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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<sub>2</sub> emissions. The methanol pathway represents a synthesis-based route for producing SAF that can utilize various feedstocks, including electrolytically produced H<sub>2</sub> and atmospheric CO<sub>2</sub> 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<sub>8</sub>–C<sub>16</sub>). 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<sub>CO<sub>2</sub></sub>, the aviation sector accounted for over 2% of the global anthropogenic carbon dioxide (CO<sub>2</sub>) emissions in 2022.<sup>1,2</sup> These emissions are projected to triple by the year 2050, provided that no counter measures are taken.<sup>3,4</sup> 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<sub>2</sub> per litre of jet fuel.<sup>5</sup> 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%.<sup>6,7</sup> In addition to CO<sub>2</sub>, significant emissions from global aviation include nitrogen oxides (NO<sub>x</sub>), water vapor, soot, sulfate aerosols, and increased cloudiness due to contrail formation.<sup>8,9</sup> Both CO<sub>2</sub> and non-CO<sub>2</sub> emissions contribute to net surface warming and anthropogenic climate changes,<sup>10</sup> with approximately one-third of the radiative forcing attributed to CO<sub>2</sub> and the other two-thirds caused by particulate emissions and water vapor forming contrail cirrus clouds.<sup>11,12</sup>

The climate impact of aviation could be mitigated by adopting new technologies, such as electric or hydrogen (H<sub>2</sub>) fuelled aircrafts.<sup>13</sup> 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.<sup>14</sup> 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.<sup>15</sup> 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.<sup>16</sup>

Sustainable aviation fuels (SAFs) are commonly referred to as kerosene-type fuels that can be produced from renewable energy sources.<sup>17</sup> 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<sub>2</sub> 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<sub>2</sub> emissions in the aviation sector.<sup>18</sup> 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.<sup>19</sup>

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).<sup>20</sup> The

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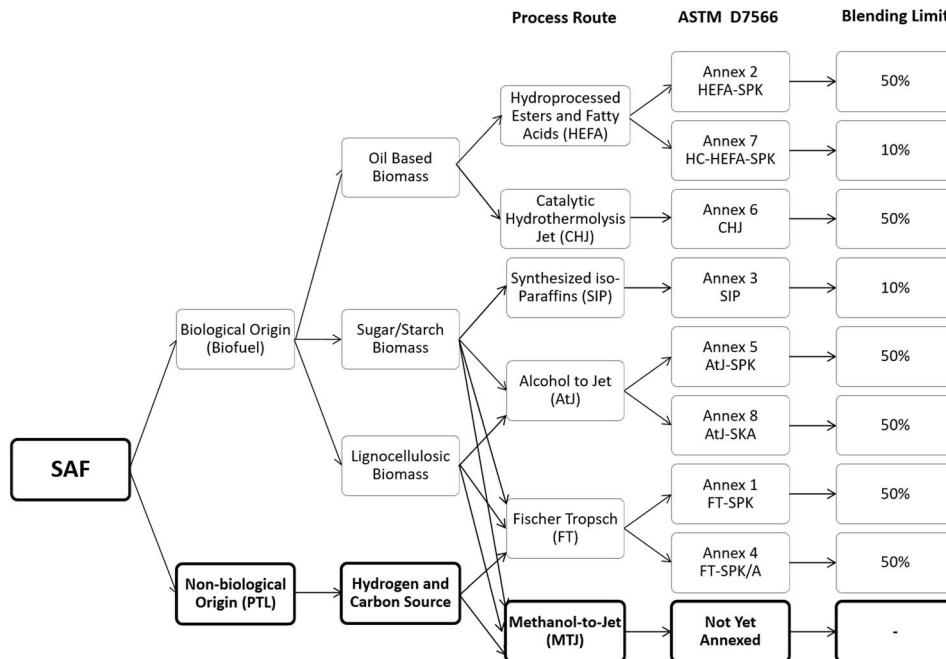


Fig. 1 Main production routes for synthetic jet fuel production.<sup>19</sup>

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.<sup>21,22</sup> 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/1, Jet A-1), specified in ASTM D1655 Standard Specification for Aviation Turbine Fuels.<sup>23</sup>

