and the porosity affecting the structure, carbon number distribution, and the stability of the resulting oligomers.[319–321] Reviews by Finiels *et al.* and Olivier-Bourbigou *et al.* provide detailed discussions on the dimerization and oligomerization mechanisms over nickel-based catalysts.[293,317] Product selectivity following a Schulz–Flory distribution, as well as product spectra deviating from this distribution, have been reported in literature, depending on the catalyst and applied process conditions.[302,311,316,322] For example, Betz *et al.* demonstrated that ethylene oligomerization over Ni/SiO_2–Al_2O_3 catalysts predominantly produces C_6, C_8, C_{10} and C_{12} fractions under conditions of 120 °C and 50 bar ethylene partial pressure, and a space velocity of 8 h^{-1}.[302]

Oligomerization of the ethylene fraction produced during the MTO process is crucial for enhancing the carbon efficiency and jet fuel selectivity of the overall MTJ process. There are two main approaches to convert ethylene into jet fuel range olefins:

(1) The two step approach based on dimerizing or trimerizing ethylene into an intermediate olefin, *e.g.* butylene and hexene, in a first reactor, followed by acid-catalysed oligomerization of the produced C_{3+} olefins to jet fuel range olefins in a second reactor.[319,323,324]

(2) The direct oligomerization of ethylene which is characterized by a low selectivity and requires substantial recycling streams, making it economically less favourable than the two step approach.[325]

Oligomerization of C_3–C_6 olefins has been investigated in literature over various heterogenous solid acid catalysts, including zeolites (*e.g.*, H-ZSM-5, H-beta),[299,326] amorphous silica–alumina (ASA, SiO_2–Al_2O_3),[327] sulfonic acid polymeric resins (*e.g.*, Amberlyst),[302,328] and SPA.[294,329] Among these, zeolites and sulfonic resins have been extensively studied for converting olefins to fuel-range hydrocarbons.[19] Zeolites are favoured for operations at increased temperatures of about 250 °C, facilitating multiple reaction types including oligomerization, disproportionation, cracking, and isomerization.[19] Notably, the H-ZSM-5 zeolite is commonly used for light olefin oligomerization due to its higher thermal stability compared to polymeric resins and suitable operational temperature range between 200 °C and 300 °C.[292,328] This particular temperature range allows for secondary reactions like disproportionation, cracking, and isomerization, supporting the production of branched longer-chain hydrocarbons ideal for jet fuel.[19] Saavedra Lopez *et al.* investigated the oligomerization of propylene/isobutylene over H-Beta zeolite at a temperature range of 140–260 °C.[19] They observed that higher oligomerization temperatures result in higher conversion of propylene, but with a decreased yield of jet fuel distillate due to secondary cyclization/isomerization, hydrogenation, and cracking reactions.

Mechanistically, Brønsted acid catalysed olefin oligomerization is initiated by the protonation of olefin by a Brønsted acid site, forming a carbenium intermediate, as described in Fig. 8.[305,330] The carbenium species undergo transformations like hydride shifts, oligomerization (alkylation), methyl shifts, and protonated cyclopropane (PCP) branching, and are eventually reverted to olefins through deprotonation.[331,332] Oligomerization extends the carbenium ion chain. In contrast, β-scission is a cracking mechanism, where the chain length is reduced. The reaction rates depend on the size and stability of the carbenium ion; larger ions react more slowly than smaller methyl and ethyl ions. Hydrogen transfer within these reactions leads to the formation of lighter paraffins.[333]

The shape selectivity and acid properties of the H-ZSM-5 zeolite catalyst enable a high activity for transforming C_3–C_6 olefins into gasoline, jet fuel and diesel fractions, while exhibiting a low deactivation rate.[334] The microstructure of the catalysts, such as the mean pore size and pore size distribution, plays a role in oligomerization reactions. A study by Monama *et al.* on desilicated ZSM-5 reveals that increased mesoporosity enhances the accessibility to acid sites, and improves the oligomerization activity for 1-hexene and propylene.[309] Larger pores in beta zeolite and desilicated ZSM-5, compared to small-sized pores of ZSM-5, improve access to acid sites for larger molecules and facilitate the desorption and diffusion of reaction products.[309,335] Thus, mesoporosity not only facilitates the diffusion of reactants and products, but also promotes the formation of longer chain hydrocarbons and extends catalyst lifetime.[309,336,337] Bickel and Gounder showed that propylene dimerization rates in H-ZSM-5 zeolites decrease with larger crystallite sizes, highlighting the importance of diffusion limitations and the impact of internally formed organic phases within micropores.[338]

Modification of the oligomerization catalyst, by alteration in composition, structure, and acidity, can impact the catalyst performance.[339–341] One notable modification involves incorporation of Ni into the H-ZSM-5 zeolite, which favours the formation of high molecular weight oligomers, particularly beneficial for diesel production. A study by Li *et al.* for propylene oligomerization revealed that a modified H-ZSM-5 catalyst with a Ni content of 2.21 wt% achieved a selectivity of 79% towards diesel compared to a selectivity of 68% for H-ZSM-5.[303] The addition of Ni can also confer activity for ethylene oligomerization, as discussed previously. Additionally, advancements like the dealumination of ZSM-5 zeolites were found to enhance ethylene conversion and favour jet fuel range production.[325]

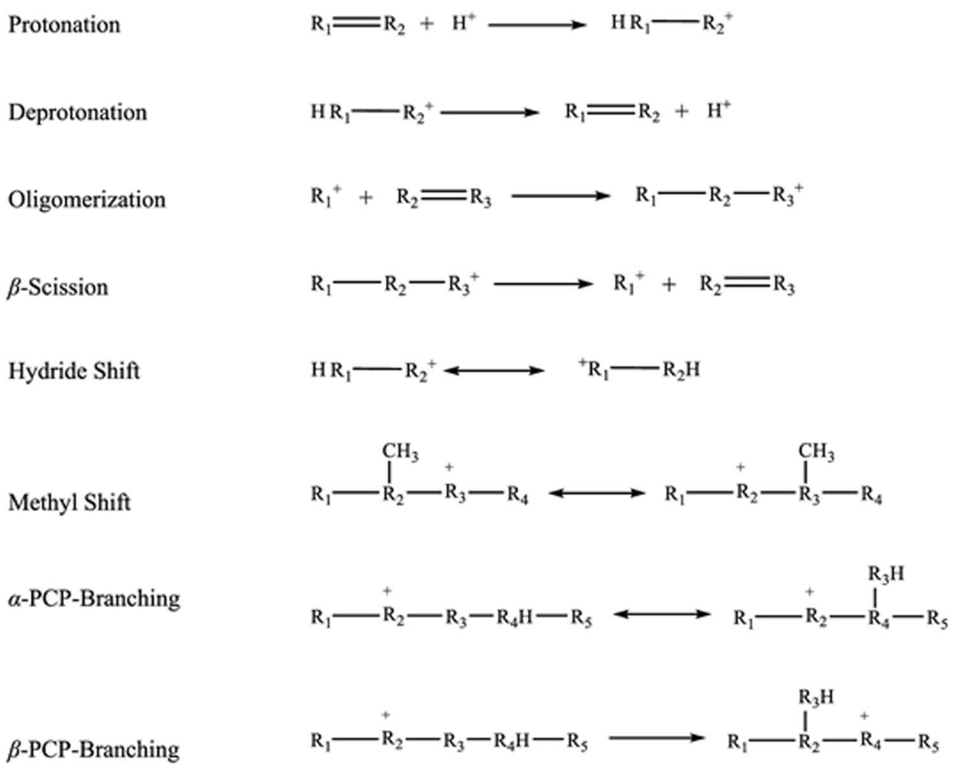

Fig. 8 Proposed reactions for propylene oligomerization on acid zeolites (reproduced from ref. 330 with permission from John Wiley and Sons, copyright 2019).

Research by Mlinar *et al.* indicated that a lower Si/Al ratio in catalysts enhances selectivity towards dimer formation rather than cracking products.[304] However, a lower Si/Al ratio with increased concentration of Brønsted acid sites could negatively impact the oligomerization selectivity and increase the productivity of aromatics.[304,342]

Catalytic activity and selectivity are significantly influenced by temperature, reactant partial pressure, and contact time between the reaction mixture and the acid sites of the catalyst.[343] A study by Coelho *et al.* on 1-butylene oligomerization over a H-ZSM-5 catalyst indicates an increase of oligomerization selectivity with temperature increased up to a threshold of 200 C, beyond which cracking dominates over oligomerization.[344] Furthermore, their findings indicate an increase in conversion at higher reactant partial pressure. In their investigation of butylene oligomerization to liquid fuels at 1.5 bar and 275 °C on H-ZSM-5 with $SiO_2/Al_2O_3 = 30$, Díaz *et al.* demonstrated that increasing the space time ($0.5–10\ g_{catalyst}\ h\ mol_c{}^{-1}$) results in higher butylene conversion, associated with higher selectivity for C_5–C_7 and lower selectivity for C_8–C_{12}.[306] This can be attributed to the cracking of C_8–C_{12} fractions, while the selectivity for by-products like paraffins remained unchanged. In conclusion, optimizing the conditions of reaction temperature, partial pressure and contact time is necessary to promote the formation of olefins with a carbon chain length suitable for jet fuel (C_8–C_{16}) and reduce the formation of cracking and hydrogen transfer products. The ethylene content of the oligomerization feed is decisive for the design of the oligomerization subprocess within MTJ, as it determines whether a one-stage oligomerization over solid acid catalysts is sufficient for obtaining a high jet fuel yield.

2.3.2 Process layout. The MOGD process introduced the idea of using H-ZSM-5 zeolite and similar zeolites as potential alternatives to traditional SPA catalysts for olefin oligomerization in the 1970s and 1980s.[307,345–348] Integrated with ExxonMobil's MTO process, the MOGD process can convert light olefins in the C_3–C_6 range into hydrocarbon products such as jet fuel. The specific conditions for oligomerization reported in literature are in the range of 200 °C to 300 °C and 40 bar applied in a system of four fixed-bed reactors, out of which three are operational and one in regeneration mode.[80,270,349] The MOGD process, shown in Fig. 9, produces high yields of distillate fuels (82%), alongside gasoline (15%) and light gases (3%), with the flexibility to adjust the distillate/gasoline ratio by adjusting the olefin yield from the MTO process.[270,350] The integration of the MTO and MOGD processes therefore also demonstrates the potential of producing jet fuel out of methanol.[69,349]

The conversion of olefins to distillate (COD) process, developed by PetroSA in South Africa, converts C_3–C_6 olefins produced in FT synthesis into higher olefins, with the purpose of producing fuels such as gasoline and diesel.[327,351] The COD process was investigated over ASA, SPA and H-ZSM-5 catalysts.[327,352,353] Among those, H-ZSM-5 is notable for producing a higher cetane number post hydrogenation reaction.[69] The COD oligomerization of FT light olefins over H-ZSM-5 is conducted at operating conditions of 210 °C to 253 °C, 56 bar to 57 bar, and WHSV 0.5 h^{-1}.[353] The FT feedstock in the COD process consists of over 80% olefins and 13% to 17% paraffins. The propylene conversion within the COD process ranges from 92% to 99%.[354] In conclusion, insights gained from the MOGD and COD processes, which are established technologies with a relatively high TRL, could be used within the MTJ process to enable the conversion of C_3–C_6 olefins into jet fuel range hydrocarbons over H-ZSM-5.

2.3.3 Products. The oligomerization subprocess within the MTJ route aims to maximize the yield of hydrocarbons fractions ranging from C_8–C_{16} while minimizing the formation of

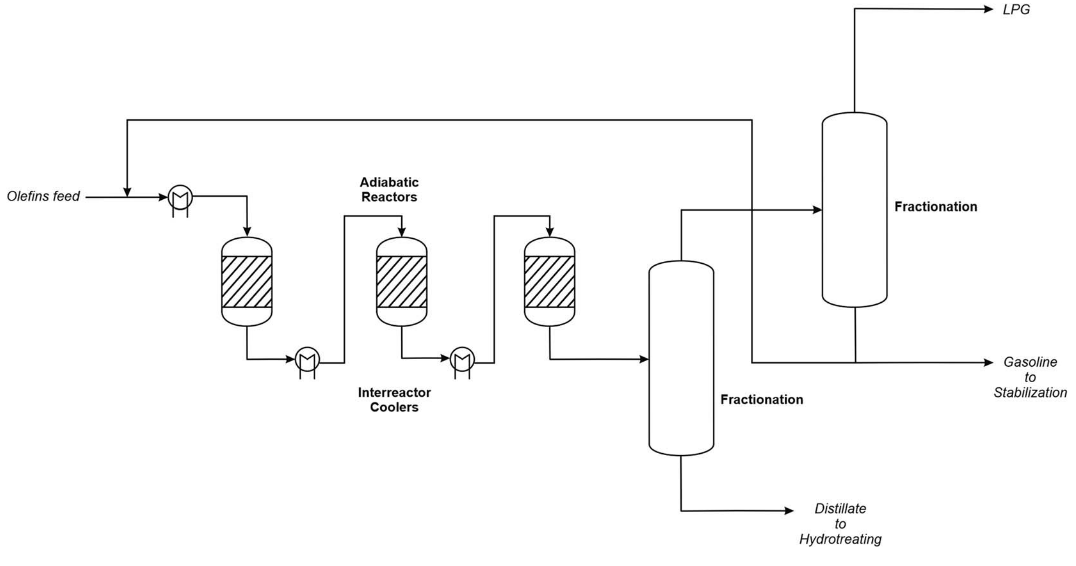

Fig. 9 Simplified process flow diagram of the MOGD process.[278]

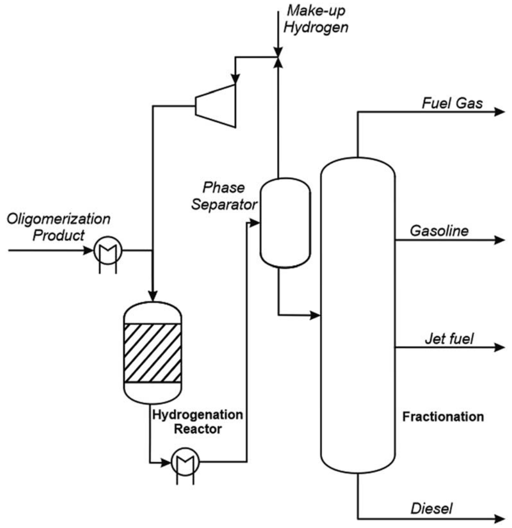

Fig. 10 Simplified process flow diagram of the hydrogenation of the oligomerization products.[341]

byproducts such as gasoline and diesel. The product distribution of oligomerization subprocess and the preferred oligomerization strategy depend on the olefin distribution produced in the MTO subprocess, emphasizing the importance of studying these two subprocesses in an integrated manner.