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.<sup>24</sup> 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.<sup>25</sup> The aviation industry aims to progress towards the use of 100% SAF that comply with safety and operability requirements of the ASTM qualification process.<sup>26</sup>

In 2024, SAF represented only 0.3% of global jet fuel produced.<sup>27</sup> 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.<sup>28,29</sup> 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.<sup>28,29</sup> 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.<sup>30</sup> 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<sup>20,23</sup>

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 <sup>2</sup> s <sup>−1</sup> )	<8	<8
Density at 15 °C (kg m <sup>−3</sup> )	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 <sup>−1</sup>	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.<sup>31</sup> Currently, the annual production capacity of SAF in the EU stands at just over 1 Mt per a.<sup>32</sup> 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,<sup>32,33</sup> 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,<sup>6,13,18,29,34–37</sup> 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.<sup>18</sup> A more extensive review by Khanal *et al.* provides a detailed analysis of SAF production *via* various biofuel routes.<sup>36</sup>

Among ASTM approved SAF production routes, the hydro-processed esters and fatty acids (HEFA) process, currently dominates the SAF market with more than 90% of the total share.<sup>29,38</sup> HEFA jet fuel and HVO diesel are produced *via* hydrotreatment and subsequent isomerization of fats, oils, and greases (FOG), or other bio-oils.<sup>39</sup> 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,<sup>40</sup> with a recent demonstration plant by LanzaJet at a production scale of 30 000 t/a.<sup>41</sup> Additionally, the ATJ process has been demonstrated using isobutanol derived from cellulosic non-edible crops biomass.<sup>42</sup> 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.<sup>20</sup>

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.<sup>6,43</sup> Additionally, the expansion in bio-based jet fuel frequently prompts concerns regarding food *versus* fuel and land-use change.<sup>18</sup> 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.<sup>44–46</sup> Currently, the economic viability of these processes is hindered due to the high production costs of green H<sub>2</sub>.<sup>47</sup> However, it is expected that these costs will decrease with the improvement of the major electrolysis technologies.<sup>48</sup> 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.<sup>49,50</sup> 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.<sup>17</sup>

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.<sup>51</sup> 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<sub>2</sub>, into liquid fuels such as SAF.<sup>52</sup> Synthesis gas can either be produced from biological or non-biological origin.<sup>53,54</sup> 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.<sup>55,56</sup>

FT technology can be integrated into PTL production route, where synthesis gas is generated from CO<sub>2</sub>, electricity, and water instead of biogenic feedstocks. However, FT synthesis faces some challenges regarding syngas generation due to the high energy intensity of CO<sub>2</sub>-to-CO-conversion by reverse water gas shift reaction (rWGS) or the low TRL of co-electrolysis.<sup>57,58</sup> Moreover, its high exothermic heat and complex reaction kinetics present a challenge for direct coupling of the process to fluctuating renewable power.<sup>59,60</sup>

While many review articles dealing with the characteristics of FT synthesis for SAF production are available today,<sup>52,53,61,62</sup> 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<sub>2</sub> and CO<sub>2</sub> *via* the methanol pathway involves four main subprocesses: methanol synthesis, methanol-to-olefins (MTO) conversion, oligomerization, and hydrogenation.<sup>19,63,64</sup>

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<sub>2</sub> and CO<sub>x</sub> 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



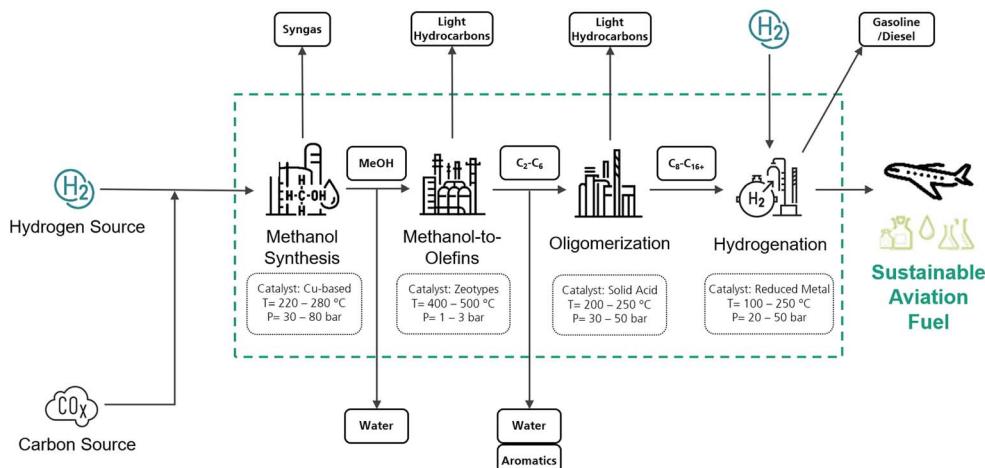


Fig. 2 Sustainable aviation fuel production from hydrogen and carbon source via the methanol pathway. The grey streams represent potential by-products that may occur in the process.<sup>18,56,57</sup>

pressure range of 220–280 °C and 30–80 bar, respectively.<sup>58</sup> 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.<sup>65</sup> The product stream of the MTO synthesis is quenched, and water is separated and partially recycled to the MTO reactor. C<sub>2</sub>–C<sub>6</sub> olefins are separated from lighter and heavier components using fractionation columns.<sup>66–68</sup> In the subsequent oligomerization step, the chain length of the olefins (C<sub>2</sub>–C<sub>6</sub>) is increased over solid acid catalyst at synthesis conditions of 200–250 °C and 30–50 bar.<sup>69</sup> 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<sub>2</sub> and hydrogenated over a reduced metal catalyst at 100–250 °C and 20–50 bar to saturate the olefinic double bonds.<sup>69</sup> The product is cooled and the excess H<sub>2</sub> is recycled back to the fixed-bed hydrogenation reactor.<sup>70</sup> Finally, the jet fuel product, with a typical carbon range of mainly C<sub>8</sub>–C<sub>16</sub>, is separated from lighter and heavier hydrocarbons using fractionation columns.<sup>71</sup>

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<sub>2</sub>, CO<sub>2</sub> can be utilized directly without the need of a reverse water gas shift stage or co-electrolysis.<sup>72</sup>

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

(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.<sup>17,71</sup> 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.<sup>78,79</sup>

Each of the individual subprocesses of the MTJ process chain are currently operational on industrial scale in various plants and refineries.<sup>80–82</sup> 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.<sup>17,71</sup>

Various companies and institutions are working on the process development of MTJ, such as ExxonMobil, UOP and Topsoe.<sup>83–85</sup> Several research projects are investigating this topic, such as SAFari and M2SAF.<sup>86,87</sup> Moreover, several techno-economic analyses have investigated the MTJ process, although the optimization towards jet fuel mainly includes strong simplifications.<sup>49,88–91</sup> 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.<sup>17,90</sup> 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.<sup>88–90</sup> 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.<sup>89</sup> 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.<sup>92</sup> Overall, the estimated production costs are subjected to varying assumptions regarding feedstock costs, plant capacity and the boundary conditions, with water electrolysis and CO<sub>2</sub> capture accounting to 74–79%.<sup>88–90</sup> Moreover, it is important to note that these studies underly



systematic uncertainties caused by technical assumptions, such as conversions, selectivities and chain growth probability.<sup>17,90</sup>

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.<sup>93,94</sup> Methanol is used as a platform molecule to produce fuels and chemicals, with the main consumption driven by China.<sup>95</sup> 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).<sup>96,97</sup> 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.<sup>43</sup> 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<sub>2</sub>, CO and CO<sub>2</sub> covering a wide concentration range.<sup>98</sup> Importantly, the CO/CO<sub>2</sub> 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.<sup>72,98</sup>