2.4 Hydrogenation

Olefins are highly reactive compounds capable to form deposits in jet engines.[71] Therefore, the hydrogenation of the olefins produced from the oligomerization process to paraffins is a crucial step within the MTJ route to enhance the stability and performance of jet fuel.[355–357] The hydrogenation process involves the addition of H_2 to unsaturated olefins:

$$C_nH_{2n} + H_2 \rightarrow C_nH_{2n+2}$$

The reaction is catalysed by reduced metals, such as Ni, Pd or Pt supported on alumina or activated carbon.[358–360] The exothermic reaction is usually carried out in a fixed-bed reactor at temperature and pressure ranges between 50 °C and 370 °C as well as 5 bar and 50 bar, respectively.[69,70,357,361] Specific hydrogenation conditions depend on the active metal, feedstock and targeted product. The H_2 gas is fed in stoichiometric excess to achieve an approximately complete conversion of olefins to paraffins. Excess H_2 is recovered downstream the reactor by a gas/liquid separator and recycled to the reactor inlet (see Fig. 10).[24,358] Downstream the separator, hydrocarbons are fractionated to segregate light hydrocarbons ($<C_8$), jet fuel range hydrocarbons (approximately C_8–C_{16}), and heavier hydrocarbons. An isomerization unit is not required, as acid-catalysed olefin oligomerization within the MTJ process produces branched olefins.[71] Meeting the final jet fuel properties, such as flashpoint, freezing point and distillation curve, the final separation after hydrogenation shall be defined by the ASTM standard for MTJ.[20]

3 Potential for process integration and intensification

Process intensification strategies aim to enhance efficiency, reduce equipment requirements, and decrease environmental impact of chemical processes by integrating subprocesses or using innovative equipment.[362–364] In the context of SAF production, these strategies should be evaluated by their impact on the overall jet fuel yield and process efficiency. The previous sections illustrated several state-of-the-art process layouts for the subprocesses involved in the MTJ route, highlighting the potential for further research and development regarding process integration and intensification. To intensify the process chain, these subprocesses need to be integrated in terms of recycle streams and heat integration strategies. This section discusses key challenges and research questions for process integration and intensification concepts significantly influencing the future implementation of the MTJ process. A simplified block diagram is shown in Fig. 11 to illustrate different recycle possibilities and process configurations discussed in this section.

A key aspect with significant potential for overall energy efficiency improvements in the MTJ process is related to the feedstock of the MTO process. On the one hand, distillation of crude methanol within the methanol synthesis subprocess requires substantial heat. On the other hand, co-feeding water with methanol helps to reduce the catalyst deactivation and manage the heat of the exothermic MTO synthesis.[365,366] Therefore, directly using crude methanol as feedstock for the MTO process can save energy and costs associated with distillation.[71] Additionally, the reaction heat generated during methanol synthesis could potentially be utilized elsewhere in the process, enhancing the overall MTJ process efficiency. It is crucial to consider that the presence of impurities in crude methanol may influence the initiation of the olefinic cycle and the subsequent MTO conversion process. Oxygenates with carbon–carbon (C–C) bonds may accelerate the MTO conversion, and higher alcohols are expected to dehydrate into their respective olefins.[367] Consequently, future research is needed to investigate the impact of these impurities on MTO conversion and their potential effects on catalyst deactivation. However, implementing this strategy would require for methanol synthesis and MTO subprocesses being located geographically close to each other.

Particularly important is optimizing the yield of the MTO subprocess towards C_2 and C_3–C_6 olefins, as this significantly affects the subsequent reaction mechanisms and product distribution in the oligomerization subprocess and can impact the overall yield of the jet fuel product. Feeding DME into the MTO subprocess could improve olefins yield.[218,219] To enhance energy efficiency and decrease equipment cost of the additional conversion step from methanol to DME, integrated concepts are currently under investigation which could be applied in this context.[368–370] Further research should be carried out to investigate the impact of the MTO feed, particularly crude methanol and/or DME, on the reaction mechanism, selectivity, reaction

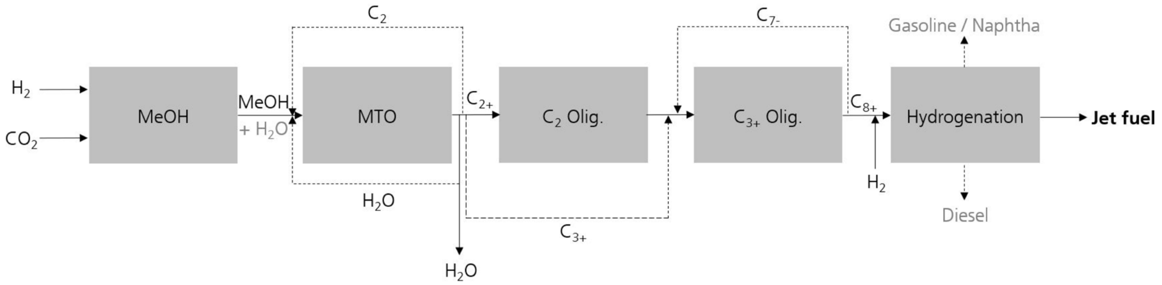

Fig. 11 A simplified block diagram illustrating various recycle options and process configuration discussed in Section 3 regarding the potential for process integration and intensification starting from CO_2 and H_2.

kinetics, and catalyst stability, in order to optimize the feedstock of MTO processes for SAF production.

As the MTO product could consist of up to 30 wt% ethylene,[251] it emerges as an intermediate product that requires careful management to achieve high jet fuel yields. A main challenge in co-oligomerizing a mixture of ethylene and other light olefins (*e.g.*, propylene and butylene) lies in the differing oligomerization mechanisms and the types of catalysts required.[294] Literature discusses three main approaches for the further conversion of ethylene within the MTJ process:

(1) Recycling ethylene back into the MTO reactor[213]

(2) Direct ethylene oligomerization[325]

(3) Two-step oligomerization[319,323,324]

While recycling ethylene to the MTO synthesis is feasible only in limited amounts and may not significantly improve overall carbon efficiency, direct ethylene oligomerization into jet fuel range olefins suffers from low selectivity and conversion, necessitating substantial recycling, which makes it an energy-intensive option.[319,324,325] In contrast, the two-step oligomerization could be more efficient, as it allows for a more selective conversion of ethylene to the desired jet fuel range olefins.[325] This method involves oligomerizing the ethylene fraction in a separate reactor with transition metal catalysts to produce higher olefins (primarily in the C_4 and C_6 range).[319] These higher olefins can then be sent to the second oligomerization reactor loaded with an acid catalyst. In conclusion, the limitations of recycling ethylene back into the MTO process suggest a need for further investigation of alternative strategies, particularly the two-step oligomerization approach, especially when substantial amounts of ethylene are produced in MTO.

The oligomerization reaction mechanism and product distribution are significantly influenced by the distribution of light olefins produced in the MTO process. Theoretically, the oligomerization product mixture could be sent entirely to the hydrogenation subprocess. However, unconverted light olefins are valuable intermediates. Thus, recycling these compounds back to the MTO or oligomerization subprocesses has the potential to significantly improve the overall jet fuel yield. On the one hand, co-feeding small concentrations of light olefins, such as propylene and butylene, with the methanol feedstock into the MTO subprocess enhances the olefinic cycle, leading to a higher yield of the desired light olefin chain lengths of C_{3+}.[242,249,250] On the other hand, the co-oligomerization of a mixed olefin feedstock results in a more uniform product distribution and improved overall selectivity towards jet fuel range hydrocarbons.[19,308] This enables multiple options for recycling light olefins (C_2–C_7) that fall short of the jet fuel chain length downstream of oligomerization. Thus, a critical area for further investigation is identified as the evaluation of extent and impact of recycling streams on energy demand, alongside improvements in product distribution and process efficiency.

By integrating and intensifying the oligomerization and hydrogenation processes, efficiency improvements and reductions in equipment requirements can be achieved. As an example, Topsoe introduced a method combining these steps into a single hydro-oligomerization (Hydro-OLI) step.[83] The process utilizes a reactor system with stacked catalyst beds, incorporating a hydrogenation metal (*e.g.*, Pd, Rh, Ni) and a zeolite. While this combination produces less heat than higher oligomerization processes and converts olefins into mainly C_8–C_{16} hydrocarbons, it has the disadvantage of eliminating the possibility to recycle short olefins back to the reactor, as all olefins are saturated into paraffins. Moreover, the integration can reduce separation efforts and enhance energy efficiency. However, such improvements depend on maintaining a comparable jet fuel yield or aiming to produce various hydrocarbon product streams. Additionally, using reactive distillation for combined oligomerization and hydrogenation has been demonstrated in the literature.[357] This concept shows the potential to improve the energy and mass efficiency of the process and reduce equipment costs, but requires further research and development within the MTJ process.

Another intensification approach is the one-pot hydrogenation of CO_2 to olefins.[371] The direct conversion of CO_2 and H_2 into hydrocarbons within a single reactor has the potential to reduce the overall energy demand and simplify the process layout compared to individual synthesis steps.[372,373] This method can be implemented *via* two primary pathways:

(1) The combination of the RWGS reaction with FT synthesis (CO_2-FT route)

(2) The integration of the methanol synthesis with the MTO synthesis (MeOH-mediated route)

While the limitations and potentials of the CO_2-FT route were already discussed in Section 1 of this article, state of science of the MeOH-mediated pathway will be discussed briefly here. For this route, the methanol and MTO synthesis can be combined using a bifunctional catalyst, consisting of a metal catalyst for methanol synthesis and a zeolite catalyst for the MTO reaction, at operating conditions of 350 °C to 400 °C and 15 bar to 30 bar.[374] This route is capable of producing light olefins with a high selectivity due to the metal/zeolite composite catalysts used.[375] However, the low C–C coupling activity as well as the formation of the byproduct water enhancing deactivation of the metal catalyst hinder the technical implementation of this pathway.[372,376] Moreover, the direct CO_2 to olefins conversion suffers from lower conversion compared to the established two-step methanol synthesis and MTO processes.[211,377] Given the currently low TRL for the direct CO_2 to olefins conversion, further research focusing on the development of efficient bifunctional and multifunctional catalysts that perform effectively under the required conditions for both methanol and MTO synthesis, while maintaining stability, remains critical for advancing this technology.

In terms of the geographical distribution of the MTJ process chain, two different approaches are possible: first, producing methanol from CO_2 and H_2 at one site and then transporting the methanol as an intermediate to a location for further jet fuel production; or second, producing jet fuel from CO_2 and H_2 in an integrated process at a single site. The first approach offers flexibility by allowing sourcing "green" methanol from the global market, independent of security of supply limitations. On the other hand, the second approach, would enable improved heat integration opportunities and higher overall process energy efficiency. Additionally, it is crucial to emphasize that the recycling of byproducts (such as fuel gas and processed purge gas) through reforming can only be effectively implemented in plant designs where methanol synthesis and MTJ processes are located at the same site. The extend of the dynamic operation of methanol synthesis to utilize the fluctuating energy supply for both approaches should be investigated in a simulation study.[73–76,378] Furthermore, scenario-specific technoeconomic assessments are recommended to evaluate economic scenarios for global SAF production.

4 Conclusions

The aviation sector faces a pressing need for sustainable alternatives to fossil feedstock-based jet fuel to mitigate its environmental impact. SAFs offer a viable drop-in solution and can be produced from various feedstocks. The MTJ pathway represents a promising route, as it offers high jet fuel yields and low byproduct formation. This review explores the current state-of-the-art of the MTJ process concepts involving the conversion of H_2 and CO_x into jet fuel through methanol synthesis, MTO synthesis, oligomerization, and hydrogenation. The main findings highlight the necessity of an integrated process to achieve high yields of SAF and economic viability.

The MTJ process chain begins with methanol synthesis with the option of dynamic operation to add flexibility to the MTJ process in coupling with fluctuating renewable energies.

Methanol is then converted to light olefins in the MTO synthesis determining jet fuel selectivity and yield. H-ZSM-5 and SAPO-34 are the commonly used catalysts for the MTO subprocess operated in a fixed bed or fluidized-bed reactor, respectively. Among these catalysts, H-ZSM-5 catalyst seems more promising for SAF production as it shows a higher selectivity to C_3–C_6 olefins compatible for the MTJ process, while exhibiting a lower tendency for coke formation and a lower selectivity towards the formation of ethylene. The olefin yield and catalyst lifetime can be improved through various strategies, including catalyst modification, olefin co-feeding, MeOH dilution and product back-mixing. The most widely accepted mechanism for the MTO reaction network is the dual-cycle mechanism, composed of the olefinic cycle and aromatic cycle. However, representative modelling of the reaction mechanism is challenging, due to the complex reaction network and challenges regarding the analytical evaluation of experimental results. Most published kinetic models on MTO synthesis are based on simplified assumptions or target solely for selective propylene production. Further research is required to develop appropriate kinetic models optimized for the process conditions relevant for an MTJ application.

The oligomerization process is used to transform lighter olefins (C_2–C_6) into longer-chain olefins (C_8–C_{16}). Available scientific literature mainly targets ethylene oligomerization over transition metal catalysts and C_3–C_6 olefins oligomerization over acidic catalysts, due to mechanistic differences in the oligomerization of ethylene and higher olefins. Thus, the oligomerization of MTO products comprising both C_2 and C_3–C_6 olefins needs special consideration regarding catalyst and process design. The oligomerization of C_3–C_6 olefins over heterogeneous solid acid catalysts such as zeolites, amorphous silica–alumina, and sulfonic acid polymeric resins has also been explored, with zeolites favoured for their thermal stability and suitable operational temperature range. Optimized reaction conditions, including temperature, reactant partial pressure, and contact time, are crucial for promoting the formation of jet fuel range olefins. The feed composition from the MTO subprocess significantly influences the reaction mechanism, product distribution, and selectivity in the oligomerization subprocess; therefore, both subprocesses should be investigated in an integrated manner. Thus, dedicated kinetic studies on both MTO and oligomerization step within the context of MTJ conversion will be necessary to reduce the uncertainty associated with future techno-economic analyses and process simulations. Industrial processes such as MOGD and COD have integrated oligomerization with other technologies to convert light olefins into gasoline and diesel, demonstrating the potential for jet fuel production through the MTJ process.

The product mixture of the oligomerization process is finally hydrogenated over reduced metal catalysts to enhance the stability and performance of jet fuel. The hydrogenation subprocess is the least challenging, as state-of-the-art technologies can be applied for SAF production.

Key challenges for the practical implementation of the MTJ process chain remain in optimizing the integration and intensification between the subprocesses, particularly in the MTO subprocess and the subsequent oligomerization subprocess, with regard to jet fuel yield. Several process intensification and integration aspects have been highlighted for further research by the scientific community within this review:

(1) The direct use of crude methanol produced from the methanol synthesis process into the MTO reactor could achieve savings in energy and costs associated with methanol distillation. The impact of side products as well as the increased water content within the crude methanol on selectivity should be investigated.

(2) Recycling of C_2–C_7 olefins downstream the oligomerization step that fall short of the jet fuel range either to the MTO reactor or the oligomerization reactor to improve the overall jet fuel yield of the MTJ process should be examined. Here, special attention to the impact of recycle streams towards energy demand, product distribution and process efficiency should be drawn.

(3) The two-step oligomerization approach for managing the ethylene fraction produced within the MTO synthesis presents a promising area for further investigations to improve the MTJ yield and process efficiency.

(4) The combination of the oligomerization and hydrogenation within one reactor unit could reduce equipment costs and enhance energy efficiency. However, this depends on maintaining a comparable jet fuel yield or aiming to produce different side products.

Identifying the optimal combination of MTO and oligomerization technology is the key challenge in optimizing the MTJ process. This aspect should be investigated in further research utilizing process simulation studies to accurately evaluate the overall process efficiency. Finally, future research should focus on refining new process integration and intensification strategies to improve the economic feasibility, efficiency, and environmental impact of the MTJ process. Overall MTJ yield and process efficiency could be significantly improved by further optimizing parameters like feedstock composition, operating conditions, and process integration.

Abbreviations

AEL	Alkaline Electrolysis
AEM	Anion Exchange Membrane Electrolysis
ASA	Amorphous Silica–Alumina
ASTM	American Society for Testing and Materials
ATJ	Alcohol-to-Jet
BAS	Brønsted Acid Site
COD	Conversion of Olefins to Distillate
CCU	Carbon Capture and Utilization
DAC	Direct Air Capture
DME	Dimethyl Ether
DOC	Direct Ocean Capture
DTO	DME-to-Olefins
eSAF	Electro Sustainable Aviation Fuel
FT	Fischer–Tropsch
GHG	Greenhouse Gas
HEFA	Hydroprocessed Esters and Fatty Acids
HTE	High-Temperature Electrolysis
IATA	International Air Transport Association
LAS	Lewis Acid Site
LCOP	Levelized Cost of Production LCOP
LHV	Lower Heating Value
MOGD	Mobil Olefins to Gasoline and Distillate
MTA	Methanol-to-Aromatics
MTG	Methanol-to-Gasoline
MTH	Methanol-to-Hydrocarbons
MTJ	Methanol-to-Jet
MTO	Methanol-to-Olefins
MTP	Methanol-to-Propylene
NOx	Nitrogen Oxides
PEMEL	Proton Exchange Membrane Electrolysis
rWGS	Reverse Water Gas Shift
SAF	Sustainable Aviation Fuel
SPA	Solid Phosphoric Acid
TOS	Time on Stream
TRL	Technology Readiness Level

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Author contributions

Ali Elwalily: conceptualization, methodology, investigation, formal analysis, writing – original draft, writing – review & editing, visualization, Emma Verkama: writing – original draft, writing – review & editing, Franz Mantei: conceptualization, writing – review & editing, project administration, Adiya Kaliyeva: investigation, formal analysis, Andrew Pounder: investigation, formal analysis, Jörg Sauer: conceptualization, writing – review & editing, supervision, Florian Nestler: conceptualization, writing – original draft, writing – review & editing, supervision.

Conflicts of interest

There are no conflicts of interest to declare.

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References

1 A. Barke, T. Bley, C. Thies, C. Weckenborg, T. S. Spengler, A. Barke, T. Bley, C. Thies, C. Weckenborg and T. S. Spengler, Are Sustainable Aviation Fuels a Viable Option for Decarbonizing Air Transport in Europe? An Environmental and Economic Sustainability Assessment, *Appl. Sci.*, 2022, **12**, 597.

2 IEA, Oil Market Report – April 2024 – Analysis – IEA, https://www.iea.org/reports/oil-market-report-april-2024, accessed 11 July 2024.

3 A. R. Gnadt, R. L. Speth, J. S. Sabnis and S. R. Barrett, Technical and environmental assessment of all-electric 180-passenger commercial aircraft, *Prog. Aero. Sci.*, 2019, **105**, 1–30.

4 International Civil Aviation Organisation (ICAO), Trends in Emissions that affect Climate Change, https://www.icao.int/environmental-protection/Pages/ClimateChange_Trends.aspx, accessed 16 April 2025.

5 M. Braun-Unkhoff, U. Riedel and C. Wahl, About the emissions of alternative jet fuels, *CEAS Aeronaut. J.*, 2017, **8**, 167–180.

6 P. Su-ungkavatin, L. Tiruta-Barna and L. Hamelin, Biofuels, electrofuels, electric or hydrogen?: A review of current and emerging sustainable aviation systems, *Prog. Energy Combust. Sci.*, 2023, **96**, 101073.

7 Eurocontrol, The aviation network – Decarbonisation issues, https://www.eurocontrol.int/publication/aviation-network-decarbonisation-issues, accessed 16 April 2025.

8 D. S. Lee, D. W. Fahey, P. M. Forster, P. J. Newton, R. C. Wit, L. L. Lim, B. Owen and R. Sausen, Aviation and global climate change in the 21st century, *Atmos. Environ.*, 2009, **43**, 3520–3537.

9 D. S. Lee, M. R. Allen, N. Cumpsty, B. Owen, K. P. Shine and A. Skowron, Uncertainties in mitigating aviation non-CO2 emissions for climate and air quality using hydrocarbon fuels, *Environ. Sci.: Atmos.*, 2023, **3**, 1693–1740.

10 D. S. Lee, D. W. Fahey, A. Skowron, M. R. Allen, U. Burkhardt, Q. Chen, S. J. Doherty, S. Freeman, P. M. Forster, J. Fuglestvedt, A. Gettelman, R. R. De León, L. L. Lim, M. T. Lund, R. J. Millar, B. Owen, J. E. Penner, G. Pitari, M. J. Prather, R. Sausen and L. J. Wilcox, The contribution of global aviation to anthropogenic climate forcing for 2000 to 2018, *Atmos. Environ.*, 2021, **244**, 117834.

11 C. Bergero, G. Gosnell, D. Gielen, S. Kang, M. Bazilian and S. J. Davis, Pathways to net-zero emissions from aviation, *Nat Sustainability*, 2023, **6**, 404–414.

12 M. Klöwer, M. R. Allen, D. S. Lee, S. R. Proud, L. Gallagher and A. Skowron, Quantifying aviation's contribution to global warming, *Environ. Res. Lett.*, 2021, **16**, 104027.

13 P. J. Ansell, Review of sustainable energy carriers for aviation: Benefits, challenges, and future viability, *Prog. Aero. Sci.*, 2023, **141**, 100919.

14 M. Ozkan, A. B. Narappa, T. Namboodiri, Y. Chai, M. Babu, J. S. Jennings, Y. Gao, S. Tasneem, J. Lam, K. R. Talluri, R. Shang, C. S. Ozkan and J. M. Watkins, Forging a sustainable sky: Unveiling the pillars of aviation e-fuel production for carbon emission circularity, *iScience*, 2024, **27**, 109154.

15 S. Manigandan, T. R. Praveenkumar, J. Ir Ryu, T. Nath Verma and A. Pugazhendhi, Role of hydrogen on aviation sector: A review on hydrogen storage, fuel flexibility, flame stability, and emissions reduction on gas turbines engines, *Fuel*, 2023, **352**, 129064.

16 P. Mäki-Arvela, A. Aho, I. Simakova and D. Y. Murzin, Sustainable Aviation Fuel from Syngas through Higher Alcohols, *ChemCatChem*, 2022, **14**, e202201005.

17 S. Bube, N. Bullerdiek, S. Voß and M. Kaltschmitt, Kerosene production from power-based syngas – A technical comparison of the Fischer-Tropsch and methanol pathway, *Fuel*, 2024, **366**, 131269.

18 N. Detsios, S. Theodoraki, L. Maragoudaki, K. Atsonios, P. Grammelis and N. G. Orfanoudakis, Recent Advances on Alternative Aviation Fuels/Pathways: A Critical Review, *Energies*, 2023, **16**, 1904.

19 J. Saavedra Lopez, R. A. Dagle, V. L. Dagle, C. Smith and K. O. Albrecht, Oligomerization of ethanol-derived propene and isobutene mixtures to transportation fuels: catalyst and process considerations, *Catal. Sci. Technol.*, 2019, **9**, 1117–1131.

20 D02 Committee, *Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons, D7566*, ASTM International, West Conshohocken, PA, 2023.

21 D02 Committee, *Practice for Evaluation of New Aviation Turbine Fuels and Fuel Additives, D4054*, ASTM International, West Conshohocken, PA, 2023.

22 M. A. Rumizen, Qualification of Alternative Jet Fuels, *Front. Energy Res.*, 2021, **9**, DOI: 10.3389/fenrg.2021.760713.

23 D02 Committee, *Specification for Aviation Turbine Fuels, D1655*, ASTM International, West Conshohocken, PA, 2023.

24 S. Geleynse, K. Brandt, M. Garcia-Perez, M. Wolcott and X. Zhang, The Alcohol-to-Jet Conversion Pathway for Drop-In Biofuels: Techno-Economic Evaluation, *ChemSusChem*, 2018, **11**, 3728–3741.

25 A. Anuar, V. K. Undavalli, B. Khandelwal and S. Blakey, Effect of fuels, aromatics and preparation methods on seal swell, *J. Aeronaut. Sci.*, 2021, **125**, 1542–1565.

26 S. Kramer, G. Andac, J. Heyne, J. Ellsworth, P. Herzig and K. C. Lewis, Perspectives on Fully Synthesized Sustainable Aviation Fuels: Direction and Opportunities, *Front. Energy Res.*, 2022, **9**, DOI: 10.3389/fenrg.2021.782823.

27 IATA, International Air Transport Association, https://www.iata.org/en/pressroom/2024-releases/2024-12-10-03/, accessed 30 January 2025.

28 Y. Zhou, S. Searle and N. Pavlenko, *Current and Future Cost of E-Kerosene in the United States and Europe*, Internation Council on Clean Transportation, 2022.

29 M. J. Watson, P. G. Machado, A. V. Da Silva, Y. Saltar, C. O. Ribeiro, C. Nascimento and A. W. Dowling, Sustainable aviation fuel technologies, costs, emissions, policies, and markets: A critical review, *J. Clean. Prod.*, 2024, **449**, 141472.

30 RefuelEU aviation initiative: Council adopts new law to decarbonise the aviation sector, https://www.consilium.europa.eu/en/press/press-releases/2023/10/09/refueleu-aviation-initiative-council-adopts-new-law-to-decarbonise-the-aviation-sector/, accessed 16 May 2024.

31 European Commission – European Alternative Fuels Observatory, Sustainable Aviation Fuels (SAF) and other Alternative Fuels Used for Aviation, https://alternative-fuels-observatory.ec.europa.eu/transport-mode/aviation/

general-information-and-context, accessed 30 January 2025.

32 European Union Aviation Safety Agency (EASA), European Aviation Environmental Report, 2025, https://www.easa.europa.eu/en/domains/environment/eaer, accessed 30 January 2025.

33 SkyNRG, Sustainable Aviation Fuel Market Outlook 2024, https://skynrg.com/skynrg-releases-sustainable-aviation-fuel-market-outlook-2024/, accessed 30 January 2025.

34 E. Cabrera and J. M. M. de Sousa, Use of Sustainable Fuels in Aviation—A Review, *Energies*, 2022, **15**, 2440.

35 G. Quante, Renewable fuel options for aviation A System-Wide comparison of Drop-In and non Drop-In fuel option, *Fuel*, 2023, **333**, 126269.

36 M. F. Shahriar and A. Khanal, The current techno-economic, environmental, policy status and perspectives of sustainable aviation fuel (SAF), *Fuel*, 2022, **325**, 124905.

37 C. Gutiérrez-Antonio, F. I. Gómez-Castro, J. A. de Lira-Flores and S. Hernández, A review on the production processes of renewable jet fuel, *Renew. Sustain. Energy Rev.*, 2017, **79**, 709–729.

38 SkyNRG, *A Market Outlook on Sustainable Aviation Fuel*, 2022.

39 S. Richter, M. Braun-Unkhoff, C. Naumann and U. Riedel, Paths to alternative fuels for aviation, *CEAS Aeronaut. J.*, 2018, **9**, 389–403.

40 LanzaJet|LanzaJet Celebrates Grand Opening of Freedom Pines Fuels…, https://www.lanzajet.com/news-insights/lanzajet-celebrates-grand-opening-of-freedom-pines-fuels-plant-the-worlds-first-ethanol-to-sustainable-aviation-fuel-production-facility, accessed 12 April 2024.

41 LanzaJet, LanzaJet Freedom Pines Fuels, https://www.lanzajet.com/freedom-pines, accessed 17 May 2024.

42 C. Ryan, *Overview of Gevos Biobased Isobutanol Production Process*, Gevo Inc., 2021.

43 Regulation – EU – 2023/2405 – Regulation (EU) 2023/2405 on ensuring a level playing field for sustainable air transport (ReFuelEU Aviation), https://eur-lex.europa.eu/eli/reg/2023/2405/oj, accessed 22 August 2024.

44 C. Douglas and B. James, *The State of: Electrofuels for Aviation*, World Fund, 2022, https://benjames.io/WorldFund_Investment_Briefing_Electrofuels_for_Aviation.pdf, accessed 26 October 2023.

45 V. Batteiger, K. Ebner, A. Habersetzer, L. Moser, P. Schmidt, W. Weindorf and T. Rakscha, Power-to-Liquids, https://www.umweltbundesamt.de/sites/default/files/medien/376/publikationen/background_paper_power-to-liquids_aviation_2022.pdf, accessed, 5 June, 2025.

46 F. Ueckerdt, C. Bauer, A. Dirnaichner, J. Everall, R. Sacchi and G. Luderer, Potential and risks of hydrogen-based e-fuels in climate change mitigation, *Nat. Clim. Change*, 2021, **11**, 384–393.

47 S. Brynolf, M. Taljegard, M. Grahn and J. Hansson, Electrofuels for the transport sector: A review of production costs, *Renew. Sustain. Energy Rev.*, 2018, **81**, 1887–1905.

48 F. Frieden and J. Leker, Future costs of hydrogen: a quantitative review, *Sustain. Energy Fuels*, 2024, **8**, 1806–1822.

49 P. Schmidt, V. Batteiger, A. Roth, W. Weindorf and T. Raksha, Power-to-Liquids as Renewable Fuel Option for Aviation: A Review, *Chem. Ing. Tech.*, 2018, **90**, 127–140.

50 M. F. Rojas-Michaga, S. Michailos, E. Cardozo, M. Akram, K. J. Hughes, D. Ingham and M. Pourkashanian, Sustainable aviation fuel (SAF) production through power-to-liquid (PtL): A combined techno-economic and life cycle assessment, *Energy Convers. Manage.*, 2023, **292**, 117427.

51 International Renewable Energy Agency (IRENA), *Reaching Zero with Renewables: Biojet Fuels*, IRENA, 2021.

52 A. de Klerk, G. Chauhan, C. Halmenschlager, F. Link, N. Montoya Sánchez, B. Gartley, H. E. M. El-Sayed, R. Sehdev and R. Lehoux, Sustainable aviation fuel: Pathways to fully formulated synthetic jet fuel via Fischer-Tropsch synthesis//Sustainable aviation fuel: Pathways to fully formulated synthetic jet fuel via Fischer–Tropsch synthesis, *Energy Sci. Eng.*, 2022, **12**, 394–409.

53 D. T. Pio, A. Vilas-Boas, V. D. Araújo, N. Rodrigues and A. Mendes, Decarbonizing the aviation sector with Electro Sustainable Aviation Fuel (eSAF) from biogenic CO2 captured at pulp mills, *Chem. Eng. J.*, 2023, **463**, 142317.