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.<sup>99</sup> Depending on the feedstock applied, these processes generate cradle-to-gate CO<sub>2</sub> emissions between 0.85 t<sub>CO<sub>2</sub>,eq</sub>/t<sub>MeOH</sub> and 2.97 t<sub>CO<sub>2</sub>,eq</sub>/t<sub>MeOH</sub> for a basic natural gas or coal based process, respectively.<sup>99,100</sup> Assuming thermal treatment of methanol end-of-life additional 1.38 t<sub>CO<sub>2</sub>,eq</sub>/t<sub>MeOH</sub> would be emitted through a stoichiometric oxidation. Thus, to decrease the CO<sub>2</sub> emissions caused by methanol production and utilization, carbon neutral production routes including carbon cycles need to be established.<sup>101</sup> Biogenic or atmospheric carbon oxides reacted with carbon-neutrally produced H<sub>2</sub> by water electrolysis is currently seen as a promising pathway to satisfy the methanol world market in the future.<sup>102</sup> Whilst these Power-to-Methanol (PTM) processes offer the potential of carbon neutrally produced methanol, the partial or entire replacement of CO by CO<sub>2</sub> in the syngas entails disadvantages originating from the high chemical stability of CO<sub>2</sub> 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.<sup>93,103</sup> Depending on the way of processing, biomass can deliver both, pure CO<sub>2</sub>, *e.g.* in case of fermentation, or a syngas containing CO<sub>2</sub>, CO, H<sub>2</sub> and nitrogen (N<sub>2</sub>), *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<sub>2</sub>.<sup>72,104-106</sup> Thus, this process is advantageous with regard to the supply of existing methanol synthesis plants.<sup>98</sup> When the gasification is performed with pure O<sub>2</sub> instead of air, the N<sub>2</sub> content in the syngas can be reduced, offering an advantageously low inert gas content.<sup>107</sup>

By application of various reforming technologies, a CO and H<sub>2</sub> containing syngas can be produced from biomethane.<sup>103,108-111</sup> Biogenic CO<sub>2</sub> can be captured *via* amine wash from fermentation processes or combustion processes.<sup>112</sup> However, in this case surplus H<sub>2</sub> 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.<sup>72,110,113</sup> Thus, these trace compounds need to be removed from the syngas before entering the synthesis process.

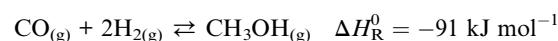
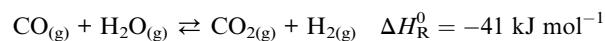
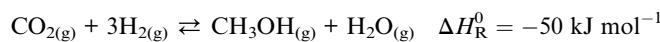
Alternatively to biomass, CO<sub>2</sub> can be obtained from the atmosphere or sea water by direct air capture (DAC) or direct ocean capture (DOC), respectively.<sup>114-118</sup> While these technologies still need to be scaled up to reach reasonable costs, they offer the potential of providing CO<sub>2</sub> at any location.<sup>116</sup>

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,<sup>119,120</sup> steel mills<sup>121-124</sup> or waste incineration plants.<sup>125,126</sup> 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.<sup>102</sup>

If H<sub>2</sub> cannot be obtained by thermochemical methods, current state of the art involves electrochemical H<sub>2</sub> 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).<sup>127,128</sup>

**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<sub>2</sub>O<sub>3</sub> catalysts were enabled for their industrial application.<sup>129</sup> Despite ongoing research for more stable and active catalysts based on different metals such as indium or noble metals,<sup>130-132</sup> this catalyst system remains the industrial standard today.<sup>133,134</sup>

Methanol synthesis on conventional catalysts can be described macroscopically by CO hydrogenation, CO<sub>2</sub> hydrogenation and water-gas-shift reaction (WGS):