54 G. Manente, A. Ficarella and A. Rahim, Power-to-liquid versus biomass-derived kerosene: a comparative study, *J. Phys.: Conf. Ser.*, 2023, **2648**, 12018.

55 H. Jahangiri, A. A. Lappas, M. Ouadi and E. Heracleous, *Production of Biofuels via Fischer-Tropsch Synthesis: Biomass-To-Liquids*, 2023, pp. 449–509.

56 B. H. H. Goh, C. T. Chong, H. C. Ong, T. Seljak, T. Katrašnik, V. Józsa, J.-H. Ng, B. Tian, S. Karmarkar and V. Ashokkumar, Recent advancements in catalytic conversion pathways for synthetic jet fuel produced from bioresources, *Energy Convers. Manage.*, 2022, **251**, 114974.

57 A. Keunecke, M. Dossow, V. Dieterich, H. Spliethoff and S. Fendt, Insights into Fischer–Tropsch catalysis: current perspectives, mechanisms, and emerging trends in energy research, *Front. Energy Res.*, 2024, **12**, DOI: 10.3389/fenrg.2024.1344179.

58 V. Dieterich, A. Buttler, A. Hanel, H. Spliethoff and S. Fendt, Power-to-liquid via synthesis of methanol, DME or Fischer–Tropsch-fuels: a review, *Energy Environ. Sci.*, 2020, **13**, 3207–3252.

59 A. Mena Subiranas, *Combining Fischer-Tropsch Synthesis (FTS) and Hydrocarbon Reactions in One Reactor*, 2008.

60 J. Wentrup, G. R. Pesch and J. Thöming, Dynamic operation of Fischer-Tropsch reactors for power-to-liquid concepts: A review, *Renew. Sustain. Energy Rev.*, 2022, **162**, 112454.

61 J. Peacock, R. Cooper, N. Waller and G. Richardson, Decarbonising aviation at scale through synthesis of sustainable e-fuel: A techno-economic assessment, *Int. J. Hydrogen Energy*, 2024, **50**, 869–890.

62 A. Meurer and J. Kern, Fischer–Tropsch Synthesis as the Key for Decentralized Sustainable Kerosene Production, *Energies*, 2021, **14**, 1836.

63 X. Sun, dissertation, Technische Universität München, 2013.

64 H. Kuechler, S. Brown, A. Verberckmoes, M. Puttemans and S. Silberberg, *US Pat.*, US7678953B2, 2006.

65 J. Haid and U. Koss, Lurgi's Mega-Methanol technology opens the door for a new era in down-stream applications, *Studies in Surface Science and Catalysis*, 2001, vol. 136, pp. 399–404.

66 N. P. Andrade, M. Andrade, M. Rebouças, R. P. Brito and K. D. Brito, Intensification proposals for the downstream separation of the methanol-to-olefins process, *Chem. Eng. Process. Process Intensif.*, 2024, **196**, 109639.

67 Z. Wang, H. Liu and J. Wang, Optimization of the separation unit of methanol to propylene (MTP) process and its application, *Chin. J. Chem. Eng.*, 2019, **27**, 1089–1093.

68 Y.-H. Chen, W. Hsieh, H. Chang and C.-D. Ho, Design and economic analysis of industrial-scale methanol-to-olefins plants, *J. Taiwan Inst. Chem. Eng.*, 2022, **130**, 103893.

69 N. M. Eagan, M. D. Kumbhalkar, J. S. Buchanan, J. A. Dumesic and G. W. Huber, Chemistries and processes for the conversion of ethanol into middle-distillate fuels, *Nat. Rev. Chem.*, 2019, **3**, 223–249.

70 S. Moussa, M. A. Arribas, P. Concepción and A. Martínez, Heterogeneous oligomerization of ethylene to liquids on bifunctional Ni-based catalysts: The influence of support properties on nickel speciation and catalytic performance, *Catal. Today*, 2016, **277**, 78–88.

71 P. Hirunsit, A. Senocrate, C. E. Gómez-Camacho and F. Kiefer, From CO2 to Sustainable Aviation Fuel: Navigating the Technology Landscape, *ACS Sustainable Chem. Eng.*, 2024, 12143–12160.

72 *Methanol: the Basic Chemical and Energy Feedstock of the Future. Asinger's Vision Today*, ed. M. Bertau, Springer, Berlin, Heidelberg, 2014.

73 P. Rentschler, C. Klahn and R. Dittmeyer, The Need for Dynamic Process Simulation: A Review of Offshore Power-to-X Systems, *Chem. Ing. Tech.*, 2024, **96**, 114–125.

74 S. Mucci, A. Mitsos and D. Bongartz, Cost-optimal Power-to-Methanol: Flexible operation or intermediate storage?, *J. Energy Storage*, 2023, **72**, 108614.

75 S. Mucci, A. Mitsos and D. Bongartz, Power-to-X processes based on PEM water electrolyzers: A review of process integration and flexible operation, *Comput. Chem. Eng.*, 2023, **175**, 108260.

76 C. Chen and A. Yang, Power-to-methanol: The role of process flexibility in the integration of variable renewable energy into chemical production, *Energy Convers. Manage.*, 2021, **228**, 113673.

77 C. Hank, S. Gelpke, A. Schnabl, R. J. White, J. Full, N. Wiebe, T. Smolinka, A. Schaadt, H.-M. Henning and C. Hebling, Economics & carbon dioxide avoidance cost of methanol production based on renewable hydrogen and recycled carbon dioxide – power-to-methanol, *Sustain. Energy Fuels*, 2018, **2**, 1244–1261.

78 C. Voigt, J. Kleine, D. Sauer, R. H. Moore, T. Bräuer, P. Le Clercq, S. Kaufmann, M. Scheibe, T. Jurkat-Witschas, M. Aigner, U. Bauder, Y. Boose, S. Borrmann, E. Crosbie, G. S. Diskin, J. DiGangi, V. Hahn, C. Heckl, F. Huber, J. B. Nowak, M. Rapp, B. Rauch, C. Robinson, T. Schripp, M. Shook, E. Winstead, L. Ziemba, H. Schlager and B. E. Anderson, Cleaner burning aviation fuels can reduce contrail cloudiness, *Commun. Earth Environ.*, 2021, **2**, 114.

79 R. S. Märkl, C. Voigt, D. Sauer, R. K. Dischl, S. Kaufmann, T. Harlaß, V. Hahn, A. Roiger, C. Weiß-Rehm, U. Burkhardt, U. Schumann, A. Marsing, M. Scheibe, A. Dörnbrack, C. Renard, M. Gauthier, P. Swann, P. Madden, D. Luff, R. Sallinen, T. Schripp and P. Le Clercq, Powering aircraft with 100\,% sustainable aviation fuel reduces ice crystals in contrails, *Atmos. Chem. Phys.*, 2024, **24**, 3813–3837.

80 J. Ruokonen, H. Nieminen, A. R. Dahiru, A. Laari, T. Koiranen, P. Laaksonen, A. Vuokila and M. Huuhtanen, Modelling and Cost Estimation for Conversion of Green Methanol to Renewable Liquid Transport Fuels via Olefin Oligomerisation, *Processes*, 2021, **9**, 1046.

81 S. Yurchak, in *Methane Conversion*, ed. D. M. Bibby, C. D. Chang, R. F. Howe and S. Yurchak, Elsevier, 1988, pp. 251–272.

82 S. A. Tabak and S. Yurchak, Conversion of methanol over ZSM-5 to fuels and chemicals, *Catal. Today*, 1990, **6**, 307–327.

83 P. Beato, *WO Pat.*, WO2022063994A1, 2022.

84 M. J. Vincent and K. H. Kuechler, *US Pat.*, US20220396741A1, 2022.

85 A. Mathur, D. Chakrabarti, J. M. Blommel, R. K. Hoehn, J. S. Paustian and M. Serban, *US Pat.*, US20240247198A1, 2024.

86 SAFari – Erneuerbare Kraftstoffe, **https://erneuerbarekraftstoffe.de/projects/safari/**, accessed 16 April 2025.

87 M2SAF – Erneuerbare Kraftstoffe, **https://erneuerbarekraftstoffe.de/projects/m2saf/**, accessed 16 April 2025.

88 D. M. Saad, T. Terlouw, R. Sacchi and C. Bauer, Life Cycle Economic and Environmental Assessment of Producing Synthetic Jet Fuel Using CO2/Biomass Feedstocks, *Environ. Sci. Technol.*, 2024, **58**, 9158–9174.

89 V. Eyberg, V. Dieterich, S. Bastek, M. Dossow, H. Spliethoff and S. Fendt, Techno-economic assessment and comparison of Fischer–Tropsch and Methanol-to-Jet processes to produce sustainable aviation fuel via Power-to-Liquid, *Energy Convers. Manage.*, 2024, **315**, 118728.

90 S. Bube, S. Voß, G. Quante and M. Kaltschmitt, Cost analysis of kerosene production from power-based syngas via the Fischer-Tropsch and methanol pathway, *Fuel*, 2025, **384**, 133901.

91 K. Atsonios, J. Li and V. J. Inglezakis, Process analysis and comparative assessment of advanced thermochemical pathways for e-kerosene production, *Energy*, 2023, **278**, 127868.

92 Project skypower, Accelerating the take-off for e-SAF in Europe. Inside report, 2024, **https://project-skypower.org**, accessed 25 March 2025.

93 IRENA and Methanol Institute, Innovation Outlook, **https://www.irena.org/publications/2021/Jan/Innovation-Outlook-Renewable-Methanol**.

94 M. Wiatros-Motyka and S. Lai, Methanol Production and Markets, **https://www.sustainable-carbon.org/report/methanol-production-and-markets/**.

95 C. F. Shih, T. Zhang, J. Li and C. Bai, Powering the Future with Liquid Sunshine, *Joule*, 2018, **2**, 1925–1949.

96 M. Bergren, *Methanol to Energy – Challenges and Opportunities*, Frankfurt, 2017.

97 M. Alvarado, The changing face of the global methanol industry.

98 F. Nestler, M. Krüger, J. Full, M. J. Hadrich, R. J. White and A. Schaadt, Methanol Synthesis – Industrial Challenges within a Changing Raw Material Landscape, *Chem. Ing. Tech.*, 2018, **90**, 1409–1418.

99 A. M. Bazzanella and F. Ausfelder, Low carbon energy and feedstock for the European chemical industry, **http://dechema.de/Low_carbon_chemical_industry.html**.

100 J. Wei, Q. Ge, R. Yao, Z. Wen, C. Fang, L. Guo, H. Xu and J. Sun, Directly converting CO2 into a gasoline fuel, *Nat. Commun.*, 2017, **8**, 15174.

101 D. Saygin and D. Gielen, Zero-Emission Pathway for the Global Chemical and Petrochemical Sector, *Energies*, 2021, **14**, 3772.

102 C. Hank, M. Holst, T. Connor, C. Kost, S. Längle, A. Schaadt and T. Smolinka, Site-specific, comparative analysis for suitable Power-to-X pathways and products in developing and emerging countries, **https://files.h2-global.de/H2G_Fraunhofer-ISE_Site-specific-comparative-analysis-for-suitable-Power-to-X-pathways-and-products-in-developing-and-emerging-countries.pdf**.

103 S. Ghosh, V. Uday, A. Giri and S. Srinivas, Biogas to methanol: A comparison of conversion processes involving direct carbon dioxide hydrogenation and via reverse water gas shift reaction, *J. Clean. Prod.*, 2019, **217**, 615–626.

104 P. Gautam, Neha, S. N. Upadhyay and S. K. Dubey, Bio-methanol as a renewable fuel from waste biomass: Current trends and future perspective, *Fuel*, 2020, **273**, 117783.

105 A. Poluzzi, G. Guandalini, S. Guffanti, C. Elsido, S. Moioli, P. Huttenhuis, G. Rexwinkel, E. Martelli, G. Groppi and M. C. Romano, Flexible Power & Biomass-to-Methanol plants: Design optimization and economic viability of the electrolysis integration, *Fuel*, 2022, **310**, 122113.

106 K. Harris, R. G. Grim, Z. Huang and L. Tao, A comparative techno-economic analysis of renewable methanol synthesis from biomass and CO2: Opportunities and barriers to commercialization, *Appl. Energy*, 2021, **303**, 117637.

107 K. Im-orb and A. Arpornwichanop, Process and sustainability analyses of the integrated biomass pyrolysis, gasification, and methanol synthesis process for methanol production, *Energy*, 2020, **193**, 116788.

108 B. Hernández and M. Martín, Optimal Process Operation for Biogas Reforming to Methanol: Effects of Dry Reforming and Biogas Composition, *Ind. Eng. Chem. Res.*, 2016, **55**, 6677–6685.

109 R. O. D. Santos, L. D. S. Santos and D. M. Prata, Simulation and optimization of a methanol synthesis process from different biogas sources, *J. Clean. Prod.*, 2018, **186**, 821–830.

110 A. Vita, C. Italiano, D. Previtali, C. Fabiano, A. Palella, F. Freni, G. Bozzano, L. Pino and F. Manenti, Methanol synthesis from biogas, *Renew. Energy*, 2018, **118**, 673–684.

111 R. Rinaldi, G. Lombardelli, M. Gatti, C. G. Visconti and M. C. Romano, Techno-economic analysis of a biogas-to-methanol process: Study of different process configurations and conditions, *J. Clean. Prod.*, 2023, 136259.

112 U. Safder, J. Loy-Benitez and C. Yoo, Techno-economic assessment of a novel integrated multigeneration system to synthesize e-methanol and green hydrogen in a carbon-neutral context, *Energy*, 2024, **290**, 130104.

113 Verein Deutscher Ingenieure, *Power-to-X - Flüssige Kohlenwasserstoffe. Entwurf*, 2023.

114 T. L. Biel-Nielsen, T. A. Hatton, S. N. B. Villadsen, J. S. Jakobsen, J. L. Bonde, A. M. Spormann and P. L. Fosbøl, Electrochemistry-Based CO2 Removal Technologies, *ChemSusChem*, 2023, **16**, e202202345.

115 M. Ozkan, S. P. Nayak, A. D. Ruiz and W. Jiang, Current status and pillars of direct air capture technologies, *iScience*, 2022, **25**, 103990.

116 N. McQueen, K. V. Gomes, C. McCormick, K. Blumanthal, M. Pisciotta and J. Wilcox, A review of direct air capture (DAC): scaling up commercial technologies and innovating for the future, *Energy Proc.*, 2021, **3**, 32001.

117 S. R. Cooley, S. Klinsky, D. R. Morrow and T. Satterfield, Sociotechnical Considerations About Ocean Carbon Dioxide Removal, *Ann. Rev. Mar. Sci*, 2023, **15**, 41–66.

118 S. Kim, M. P. Nitzsche, S. B. Rufer, J. R. Lake, K. K. Varanasi and T. A. Hatton, Asymmetric chloride-mediated electrochemical process for CO 2 removal from oceanwater, *Energy Environ. Sci.*, 2023, **16**, 2030–2044.

119 W. Wu, Z.-L. Jian, B.-Y. Chou, C.-Y. You and Y.-N. Kuo, Process Design and Techno-ECONOMIC Evaluation of a Decarbonized Cement Production Process Using Carbon Capture and Utilization, *Processes*, 2023, **11**, 2043.