In this reaction network, CO hydrogenation can be defined as the combination of CO<sub>2</sub> hydrogenation and WGS. Currently, this combination is considered as the main source of methanol over conventional Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> methanol synthesis catalysts



by various studies,<sup>135–138</sup> while the actual mechanistic nature of methanol synthesis is still debated.<sup>139–141</sup> Due to the equimolar formation of water, equilibrium conversion of CO<sub>2</sub> hydrogenation is lower compared to CO hydrogenation.<sup>142,143</sup> Moreover, water was shown to be responsible for inhibited methanol reaction kinetics<sup>144</sup> and accelerated deactivation of the catalyst.<sup>145–147</sup> As increased CO<sub>2</sub> contents in the synthesis gas enhance water formation along the reactor by both CO<sub>2</sub> hydrogenation and reverse WGS (rWGS), many studies have dealt with enhancement of the catalyst for CO<sub>2</sub>-based methanol synthesis.<sup>148–151</sup> Switching from the Al<sub>2</sub>O<sub>3</sub>-support towards ZrO<sub>2</sub> or Ga<sub>2</sub>O<sub>3</sub> is most widely applied to stabilize the Cu species on the catalytic surface.<sup>152–154</sup>

For the kinetic description of methanol synthesis, plenty different kinetic models have been proposed in scientific literature<sup>155–161</sup> among which the model by Vanden Bussche *et al.*<sup>155</sup> and Graaf *et al.*<sup>156</sup> 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.<sup>162–166</sup>

**2.1.3 Process layout and reactors.** Regarding reactor design for conventional methanol synthesis, multiple approaches are known in literature.<sup>58,167–169</sup> 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.<sup>143</sup> 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.<sup>170</sup>

Depending on plant size, syngas composition and economical aspects, many combinations of different reactor types were studied in both, scientific and patent literature.<sup>171–174</sup> To overcome the thermodynamic limitation of CO<sub>2</sub> hydrogenation, removal of water and/or methanol from the reaction mixture

either by interstage absorption,<sup>175</sup> adsorption<sup>176,177</sup> or condensation<sup>122,178–183</sup> 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.<sup>184–189</sup> However, these technologies have not yet been demonstrated on a larger scale. Another way to tackle the thermodynamic and catalytic challenges of CO<sub>2</sub>-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.<sup>190,191</sup> Similar approaches were considered as an option within patent literature.<sup>192,193</sup> However, when stable catalysts for CO<sub>2</sub>-based methanol synthesis become industrially available, these concepts could become obsolete.

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,<sup>111,194–196</sup> 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<sub>2</sub> buffers and an improved utilization of renewable power.<sup>58,73–76,113</sup>

**2.1.4 Products.** With the effects of WGS and rWGS, *i.e.* CO<sub>2</sub> and CO formation, respectively, excluded, commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts show a carbon selectivity towards methanol >99%.<sup>72,197,198</sup> Industrially, methanol purity is classified by chemical grades<sup>199,200</sup> usually achieved by distillation of raw methanol.<sup>58,113,201</sup> 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.<sup>202</sup>

The main side products documented in literature are dimethyl ether (DME), formic acid, methyl formate, methyl acetate, higher alcohols (predominantly ethanol), ketones and paraffins.<sup>171,201,203,204</sup> 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.<sup>204</sup> In this work, the CO/CO<sub>2</sub> ratio in the reactor feed was identified as the main parameter determining side product formation, with an overall tendency to decrease as CO<sub>2</sub> content increases. From the experimental data obtained, a simplified correlation was derived between the CO/CO<sub>2</sub> 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.<sup>205</sup>

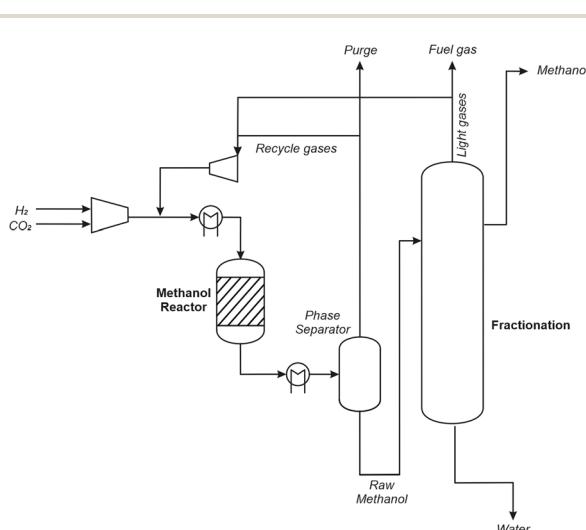


Fig. 3 Simplified process flow diagram of the methanol synthesis.<sup>145</sup>



## 2.2 Methanol-to-olefins conversion

The methanol-to-hydrocarbons (MTH) process was first developed by Mobil Oil Corporation (today ExxonMobil) in the 1970s.<sup>206</sup> 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<sub>2</sub>–C<sub>5</sub> 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.<sup>207</sup>