120 J. Gallego Dávila, R. Sacchi and M. Pizzol, Preconditions for achieving carbon neutrality in cement production through CCUS, *J. Clean. Prod.*, 2023, **425**, 138935.

121 M. Bampaou, K. Panopoulos, P. Seferlis, S. Voutetakis, I. Matino, A. Petrucciani, A. Zaccara, V. Colla, S. Dettori, T. Annunziata Branca and V. Iannino, Integration of Renewable Hydrogen Production in Steelworks Off-Gases for the Synthesis of Methanol and Methane, *Energies*, 2021, **14**, 2904.

122 M. Bampaou, S. Haag, A.-S. Kyriakides, K. D. Panopoulos and P. Seferlis, Optimizing methanol synthesis combining steelworks off-gases and renewable hydrogen, *Renew. Sustain. Energy Rev.*, 2023, **171**, 113035.

123 F. Nestler, J. Full, J.-M. Jäckle, J. Linsenmeier, J. Roob, M. J. Hadrich and A. Schaadt, Experimental Validation of Methanol Synthesis from Steel Mill Gases Using a Miniplant Setup, *Chem. Ing. Tech.*, 2022, **94**, 1466–1475.

124 L. Deng and T. A. Adams, in *13th International Symposium on Process Systems Engineering (PSE 2018)*, Elsevier, 2018, pp. 163–168.

125 C. Hakandai, H. Sidik Pramono and M. Aziz, Conversion of municipal solid waste to hydrogen and its storage to methanol, *Sustain. Energy Technol. Assessments*, 2022, **51**, 101968.

126 M. Kircher and T. Schwarz, *CO_2 and CO as Feedstock*, Springer International Publishing, Cham, 2023.

127 H. Lange, A. Klose, W. Lippmann and L. Urbas, Technical evaluation of the flexibility of water electrolysis systems to increase energy flexibility: A review, *Int. J. Hydrogen Energy*, 2023, **48**, 15771–15783.

128 M. El-Shafie, Hydrogen production by water electrolysis technologies: A review, *Results Eng.*, 2023, **20**, 101426.

129 G. C. Chinchen, P. J. Denny, J. R. Jennings, M. S. Spencer and K. C. Waugh, Synthesis of Methanol, *Appl. Catal.*, 1988, **36**, 1–65.

130 F. Sha, Z. Han, S. Tang, J. Wang and C. Li, Hydrogenation of Carbon Dioxide to Methanol over Non-Cu-based Heterogeneous Catalysts, *ChemSusChem*, 2020, **13**, 6160–6181.

131 J. Zhong, X. Yang, Z. Wu, B. Liang, Y. Huang and T. Zhang, State of the art and perspectives in heterogeneous catalysis of CO2 hydrogenation to methanol, *Chem. Soc. Rev.*, 2020, **49**, 1385–1413.

132 I. Hussain, U. Mustapha, A. T. Al-Qathmi, Z. O. Malaibari, S. Alotaibi, Samia, K. Alhooshani and S. A. Ganiyu, The critical role of intrinsic physicochemical properties of catalysts for CO2 hydrogenation to methanol: A state of the art review, *J. Ind. Eng. Chem.*, 2023, **128**, 95–126.

133 P. Schwiderowski, H. Ruland and M. Muhler, Current developments in CO2 hydrogenation towards methanol – a review related to industrial application, *Curr. Opin. Green Sustainable Chem.*, 2022, 100688.

134 Q. Wu, S. Liang, T. Zhang, B. Louis and Q. Wang, Current advances in bimetallic catalysts for carbon dioxide hydrogenation to methanol, *Fuel*, 2022, **313**, 122963.

135 K. G. Chanchlani, Methanol synthesis from H2, CO, and CO2 over Cu/ZnO catalysts, *J. Catal.*, 1992, **136**, 59–75.

136 G. C. Chinchen, K. Mansfield and M. S. Spencer, The methanol synthesis-how does it work, *Chemtech*, 1990, **20**, 692–699.

137 Y. B. Kagan, L. G. Liberov, E. V. Slivinskii, S. M. Loktev, G. I. Lin, A. Y. Rozovskii and A. N. Bashkirov, Mechanism of methanol synthesis from carbon dioxide and hydrogen, *Dokl. Phys. Chem.*, 1975, **221**, 254–256.

138 N. D. Nielsen, A. D. Jensen and J. M. Christensen, The roles of CO and CO2 in high pressure methanol synthesis over Cu-based catalysts, *J. Catal.*, 2021, **393**, 324–334.

139 X. Liu, H. Zhang, J. Du and J. Liao, Research progress of methanol production via CO2 hydrogenation: Mechanism and catalysts, *Process Saf. Environ. Prot.*, 2024, **189**, 1071–1086.

140 X. Liu, H. Wang and J. Lu, Recent progress in understanding the nature of active sites for methanol synthesis over Cu/ZnO catalysts, *J. Catal.*, 2024, **436**, 115561.

141 A. Beck, M. Zabilskiy, M. A. Newton, O. Safonova, M. G. Willinger and J. A. van Bokhoven, Following the structure of copper-zinc-alumina across the pressure gap in carbon dioxide hydrogenation, *Nat. Catal.*, 2021, **4**, 488–497.

142 R. Schlögl, *Chemical Energy Storage*, De Gruyter, Berlin, 2013.

143 F. Nestler, *Dissertation*, Karlsruhe Institut of Technology, 2022.

144 M. Sahibzada, I. S. Metcalfe and D. Chadwick, Methanol Synthesis from CO/CO2/H2 over Cu/ZnO/Al2O3 at Differential and Finite Conversions, *J. Catal.*, 1998, **174**, 111–118.

145 M. B. Fichtl, D. Schlereth, N. Jacobsen, I. Kasatkin, J. Schumann, M. Behrens, R. Schlögl and O. Hinrichsen, Kinetics of deactivation on Cu/ZnO/Al2O3 methanol synthesis catalysts, *Appl. Catal., A*, 2015, **502**, 262–270.

146 J. Wu, M. Saito, M. Takeuchi and T. Watanabe, The stability of Cu/ZnO-based catalysts in methanol synthesis from a CO2-rich feed and from a CO-rich feed, *Appl. Catal., A*, 2001, **218**, 235–240.

147 J. Ladebeck, Improve methanol synthesis, *Hydrocarb. Process.*, 1993, **72**, 89–91.

148 S. M. Fehr, K. Nguyen, C. Njel and I. Krossing, Enhancement of Methanol Synthesis by Oxidative Fluorination of Cu/ZnO Catalysts-Insights from Surface Analyses, *ACS Catal.*, 2021, **11**, 13223–13235.

149 V. Dybbert, S. M. Fehr, F. Klein, A. Schaadt, A. Hoffmann, E. Frei, E. Erdem, T. Ludwig, H. Hillebrecht and I. Krossing, Oxidative Fluorination of Cu/ZnO Methanol Catalysts, *Angew Chem. Int. Ed. Engl.*, 2019, **58**, 12935–12939.

150 I. U. Din, M. S. Shaharun, M. A. Alotaibi, A. I. Alharthi and A. Naeem, Recent developments on heterogeneous catalytic CO2 reduction to methanol, *J. CO_2 Util.*, 2019, **34**, 20–33.

151 C. Li, X. Yuan and K. Fujimoto, Development of highly stable catalyst for methanol synthesis from carbon dioxide, *Appl. Catal., A*, 2014, **469**, 306–311.

152 R. Guil-López, N. Mota, J. Llorente, E. Millán, B. Pawelec, J. L. G. Fierro and R. M. Navarro, Methanol Synthesis from CO2: A Review of the Latest Developments in Heterogeneous Catalysis, *Materials*, 2019, **12**, 3902.

153 E. Frei, A. Schaadt, T. Ludwig, H. Hillebrecht and I. Krossing, The Influence of the Precipitation/Ageing Temperature on a Cu/ZnO/ZrO 2 Catalyst for Methanol Synthesis from H 2 and CO 2, *ChemCatChem*, 2014, **6**, 1721–1730.

154 M. Saito, R&D activities in Japan on methanol synthesis from CO2 and H2, *Catal. Surv. Jpn.*, 1998, **2**, 175–184.

155 K. M. Vanden Bussche and G. F. Froment, A Steady-State Kinetic Model for Methanol Synthesis and the Water Gas Shift Reaction on a Commercial Cu/ZnO/Al2O3 Catalyst, *J. Catal.*, 1996, **161**, 1–10.

156 G. H. Graaf, E. J. Stamhuis and A. Beenackers, Kinetics of low-pressure methanol synthesis, *Chem. Eng. Sci.*, 1988, **43**, 3185–3195.

157 X. An, Y. Zuo, Q. Zhang and J. Wang, Methanol Synthesis from CO2 Hydrogenation with a Cu/Zn/Al/Zr Fibrous Catalyst, *Chin. J. Chem. Eng.*, 2009, **17**, 88–94.

158 C. Seidel, A. Jörke, B. Vollbrecht, A. Seidel-Morgenstern and A. Kienle, Kinetic modeling of methanol synthesis from renewable resources, *Chem. Eng. Sci.*, 2018, **175**, 130–138.

159 N. Park, M.-J. Park, Y.-J. Lee, K.-S. Ha and K.-W. Jun, Kinetic modeling of methanol synthesis over commercial catalysts based on three-site adsorption, *Fuel Process. Technol.*, 2014, **125**, 139–147.

160 F. Nestler, V. P. Müller, O. Salem, M. Hadrich, A. Schaadt, S. Bajohr and T. Kolb, A Novel Approach for Kinetic Measurements in Exothermic Fixed Bed Reactors: Advancements in Non-Isothermal Bed Conditions Demonstrated for Methanol Synthesis, *React. Chem. Eng.*, 2021, **6**, 1092–1107.

161 G. Bozzano and F. Manenti, Efficient methanol synthesis, *Prog. Energy Combust. Sci.*, 2016, **56**, 71–105.

162 F. Nestler, A. R. Schütze, M. Ouda, M. J. Hadrich, A. Schaadt, S. Bajohr and T. Kolb, Kinetic modelling of methanol synthesis over commercial catalysts: A critical assessment, *Chem. Eng. J.*, 2020, **394**, 124881.

163 J. J. Meyer, P. Tan, A. Apfelbacher, R. Daschner and A. Hornung, Modeling of a Methanol Synthesis Reactor for Storage of Renewable Energy and Conversion of CO2 - Comparison of Two Kinetic Models, *Chem. Eng. Technol.*, 2016, **39**, 233–245.

164 G. Leonzio, Mathematical modeling of a methanol reactor by using different kinetic models, *J. Ind. Eng. Chem.*, 2020, **85**, 130–140.

165 F. Bisotti, M. Fedeli, K. Prifti, A. Galeazzi, A. Dell'Angelo, M. Barbieri, C. Pirola, G. Bozzano and F. Manenti, Century of Technology Trends in Methanol Synthesis: Any Need for Kinetics Refitting?, *Ind. Eng. Chem. Res.*, 2021, **60**, 16032–16053.

166 J. Nyári, D. Izbassarov, Á. I. Toldy, V. Vuorinen and A. Santasalo-Aarnio, Choice of the kinetic model significantly affects the outcome of techno-economic assessments of CO2-based methanol synthesis, *Energy Convers. Manage.*, 2022, **271**, 116200.

167 J.-P. Lange, Methanol synthesis, *Catal. Today*, 2001, **64**, 3–8.

168 A. Daraie and M. R. Rahimpour, in *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*, Elsevier, 2024.

169 X. Cui and S. K. Kær, A comparative study on three reactor types for methanol synthesis from syngas and CO2, *Chem. Eng. J.*, 2020, **393**, 124632.

170 A. Schulz and S. Schirrmeister, *WO pat.*, WO 2018/019875, 2022.

171 H. Göhna and P. König, Producing methanol from CO2, *Chemtech*, 1994, **24**, 36–39.

172 M. Nassirpour and M. H. Khademi, Evaluation of different cooling technologies for industrial methanol synthesis reactor in terms of energy efficiency and methanol yield: An economic-optimization, *J. Taiwan Inst. Chem. Eng.*, 2020, **113**, 302–314.

173 A. Mirvakili, S. Chahibakhsh, M. Ebrahimzadehsarvestani, E. Soroush and M. R. Rahimpour, Modeling and assessment of novel configurations to enhance methanol production in industrial mega-methanol synthesis plant, *J. Taiwan Inst. Chem. Eng.*, 2019, **104**, 40–53.

174 Z. Eksiri, M. Mozdianfard, A. Mirvakili and M. Rahimpour, Effect of an axial-radial plate reactor modifications on a mega methanol plant production, *Int. J. Chem. React. Eng.*, 2021, **19**, 447–463.

175 K. R. Westerterp, M. Kuczynski and C. H. M. Kamphuis, The synthesis of methanol in a reactor system with interstage product removal, *Ind. Eng. Chem. Res.*, 1989, **28**, 763–771.

176 K. R. Westerterp, M. Kuczynski, T. N. Bodewes and M. S. A. Vrijland, Neue Konvertersysteme für die Methanol-Synthese, *Chem. Ing. Tech.*, 1989, **61**, 193–199.

177 K. R. Westerterp, *US Pat.*, US4731387A, 1988.

178 S. Haag, C. Drosdzol, B. Williams, V. Peña, N. Palauschek, M. Wilken, A. Günther, V. Gronemann and A. Roesch, Recent Developments in Methanol Technology by Air Liquide for CO2 Reduction and CO2 Usage, *Chem. Ing. Tech.*, 2022, **94**, 1655–1666.

179 B. Lacerda de Oliveira Campos, K. John, P. Beeskow, K. Herrera Delgado, S. Pitter, N. Dahmen and J. Sauer, A Detailed Process and Techno-Economic Analysis of Methanol Synthesis from H2 and CO2 with Intermediate Condensation Steps, *Processes*, 2022, **10**, 1535.

180 T. Oelmann, T. Schuhmann, M. Gorny, M. Strozyk, C. Drosdzol, S. Haag and F. Castillo-Welter, A new reactor concept for conversion of CO2 to methanol, *Oil Gas Eur. Mag.*, 2021, **47**, 28–32.

181 A. Ochs, F. Castillo-Welter, S. Haag, R. Frind, T. Schuhmann, M. Wagner and S. Valentin, *EP pat.*, EP3401299 A1, 2018.

182 M. G. Mohammed, N. A. Hashim, W. M. A. W. Daud, U. W. Hartley, M. K. Aroua and S. Wohlrab, Overview of the latest progress and prospects in the catalytic hydrogenation of carbon dioxide (CO2) to methanol in membrane reactors, *Int. J. Hydrogen Energy*, 2024, **77**, 936–957.

183 R. Struis, S. Stucki and M. Wiedorn, A membrane reactor for methanol synthesis, *J. Membr. Sci.*, 1996, **113**, 93–100.

184 P. Maksimov, H. Nieminen, A. Laari and T. Koiranen, Sorption enhanced carbon dioxide hydrogenation to methanol: process design and optimization, *Chem. Eng. Sci.*, 2022, 117498.

185 H. Nieminen, P. Maksimov, A. Laari, V. Väisänen, A. Vuokila, M. Huuhtanen and T. Koiranen, Process modelling and feasibility study of sorption-enhanced methanol synthesis, *Chem. Eng. Process. Process Intensif.*, 2022, **179**, 109052.

186 E. Moioli and T. Schildhauer, Tailoring the Reactor Properties in the Small-Scale Sorption-Enhanced Methanol Synthesis, *Chem. Ing. Tech.*, 2023, **95**, 631–641.

187 Z. Dehghani, M. Bayat and M. R. Rahimpour, Sorption-enhanced methanol synthesis: Dynamic modeling and optimization, *J. Taiwan Inst. Chem. Eng.*, 2014, **45**, 1490–1500.

188 F. Zejarbad, J. Gong, Z. Li, K. Jessen and T. Tsotsis, Simulation of methanol synthesis in a membrane-contactor reactor, *J. Membr. Sci.*, 2022, 120677.

189 V. Dieterich, N. Wein, H. Spliethoff and S. Fendt, Performance Requirements of Membrane Reactors for the Application in Renewable Methanol Synthesis: A Techno-Economic Assessment, *Adv. Sustainable Syst.*, 2022, 2200254.

190 O.-S. Joo, K.-D. Jung, I. Moon, A. Y. Rozovskii, G. I. Lin, S.-H. Han and S.-J. Uhm, Carbon Dioxide Hydrogenation To Form Methanol via a Reverse-Water-Gas-Shift Reaction (the CAMERE Process), *Ind. Eng. Chem. Res.*, 1999, **38**, 1808–1812.

191 O.-S. Joo, in *Energy and Fuels*, American Chemical Society, 45th edn, 2000, pp. 686–689.

192 O. Ingolfsson, F. R. Jonsson, A. Shulenberger and K.-C. Tran, *WO pat.*, WO002007108014A1, 2007.

193 S. G. Eskesen, J. B. Hansen, M. Jorgensen and P. M. Mortensen, *WO pat.*, WO23194286A1, 2023.

194 G. Zahedi, A. Elkamel and A. Lohi, Dynamic Optimization Strategies of a Heterogeneous Reactor for CO2 Conversion to Methanol, *Energy Fuels*, 2007, **21**, 2977–2983.

195 I. Løvik, M. Hillestad and T. Hertzberg, Long term dynamic optimization of a catalytic reactor system, *Comput. Chem. Eng.*, 1998, **22**, S707–S710.

196 M. N. Mohd Fuad, M. A. Hussain and A. Zakaria, Optimization strategy for long-term catalyst deactivation in a fixed-bed reactor for methanol synthesis process, *Comput. Chem. Eng.*, 2012, **44**, 104–126.

197 F. Pontzen, W. Liebner, V. Gronemann, M. Rothaemel and B. Ahlers, CO2-based methanol and DME – Efficient technologies for industrial scale production, *Catal. Today*, 2011, **171**, 242–250.

198 J. Ott, V. Gronemann, F. Pontzen, E. Fiedler, G. Grossmann, D. B. Kersebohm, G. Weiss and C. Witte, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2012.

199 International Methanol Producers & Consumers Association, *IMPCA Methanol Reference Specifications*, 2021.

200 U.S. Department of Defense, *Methanol (Methyl Alcohol). Federal Specification*, 2016.

201 E. Supp, *How to Produce Methanol from Coal*, Springer, Berlin, Heidelberg, 1990.

202 M. Semmel, M. Kerschbaum, B. Steinbach, J. Sauer and O. Salem, Optimized design and techno-economic analysis of novel DME production processes, *React. Chem. Eng.*, 2023, **8**, 2826–2840.

203 J. Zhang, S. Liang and X. Feng, A novel multi-effect methanol distillation process, *Chem. Eng. Process. Process Intensif.*, 2010, **49**, 1031–1037.

204 F. Nestler, J. Voß, A. Fastabend, T. Niemeier, H. Ruland and M. J. Hadrich, Methanol Synthesis from Sustainable Feedstocks – A Quantitative Side Product Analysis, *Chem. Ing. Tech.*, 2024, **96**, 1166–1176.

205 J. J. Senetar, I. G. Horn and A. B. Chin, *WO pat.*, WO2024238511A1, 2024.

206 C. D. Chang and A. J. Silvestri, The conversion of methanol and other O-compounds to hydrocarbons over zeolite catalysts, *J. Catal.*, 1977, **47**, 249–259.

207 M. Stöcker, Methanol-to-hydrocarbons: catalytic materials and their behavior1Dedicated to my wife Wencke Ophaug.1, *Microporous Mesoporous Mater.*, 1999, **29**, 3–48.

208 C. D. Chang, The New Zealand Gas-to-Gasoline plant: An engineering tour de force, *Catal. Today*, 1992, **13**, 103–111.

209 X. Niu, J. Gao, K. Wang, Q. Miao, M. Dong, G. Wang, W. Fan, Z. Qin and J. Wang, Influence of crystal size on the catalytic performance of H-ZSM-5 and Zn/H-ZSM-5 in the conversion of methanol to aromatics, *Fuel Process. Technol.*, 2017, **157**, 99–107.

210 H. Koempel and W. Liebner, Lurgi's Methanol To Propylene (MTP®) Report on a successful commercialisation, *Stud. Surf. Sci. Catal.*, 2007, **167**, 261–267.

211 P. Tian, Y. Wei, M. Ye and Z. Liu, Methanol to Olefins (MTO): From Fundamentals to Commercialization, *ACS Catal.*, 2015, **5**, 1922–1938.

212 K. de Wispelaere, C. S. Wondergem, B. Ensing, K. Hemelsoet, E. J. Meijer, B. M. Weckhuysen, V. van Speybroeck and J. Ruiz-Martínez, Insight into the Effect of Water on the Methanol-to-Olefins Conversion in H-SAPO-34 from Molecular Simulations and in Situ Microspectroscopy, *ACS Catal.*, 2016, **6**, 1991–2002.

213 X. Wu and R. G. Anthony, Effect of feed composition on methanol conversion to light olefins over SAPO-34, *Appl. Catal., A*, 2001, **218**, 241–250.

214 L. Liu, R. G. Tobias, K. McLaughlin and R. G. Anthony, in *Catalytic Conversions of Synthesis Gas and Alcohols to Chemicals*, ed. R. G. Herman, Springer US, Boston, MA, 1984, pp. 323–360.

215 A. J. Marchi and G. F. Froment, Catalytic conversion of methanol to light alkenes on SAPO molecular sieves, *Appl. Catal.*, 1991, **71**, 139–152.

216 P. Pérez-Uriarte, A. Ateka, M. Gamero, A. T. Aguayo and J. Bilbao, Effect of the Operating Conditions in the Transformation of DME to olefins over a HZSM-5 Zeolite Catalyst, *Ind. Eng. Chem. Res.*, 2016, **55**, 6569–6578.

217 P. Pérez-Uriarte, A. Ateka, A. T. Aguayo, A. G. Gayubo and J. Bilbao, Kinetic model for the reaction of DME to olefins over a HZSM-5 zeolite catalyst, *Chem. Eng. J.*, 2016, **302**, 801–810.

218 J. S. Martinez-Espin, M. Mortén, T. V. W. Janssens, S. Svelle, P. Beato and U. Olsbye, New insights into catalyst deactivation and product distribution of zeolites in the methanol-to-hydrocarbons (MTH) reaction with methanol and dimethyl ether feeds, *Catal. Sci. Technol.*, 2017, **7**, 2700–2716.

219 T. Cordero-Lanzac, A. G. Gayubo, A. T. Aguayo and J. Bilbao, The MTO and DTO processes as greener alternatives to produce olefins: A review of kinetic models and reactor design, *Chem. Eng. J.*, 2024, 152906.

220 F. Keil, Methanol-to-hydrocarbons: process technology, *Microporous Mesoporous Mater.*, 1999, **29**, 49–66.

221 S. Bailleul, I. Yarulina, A. E. J. Hoffman, A. Dokania, E. Abou-Hamad, A. D. Chowdhury, G. Pieters, J. Hajek, K. De

Wispelaere, M. Waroquier, J. Gascon and V. Van Speybroeck, A Supramolecular View on the Cooperative Role of Brønsted and Lewis Acid Sites in Zeolites for Methanol Conversion, *J. Am. Chem. Soc.*, 2019, **141**, 14823–14842.

222 K. Hemelsoet, J. van der Mynsbrugge, K. de Wispelaere, M. Waroquier and V. van Speybroeck, Unraveling the Reaction Mechanisms Governing Methanol-to-Olefins Catalysis by Theory and Experiment, *ChemPhysChem*, 2013, **14**, 1526–1545.

223 S. Teketel, W. Skistad, S. Benard, U. Olsbye, K. P. Lillerud, P. Beato and S. Svelle, Shape Selectivity in the Conversion of Methanol to Hydrocarbons: The Catalytic Performance of One-Dimensional 10-Ring Zeolites: ZSM-22, ZSM-23, ZSM-48, and EU-1, *ACS Catal.*, 2012, **2**, 26–37.

224 S. Teketel, U. Olsbye, K.-P. Lillerud, P. Beato and S. Svelle, Selectivity control through fundamental mechanistic insight in the conversion of methanol to hydrocarbons over zeolites, *Microporous Mesoporous Mater.*, 2010, **136**, 33–41.

225 S. Teketel, S. Svelle, K.-P. Lillerud and U. Olsbye, Shape-Selective Conversion of Methanol to Hydrocarbons Over 10-Ring Unidirectional-Channel Acidic H-ZSM-22, *ChemCatChem*, 2009, **1**, 78–81.

226 C. Baerlocher, D. Brouwer, B. Marler and L. B. McCusker, International Zeolite Association (IZA) - Database of Zeolite Structures, https://www.iza-structure.org/databases/, accessed 15 July 2024.

227 I. Yarulina, K. de Wispelaere, S. Bailleul, J. Goetze, M. Radersma, E. Abou-Hamad, I. Vollmer, M. Goesten, B. Mezari, E. J. M. Hensen, J. S. Martínez-Espín, M. Morten, S. Mitchell, J. Perez-Ramirez, U. Olsbye, B. M. Weckhuysen, V. van Speybroeck, F. Kapteijn and J. Gascon, Structure–performance descriptors and the role of Lewis acidity in the methanol-to-propylene process, *Nat. Chem.*, 2018, **10**, 804–812.

228 N. Hadi and A. Farzi, A review on reaction mechanisms and catalysts of methanol to olefins process, *Chem. Eng. Commun.*, 2022, **209**, 1664–1710.

229 M. Guisnet, L. Costa and F. R. Ribeiro, Prevention of zeolite deactivation by coking, *J. Mol. Catal. A: Chem.*, 2009, **305**, 69–83.

230 T. Liang, J. Chen, Z. Qin, J. Li, P. Wang, S. Wang, G. Wang, M. Dong, W. Fan and J. Wang, Conversion of Methanol to Olefins over H-ZSM-5 Zeolite: Reaction Pathway Is Related to the Framework Aluminum Siting, *ACS Catal.*, 2016, **6**, 7311–7325.

231 I. Yarulina, S. Bailleul, A. Pustovarenko, J. R. Martinez, K. de Wispelaere, J. Hajek, B. M. Weckhuysen, K. Houben, M. Baldus, V. van Speybroeck, F. Kapteijn and J. Gascon, Suppression of the Aromatic Cycle in Methanol-to-Olefins Reaction over ZSM-5 by Post-Synthetic Modification Using Calcium, *ChemCatChem*, 2016, **8**, 3057–3063.

232 A. Liutkova, H. Zhang, J. F. M. Simons, B. Mezari, M. Mirolo, G. A. Garcia, E. J. M. Hensen and N. Kosinov, Ca Cations Impact the Local Environment inside HZSM-5 Pores during the Methanol-to-Hydrocarbons Reaction, *ACS Catal.*, 2023, **13**, 3471–3484.

233 A. Liutkova, N. Kosinov and E. J. M. Hensen, Ca/ZSM-5 catalysts for the methanol-to-hydrocarbons reaction: Activity – Selectivity trade-off?, *J. Catal.*, 2023, **428**, 115169.

234 N. Y. Chen and W. J. Reagan, Evidence of autocatalysis in methanol to hydrocarbon reactions over zeolite catalysts, *J. Catal.*, 1979, **59**, 123–129.

235 R. M. Dessau and R. B. LaPierre, On the mechanism of methanol conversion to hydrocarbons over HZSM-5, *J. Catal.*, 1982, **78**, 136–141.

236 R. M. Dessau, On the H-ZSM-5 catalyzed formation of ethylene from methanol or higher olefins, *J. Catal.*, 1986, **99**, 111–116.

237 T. Mole, G. Bett and D. Seddon, Conversion of methanol to hydrocarbons over ZSM-5 zeolite: An examination of the role of aromatic hydrocarbons using 13carbon- and deuterium-labeled feeds, *J. Catal.*, 1983, **84**, 435–445.

238 T. Mole, J. A. Whiteside and D. Seddon, Aromatic co-catalysis of methanol conversion over zeolite catalysts, *J. Catal.*, 1983, **82**, 261–266.

239 I. M. Dahl and S. Kolboe, On the reaction mechanism for propene formation in the MTO reaction over SAPO-34, *Catal. Lett.*, 1993, **20**, 329–336.

240 I. M. Dahl and S. Kolboe, On the Reaction Mechanism for Hydrocarbon Formation from Methanol over SAPO-34: I. Isotopic Labeling Studies of the Co-Reaction of Ethene and Methanol, *J. Catal.*, 1994, **149**, 458–464.

241 I. M. Dahl and S. Kolboe, On the Reaction Mechanism for Hydrocarbon Formation from Methanol over SAPO-34: 2. Isotopic Labeling Studies of the Co-reaction of Propene and Methanol, *J. Catal.*, 1996, **161**, 304–309.

242 I. Yarulina, A. D. Chowdhury, F. Meirer, B. M. Weckhuysen and J. Gascon, Recent trends and fundamental insights in the methanol-to-hydrocarbons process, *Nat. Catal.*, 2018, **1**, 398–411.

243 S. Mitchell, A. B. Pinar, J. Kenvin, P. Crivelli, J. Kärger and J. Pérez-Ramírez, Structural analysis of hierarchically organized zeolites, *Nat. Commun.*, 2015, **6**, 8633.

244 S. Wang, Z. Qin, M. Dong, J. Wang and W. Fan, Recent progress on MTO reaction mechanisms and regulation of acid site distribution in the zeolite framework, *Chem Catal.*, 2022, **2**, 1657–1685.

245 U. Olsbye, S. Svelle, M. Bjørgen, P. Beato, T. V. W. Janssens, F. Joensen, S. Bordiga and K. P. Lillerud, Conversion of Methanol to Hydrocarbons: How Zeolite Cavity and Pore Size Controls Product Selectivity, *Angew. Chem., Int. Ed.*, 2012, **51**, 5810–5831.

246 A. D. Chowdhury, K. Houben, G. T. Whiting, M. Mokhtar, A. M. Asiri, S. A. Al-Thabaiti, S. N. Basahel, M. Baldus and B. M. Weckhuysen, Initial Carbon–Carbon Bond Formation during the Early Stages of the Methanol-to-Olefin Process Proven by Zeolite-Trapped Acetate and Methyl Acetate, *Angew. Chem., Int. Ed.*, 2016, **55**, 15840–15845.

247 S. Ilias and A. Bhan, Mechanism of the Catalytic Conversion of Methanol to Hydrocarbons, *ACS Catal.*, 2013, **3**, 18–31.

248 N. Nesterenko, J. Aguilhon, P. Bodart, D. Minoux and J.-P. Dath, in *Zeolites and Zeolite-like Materials*, Elsevier, 2016, pp. 189–263.

249 X. Sun, S. Mueller, H. Shi, G. L. Haller, M. Sanchez-Sanchez, A. C. van Veen and J. A. Lercher, On the impact of co-feeding aromatics and olefins for the methanol-to-olefins reaction on HZSM-5, *J. Catal.*, 2014, **314**, 21–31.

250 X. Sun, S. Mueller, Y. Liu, H. Shi, G. L. Haller, M. Sanchez-Sanchez, A. C. van Veen and J. A. Lercher, On reaction pathways in the conversion of methanol to hydrocarbons on HZSM-5, *J. Catal.*, 2014, **317**, 185–197.

251 H. Schulz, "Coking" of zeolites during methanol conversion: Basic reactions of the MTO-, MTP- and MTG processes, *Catal. Today*, 2010, **154**, 183–194.

252 D. Chen, K. Moljord and A. Holmen, A methanol to olefins review: Diffusion, coke formation and deactivation on SAPO type catalysts, *Microporous Mesoporous Mater.*, 2012, **164**, 239–250.

253 V. Paunović, X. Wu, L. Maggiulli, D. Ferri, P. Hemberger, A. Bodi and J. A. van Bokhoven, The formation, reactivity and transformation pathways of formaldehyde in the methanol-to-hydrocarbon conversion, *Catal. Sci. Technol.*, 2024, **14**, 1216–1228.

254 V. Paunović, V. Sushkevich, P. Rzepka, L. Artiglia, R. Hauert, S. Sik Lee and J. A. van Bokhoven, Reactivation of catalysts for methanol-to-hydrocarbons conversion with hydrogen, *J. Catal.*, 2022, **407**, 54–64.

255 S. Lee and M. Choi, Unveiling coke formation mechanism in MFI zeolites during methanol-to-hydrocarbons conversion, *J. Catal.*, 2019, **375**, 183–192.

256 S. Müller, Y. Liu, M. Vishnuvarthan, X. Sun, A. C. van Veen, G. L. Haller, M. Sanchez-Sanchez and J. A. Lercher, Coke formation and deactivation pathways on H-ZSM-5 in the conversion of methanol to olefins, *J. Catal.*, 2015, **325**, 48–59.

257 T. V. Janssens, S. Svelle and U. Olsbye, Kinetic modeling of deactivation profiles in the methanol-to-hydrocarbons (MTH) reaction: A combined autocatalytic–hydrocarbon pool approach, *J. Catal.*, 2013, **308**, 122–130.

258 Y. Liu, F. M. Kirchberger, S. Müller, M. Eder, M. Tonigold, M. Sanchez-Sanchez and J. A. Lercher, Critical role of formaldehyde during methanol conversion to hydrocarbons, *Nat. Commun.*, 2019, **10**, 1462.

259 S. S. Arora and A. Bhan, The critical role of methanol pressure in controlling its transfer dehydrogenation and the corresponding effect on propylene-to-ethylene ratio during methanol-to-hydrocarbons catalysis on H-ZSM-5, *J. Catal.*, 2017, **356**, 300–306.

260 S. Zhang, B. Zhang, Z. Gao and Y. Han, Ca modified ZSM-5 for high propylene selectivity from methanol, *React. Kinet., Mech. Catal.*, 2010, **99**, 447–453.

261 B. Niethammer, U. Arnold and J. Sauer, Suppressing the aromatic cycle of the dimethyl ether to hydrocarbons reaction on zeolites, *Appl. Catal., A*, 2023, **651**, 119021.

262 A. T. Aguayo, D. Mier, A. G. Gayubo, M. Gamero and J. Bilbao, Kinetics of Methanol Transformation into Hydrocarbons on a HZSM-5 Zeolite Catalyst at High Temperature (400−550 °C), *Ind. Eng. Chem. Res.*, 2010, **49**, 12371–12378.

263 A. G. Gayubo, A. T. Aguayo, M. Castilla, A. L. Moran and J. Bilbao, Role of Water in the Kinetic Modeling of Methanol Transformation into Hydrocarbons on Hzsm-5 Zeolite, *Chem. Eng. Commun.*, 2004, **191**, 944–967.

264 T.-Y. Park and G. F. Froment, Kinetic Modeling of the Methanol to Olefins Process. 1. Model Formulation, *Ind. Eng. Chem. Res.*, 2001, **40**, 4172–4186.

265 T.-Y. Park and G. F. Froment, Kinetic Modeling of the Methanol to Olefins Process. 2. Experimental Results, Model Discrimination, and Parameter Estimation, *Ind. Eng. Chem. Res.*, 2001, **40**, 4187–4196.

266 X. Huang, X.-G. Li, H. Li and W. Xiao, High-performance HZSM-5/cordierite monolithic catalyst for methanol to propylene reaction: A combined experimental and modelling study, *Fuel Process. Technol.*, 2017, **159**, 168–177.

267 S. H. Alaei, F. Khorasheh, M. R. Jafari Nasr and M. Arjmand, Experimental study and kinetic modeling of methanol conversion to propylene with co-feeding of C4 and C5/C6 hydrocarbon cuts over a ZSM-5 catalyst, *J. Chem. Phys.*, 2023, **158**, 124203.

268 X. Huang, D. Aihemaitijiang and W. Xiao, Co-reaction of methanol and olefins on the high silicon HZSM-5 catalyst: A kinetic study, *Chem. Eng. J.*, 2016, **286**, 150–164.

269 X. Huang, H. Li, W. Xiao and D. CHEN, Insight into the side reactions in methanol-to-olefin process over HZSM-5: A kinetic study, *Chem. Eng. J.*, 2016, **299**, 263–275.

270 A. A. Avidan, Gasoline and Distillate Fuels From Methanol, *Methane Convers.*, 1988, **36**, 307–323.

271 J. Topp-Jørgensen, in *Methane Conversion*, ed. D. M. Bibby, C. D. Chang, R. F. Howe and S. Yurchak, Elsevier, 1988, pp. 293–305.

272 B. V. Vora, Development of Catalytic Processes for the Production of Olefins, *Trans. Indian Natl. Acad. Eng.*, 2023, **8**, 201–219.

273 M. R. Gogate, Methanol-to-olefins process technology: current status and future prospects, *Pet. Sci. Technol.*, 2019, **37**, 559–565.

274 B. V. Vora, T. L. Marker, P. T. Barger, H. R. Nilsen, S. Kvisle and T. Fuglerud, in *Natural Gas Conversion IV*, ed. M. de Pontes, R. L. Espinoza, C. P. Nicolaides, J. H. Scholtz and M. S. Scurrell, Elsevier, 1997, pp. 87–98.

275 J. Q. Chen, A. Bozzano, B. Glover, T. Fuglerud and S. Kvisle, Recent advancements in ethylene and propylene production using the UOP/Hydro MTO process, *Catal. Today*, 2005, **106**, 103–107.

276 C. D. Chang, Methanol Conversion to Light Olefins, *Catal. Rev.*, 1984, **26**, 323–345.

277 G. J. Hutchings and R. Hunter, Hydrocarbon formation from methanol and dimethyl ether: a review of the experimental observations concerning the mechanism of formation of the primary products, *Catal. Today*, 1990, **6**, 279–306.

278 M. Yang, D. Fan, Y. Wei, P. Tian and Z. Liu, Recent Progress in Methanol-to-Olefins (MTO) Catalysts//Recent Progress in

Methanol-to-Olefins (MTO) Catalysts, *Adv. Mater.*, 2019, **31**, e1902181.

279 S. Jasper and M. El-Halwagi, A Techno-Economic Comparison between Two Methanol-to-Propylene Processes, *Processes*, 2015, **3**, 684–698.

280 M. Khanmohammadi, S. Amani, A. B. Garmarudi and A. Niaei, Methanol-to-propylene process: Perspective of the most important catalysts and their behavior, *Chin. J. Catal.*, 2016, **37**, 325–339.

281 A. C. Dimian and C. S. Bildea, Energy efficient methanol-to-olefins process, *Chem. Eng. Res. Des.*, 2018, **131**, 41–54.

282 C. Zhang, K. L. A. Ng, L. Yan, X. Feng, B. Jiang, Z. Liao, J. Wang and Y. Yang, Kinetic Perspective on Methanol to Propylene Process via HZSM-5 Catalyst: Balancing between Reaction and Diffusion, *Ind. Eng. Chem. Res.*, 2022, **61**, 2055–2067.

283 G. R. K. Zadeh, M. Panahi, E. Yasari, A. Rafiee, M. A. Fanaei and H. Alaei, Plantwide Simulation and Operation of a Methanol to Propylene (MTP) Process, *J. Taiwan Inst. Chem. Eng.*, 2023, **153**, 105204.

284 X. Huang, H. Li, H. Li and W. Xiao, Modeling and analysis of the Lurgi-type methanol to propylene process: Optimization of olefin recycle, *AIChE J.*, 2017, **63**, 306–313.

285 K. G. Bryan, Q. C. John, R. P. Peter and V. V. Bipin, *US Pat.*, US7408092B2, 2008.

286 N. K. Tom and V. V. Timur, *US Pat.*, US7414167B2, 2008.

287 N. K. Tom, H. W. Daniel and K. G. Bryan, *US Pat.*, US7405337B2, 2008.

288 P. Beato, *WO pat.*, WO2022063995A1, 2022.

289 P. Beato, *WO pat.*, WO22063992A1, 2022.

290 P. Beato, *WO pat.*, WO22063993A1, 2022.

291 X. Huang, D. Aihemaitijiang and W. Xiao, Reaction pathway and kinetics of C3–C7 olefin transformation over high-silicon HZSM-5 zeolite at 400–490°C, *Chem. Eng. J.*, 2015, **280**, 222–232.

292 A. Corma and S. Iborra, in *Catalysts for Fine Chemical Synthesis*, 2006, pp. 125–140.

293 H. Olivier-Bourbigou, P. A. R. Breuil, L. Magna, T. Michel, M. F. Espada Pastor and D. Delcroix, Nickel Catalyzed Olefin Oligomerization and Dimerization, *Chem. Rev.*, 2020, **120**, 7919–7983.

294 C. P. Nicholas, Applications of light olefin oligomerization to the production of fuels and chemicals, *Appl. Catal., A*, 2017, **543**, 82–97.

295 E. Koninckx, P. S. Mendes, J. W. Thybaut and L. J. Broadbelt, Ethylene oligomerization on nickel catalysts on a solid acid support: From New mechanistic insights to tunable bifunctionality, *Appl. Catal., A*, 2021, **624**, 118296.

296 S. A. Tabak, F. J. Krambeck and W. E. GARWOOD, Conversion of propylene and butylene over ZSM-5 catalyst, *AIChE J.*, 1986, **32**, 1526–1531.

297 S. Peratello, M. Molinari, G. Bellussi and C. Perego, Olefins oligomerization: thermodynamics and kinetics over a mesoporous silica–alumina, *Catal. Today*, 1999, **52**, 271–277.

298 M. R. Díaz-Rey, C. Paris, R. Martínez-Franco, M. Moliner, C. Martínez and A. Corma, Efficient Oligomerization of Pentene into Liquid Fuels on Nanocrystalline Beta Zeolites, *ACS Catal.*, 2017, **7**, 6170–6178.

299 S. Vernuccio, E. E. Bickel, R. Gounder and L. J. Broadbelt, Propene oligomerization on Beta zeolites: Development of a microkinetic model and experimental validation, *J. Catal.*, 2021, **395**, 302–314.

300 A. de Klerk, Oligomerization of 1-Hexene and 1-Octene over Solid Acid Catalysts, *Ind. Eng. Chem. Res.*, 2005, **44**, 3887–3893.

301 W. E. Garwood, in *Intrazeolite Chemistry*, ed. G. D. Stucky and F. G. Dwyer, American Chemical Society, Washington, D.C., 1983, pp. 383–396.

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

303 X. Li, D. Han, H. Wang, G. Liu, B. Wang, Z. Li and J. Wu, Propene oligomerization to high-quality liquid fuels over Ni/HZSM-5, *Fuel*, 2015, **144**, 9–14.

304 A. N. Mlinar, P. M. Zimmerman, F. E. Celik, M. Head-Gordon and A. T. Bell, Effects of Brønsted-acid site proximity on the oligomerization of propene in H-MFI, *J. Catal.*, 2012, **288**, 65–73.

305 S. Vernuccio, E. E. Bickel, R. Gounder and L. J. Broadbelt, Microkinetic Model of Propylene Oligomerization on Brønsted Acidic Zeolites at Low Conversion, *ACS Catal.*, 2019, **9**, 8996–9008.

306 M. Díaz, E. Epelde, A. T. Aguayo and J. Bilbao, Low-pressure oligomerization of 1-butene to liquid fuels on HZSM-5 zeolite catalysts: Effect of operating conditions, *J. Ind. Eng. Chem.*, 2020, **87**, 234–241.

307 P. Borges, R. R. Pinto, M. Lemos, F. Lemos, J. C. Védrine, E. G. Derouane and F. R. Ribeiro, Light olefin transformation over ZSM-5 zeolitesA kinetic model for olefin consumption, *Appl. Catal., A*, 2007, **324**, 20–29.

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

309 W. Monama, E. Mohiuddin, B. Thangaraj, M. M. Mdleleni and D. Key, Oligomerization of lower olefins to fuel range hydrocarbons over texturally enhanced ZSM-5 catalyst, *Catal. Today*, 2020, **342**, 167–177.

310 W. van der Merwe, Conversion of Spent Solid Phosphoric Acid Catalyst to Environmentally Friendly Fertilizer, *Environ. Sci. Technol.*, 2010, **44**, 1806–1812.

311 K. Toch, J. W. Thybaut, M. A. Arribas, A. Martínez and G. B. Marin, Steering linear 1-alkene, propene or gasoline yields in ethene oligomerization via the interplay between nickel and acid sites, *Chem. Eng. Sci.*, 2017, **173**, 49–59.

312 P. Liu, E. Redekop, X. Gao, W.-C. Liu, U. Olsbye and G. A. Somorjai, Oligomerization of Light Olefins Catalyzed by Brønsted-Acidic Metal–Organic Framework-808, *J. Am. Chem. Soc.*, 2019, **141**, 11557–11564.

313 C. T. O'Connor and M. Kojima, Alkene oligomerization, *Catal. Today*, 1990, **6**, 329–349.

314 R. L. Espinoza, R. Snel, C. J. Korf and C. P. Nicolaides, Catalytic oligomerization of ethene over nickel-exchanged amorphous silica–aluminas; effect of the acid strength of the support, *Appl. Catal.*, 1987, **29**, 295–303.

315 Y. Chauvin, D. Commereuc, F. Hugues and J. Thivolle-cazat, Nickel-based heterogeneous catalysts for olefin oligomerization: I. Support and anion effects, *Appl. Catal.*, 1988, **42**, 205–216.

316 J. Heveling, C. P. Nicolaides and M. S. Scurrell, Catalysts and conditions for the highly efficient, selective and stable heterogeneous oligomerisation of ethylene, *Appl. Catal., A*, 1998, **173**, 1–9.

317 A. Finiels, F. Fajula and V. Hulea, Nickel-based solid catalysts for ethylene oligomerization – a review, *Catal. Sci. Technol.*, 2014, **4**, 2412–2426.

318 R. D. Andrei, M. I. Popa, F. Fajula and V. Hulea, Heterogeneous oligomerization of ethylene over highly active and stable Ni-AlSBA-15 mesoporous catalysts, *J. Catal.*, 2015, **323**, 76–84.

319 B. H. Babu, M. Lee, D. W. Hwang, Y. Kim and H.-J. Chae, An integrated process for production of jet-fuel range olefins from ethylene using Ni-AlSBA-15 and Amberlyst-35 catalysts, *Appl. Catal., A*, 2017, **530**, 48–55.

320 M. Tanaka, A. Itadani, Y. Kuroda and M. Iwamoto, Effect of Pore Size and Nickel Content of Ni-MCM-41 on Catalytic Activity for Ethene Dimerization and Local Structures of Nickel Ions, *J. Phys. Chem. C*, 2012, **116**, 5664–5672.

321 V. Hulea and F. Fajula, Ni-exchanged AlMCM-41—An efficient bifunctional catalyst for ethylene oligomerization, *J. Catal.*, 2004, **225**, 213–222.

322 G. J. P. Britovsek, R. Malinowski, D. S. McGuinness, J. D. Nobbs, A. K. Tomov, A. W. Wadsley and C. T. Young, Ethylene Oligomerization beyond Schulz–Flory Distributions, *ACS Catal.*, 2015, **5**, 6922–6925.

323 M. A. Lilga, R. T. Hallen, K. O. Albrecht, A. R. Cooper, J. G. Frye and K. K. Ramasamy, *US Pat.*, US2017218283A1, 2017.

324 A. Lacarriere, J. Robin, D. Świerczyński, A. Finiels, F. Fajula, F. Luck and V. Hulea, Distillate-Range Products from Non-Oil-Based Sources by Catalytic Cascade Reactions, *ChemSusChem*, 2012, **5**, 1787–1792.

325 K. P. Brooks, L. J. Snowden-Swan, S. B. Jones, M. G. Butcher, G.-S. Lee, D. M. Anderson, J. G. Frye, J. E. Holladay, J. Owen, L. Harmon, F. Burton, I. Palou-Rivera, J. Plaza, R. Handler and D. Shonnard, Low-Carbon Aviation Fuel Through the Alcohol to Jet Pathway, in *Biofuels for Aviation*, Elsevier, 2016, pp. 109–150.

326 J. W. Yoon, J.-S. Chang, H.-D. Lee, T.-J. Kim and S. H. Jhung, Trimerization of isobutene over a zeolite beta catalyst, *J. Catal.*, 2007, **245**, 253–256.

327 A. de Klerk, Oligomerization of Fischer−Tropsch Olefins to Distillates over Amorphous Silica–Alumina, *Energy Fuels*, 2006, **20**, 1799–1805.

328 K. Hauge, E. Bergene, D. Chen, G. R. Fredriksen and A. Holmen, Oligomerization of isobutene over solid acid catalysts, *Catal. Today*, 2005, **100**, 463–466.

329 T. Sakuneka, A. de Klerk and A. Pienaar, Synthetic Jet Fuel Production by Combined Propene Oligomerization and Aromatic Alkylation over Solid Phosphoric Acid, *Ind. Eng. Chem. Res.*, 2008, **47**, 1828–1834.

330 S. Vernuccio and L. J. Broadbelt, Discerning complex reaction networks using automated generators, *AIChE J.*, 2019, **65**, e16663.

331 J. R. Shahrouzi, D. Guillaume, P. Rouchon and P. Da Costa, Stochastic Simulation and Single Events Kinetic Modeling: Application to Olefin Oligomerization, *Ind. Eng. Chem. Res.*, 2008, **47**, 4308–4316.

332 D. Guillaume, Network Generation of Oligomerization Reactions: Principles, *Ind. Eng. Chem. Res.*, 2006, **45**, 4554–4557.

333 F. Jin, Y. Fan, M. Yuan, F. Min, G. Wu, Y. Ding and G. F. Froment, Single-event kinetic modeling of ethene oligomerization on ZSM-5, *Catal. Today*, 2018, **316**, 129–141.

334 A. Corma, C. Martínez and E. Doskocil, Designing MFI-based catalysts with improved catalyst life for C3=andC5= oligomerization to high-quality liquid fuels, *J. Catal.*, 2013, **300**, 183–196.

335 K. A. Tarach, K. Góra-Marek, J. Martinez-Triguero and I. Melián-Cabrera, Acidity and accessibility studies of desilicated ZSM-5 zeolites in terms of their effectiveness as catalysts in acid-catalyzed cracking processes, *Catal. Sci. Technol.*, 2017, **7**, 858–873.

336 S. Moon, H.-J. Chae and M. B. Park, Oligomerization of light olefins over ZSM-5 and beta zeolite catalysts by modifying textural properties, *Appl. Catal., A*, 2018, **553**, 15–23.

337 F. Zhou, Y. Gao, G. Wu, F. Ma and C. Liu, Improved catalytic performance and decreased coke formation in post-treated ZSM-5 zeolites for methanol aromatization, *Microporous Mesoporous Mater.*, 2017, **240**, 96–107.

338 E. E. Bickel and R. Gounder, Hydrocarbon Products Occluded within Zeolite Micropores Impose Transport Barriers that Regulate Brønsted Acid-Catalyzed Propene Oligomerization, *JACS Au*, 2022, **2**, 2585–2595.

339 J. M. Escola, R. van Grieken, J. Moreno and R. Rodríguez, Liquid-Phase Oligomerization of 1-Hexene Using Al-MTS Catalysts, *Ind. Eng. Chem. Res.*, 2006, **45**, 7409–7414.

340 J. Kim, M. Choi and R. Ryoo, Effect of mesoporosity against the deactivation of MFI zeolite catalyst during the methanol-to-hydrocarbon conversion process, *J. Catal.*, 2010, **269**, 219–228.

341 X. Ding, C. Li and C. Yang, Study on the Oligomerization of Ethylene in Fluidized Catalytic Cracking (FCC) Dry Gas over Metal-Loaded HZSM-5 Catalysts, *Energy Fuels*, 2010, **24**, 3760–3763.

342 P. Sazama, J. Dědeček, V. Gábová, B. Wichterlová, G. Spoto and S. Bordiga, Effect of aluminium distribution in the framework of ZSM-5 on hydrocarbon transformation. Cracking of 1-butene, *J. Catal.*, 2008, **254**, 180–189.

343 A. Kulkarni, A. Kumar, A. S. Goldman and F. E. Celik, Selectivity for dimers in pentene oligomerization over acid zeolites, *Catal. Commun.*, 2016, **75**, 98–102.

344 A. Coelho, G. Caeiro, M. Lemos, F. Lemos and F. R. Ribeiro, 1-Butene oligomerization over ZSM-5 zeolite: Part 1 – Effect of reaction conditions, *Fuel*, 2013, **111**, 449–460.

345 E. G. William, D. C. Philip and A. B. James, *US Pat.*, US4150062A, 1979.

346 E. G. William and L. Wooyoung, *US Pat.*, US4227992A, 1980.

347 A. T. Samuel, *US Pat.*, US4254295A, 1981.

348 A. T. Samuel, S. W. Bernard and O. Hartley, *US Pat.*, US4504693, 1985.

349 K. S. Ng, D. Farooq, A. Yang, K. S. Ng, D. Farooq and A. Yang, Global biorenewable development strategies for sustainable aviation fuel production, *Renew. Sustain. Energy Rev.*, 2021, **150**, 111502.

350 A. T. Samuel, *US Pat.*, US4560537, 1985.

351 E. Kohler, F. Schmidt, H. J. Wernicke, M. de Pontes and H. L. Roberts, Converting olefins to diesel: the COD process, *Int. J. Hydrocarb. Technol.*, 1995, **95**, 37–40.

352 A. de Klerk, Distillate Production by Oligomerization of Fischer−Tropsch Olefins over Solid Phosphoric Acid, *Energy Fuels*, 2006, **20**, 439–445.

353 A. de Klerk, Properties of Synthetic Fuels from H-ZSM-5 Oligomerization of Fischer–Tropsch Type Feed Materials, *Energy Fuels*, 2007, **21**, 3084–3089.

354 C. M. Halmenschlager, M. Brar, I. T. Apan and A. de Klerk, Oligomerization of Fischer–Tropsch Tail Gas over H-ZSM-5, *Ind. Eng. Chem. Res.*, 2016, **55**, 13020–13031.

355 M. Brémaud, L. Vivier, G. Pérot, V. Harlé and C. Bouchy, Hydrogenation of olefins over hydrotreating catalysts: Promotion effect on the activity and on the involvement of H2S in the reaction, *Appl. Catal., A*, 2005, **289**, 44–50.

356 D. Lamprecht, Hydrogenation of Fischer−Tropsch Synthetic Crude, *Energy Fuels*, 2007, **21**, 2509–2513.

357 A. C. Villareal-Hernández, M. D. Ramírez-Mendiola, J. J. Quiroz-Ramírez, E. Sánchez-Ramírez, B. Huerta-Rosas, G. Contreras-Zarazua and J. G. Segovia-Hernández, Intensification of the Oligomerization and Hydrogenation Stage for Biojet Fuel Production: Preliminary Outlines, *Ind. Eng. Chem. Res.*, 2023, **62**, 8820–8833.

358 L. Tao, J. N. Markham, Z. Haq and M. J. Biddy, Techno-economic analysis for upgrading the biomass-derived ethanol-to-jet blendstocks, *Green Chem.*, 2017, **19**, 1082–1101.

359 A. de Klerk, Fischer–Tropsch refining: technology selection to match, *Molecules*, 2008, **10**(12), 1249–1279.

360 R. G. Patrick, W. P. Matthew, M. G. Josefa, A. O. Yassin, E. M. Leo, D. T. Joshua and E. H. David, *US Pat.*, US8378160B2, 2013.

361 A. L. Michael, T. H. Richard, O. A. Karl, R. C. Alan, G. F. John and R. Karthi, *US Pat.*, US 20160194257A1, 2016.

362 T. van Gerven and A. Stankiewicz, Structure, Energy, Synergy, Time—The Fundamentals of Process Intensification, *Ind. Eng. Chem. Res.*, 2009, **48**, 2465–2474.

363 T. Cholewa, M. Semmel, F. Mantei, R. Güttel and O. Salem, Process Intensification Strategies for Power-to-X Technologies, *ChemEngineering*, 2022, **6**, 13.

364 A. G. Romero-Izquierdo, F. I. Gómez-Castro, C. Gutiérrez-Antonio, S. Hernández and M. Errico, Intensification of the alcohol-to-jet process to produce renewable aviation fuel, *Chem. Eng. Process. Process Intensif.*, 2021, **160**, 108270.

365 J. Valecillos, G. Elordi, A. T. Aguayo and P. Castaño, The intrinsic effect of co-feeding water on the formation of active/deactivating species in the methanol-to-hydrocarbons reaction on ZSM-5 zeolite, *Catal. Sci. Technol.*, 2021, **11**, 1269–1281.

366 M. Luo, Y. Fu, B. Hu, D. Wang, B. Wang and G. Mao, Water inhibits the conversion and coking of olefins on SAPO-34, *Appl. Catal., A*, 2019, **570**, 209–217.

367 J. Amsler, P. N. Plessow and F. Studt, Effect of Impurities on the Initiation of the Methanol-to-Olefins Process: Kinetic Modeling Based on Ab Initio Rate Constants, *Catal. Lett.*, 2021, **151**, 2595–2602.

368 M. Gierse, I. Bogatykh, B. Steinbach, J. Sauer, J.-U. Repke and O. Salem, Demonstration and experimental model validation of the DME synthesis by reactive distillation in a pilot-scale pressure column, *React. Chem. Eng.*, 2023, **8**, 2309–2322.

369 M. Gierse, M. Kerschbaum, B. Steinbach, J. Sauer and O. Salem, Optimized design and techno-economic analysis of novel DME production processes, *React. Chem. Eng.*, 2023, **8**, 2826–2840.

370 S. Malte, S. Benedikt and O. Mohamed, *WO pat.*, WO2023241919A1, 2023.

371 T. Cordero-Lanzac, I. Capel Berdiell, A. Airi, S. Chung, J. L. Mancuso, E. A. Redekop, C. Fabris, L. Figueroa-Quintero, N. de Miguel, C. Juan, J. Narciso, E. V. Ramos-Fernandez, S. Svelle, V. van Speybroeck, J. Ruiz-Martínez, S. Bordiga and U. Olsbye, Transitioning from Methanol to Olefins (MTO) toward a Tandem CO2 Hydrogenation Process: On the Role and Fate of Heteroatoms (Mg, Si) in MAPO-18 Zeotypes, *JACS Au*, 2024, **4**, 744–759.

372 P. Gao, L. Zhang, S. Li, Z. Zhou and Y. Sun, Novel Heterogeneous Catalysts for CO2 Hydrogenation to Liquid Fuels, *ACS Cent. Sci.*, 2020, **6**, 1657–1670.

373 Y. Gambo, S. Adamu, R. A. Lucky, M. S. Ba-Shammakh and M. M. Hossain, Tandem catalysis: A sustainable alternative for direct hydrogenation of CO2 to light olefins, *Appl. Catal., A*, 2022, **641**, 118658.

374 C. G. Okoye-Chine, C. O. L. Mbuya, N. C. Shiba and K. O. Otun, Effective catalysts for hydrogenation of CO2 into lower olefins: A review, *Carbon Capture Sci. Technol.*, 2024, **13**, 100251.

375 E. C. Ra, K. Y. Kim, E. H. Kim, H. Lee, K. An and J. S. Lee, Recycling Carbon Dioxide through Catalytic Hydrogenation: Recent Key Developments and Perspectives, *ACS Catal.*, 2020, **10**, 11318–11345.

376 R.-P. Ye, J. Ding, W. Gong, M. D. Argyle, Q. Zhong, Y. Wang, C. K. Russell, Z. Xu, A. G. Russell, Q. Li, M. Fan and Y.-G. Yao, CO2 hydrogenation to high-value products via heterogeneous catalysis, *Nat. Commun.*, 2019, **10**, 5698.

377 B. Pawelec, R. Guil-López, N. Mota, J. L. G. Fierro and R. M. Navarro Yerga, Catalysts for the Conversion of CO2 to Low Molecular Weight Olefins—A Review, *Materials*, 2021, **14**, 6952.

378 K. Räuchle, L. Plass, H.-J. Wernicke and M. Bertau, Methanol for Renewable Energy Storage and Utilization, *Energy Technol.*, 2016, **4**, 193–200.