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),<sup>208</sup> methanol-to-aromatics (MTA),<sup>209</sup> MTP,<sup>210</sup> and MTO processes.<sup>211</sup> 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.<sup>82</sup> Thus, the MTH synthesis can also be applied to produce renewable synthetic fuel when “green” methanol is used as a feedstock.<sup>80</sup> 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.<sup>212</sup> 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.<sup>213–215</sup> 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.<sup>216,217</sup> 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.<sup>218</sup> Additionally, Cordero-Lanzac and co-workers found that the DTO process produces less water and is less exothermic compared to the MTO process.<sup>219</sup> 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.

**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.<sup>220</sup> The topology and acidity of the zeolite catalyst significantly influence the selectivity of MTO synthesis.<sup>221–223</sup> 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.<sup>224</sup> Notably, a high selectivity to C<sub>3+</sub> olefins has been reported in MTO over 1-D framework zeolites, such as H-ZSM-48 and H-ZSM-22.<sup>223,225</sup> High C<sub>3+</sub> 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.<sup>226</sup>

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).<sup>227</sup> BAS density affects the catalytic activity and catalyst lifetime.<sup>228</sup> 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.<sup>229</sup> 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.<sup>230</sup> Hydrogen transfer reactions can be suppressed by reducing the Brønsted acidity of the ZSM-5 zeolite, *e.g.*, by incorporating a Ca promoter.<sup>231</sup> 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.<sup>221,227,231–233</sup> 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.<sup>221</sup> As described by Bailleul *et al.*,<sup>221</sup> 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.<sup>232,233</sup> In conclusion,

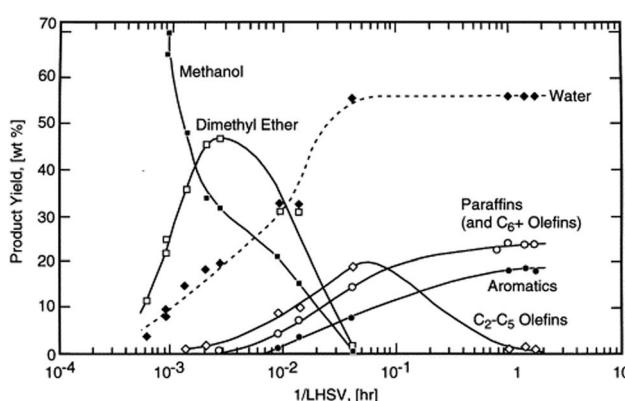


Fig. 4 Formation and consumption of the species involved into MTO synthesis over residence time (reproduced from ref. 181 with permission from Elsevier, copyright 1999).



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.<sup>207,234-241</sup> 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.<sup>242-244</sup> Today, the dual-cycle mechanism (DCM) is the most widely accepted for the mechanistic description of the MTH reaction.<sup>245,246</sup> As schematically shown in Fig. 5, it suggests an autocatalytic olefinic and aromatic cycle to run in parallel.<sup>247</sup> 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.<sup>247,248</sup> 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.<sup>249,250</sup> A small olefin recycle to the MTO unit could therefore be beneficial within the MTI 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.<sup>251,252</sup> 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.<sup>253-256</sup> H-ZSM-5 demonstrates a higher resistance to coking compared to SAPO-34.<sup>245</sup> 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.<sup>257</sup> 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.<sup>257</sup> 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.<sup>253</sup>

Despite being present in low concentrations during MTO synthesis, formaldehyde contributes to the coke-induced deactivation of the zeolite catalyst.<sup>218</sup> 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.<sup>258</sup> 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,<sup>259</sup> olefin co-feeding,<sup>250</sup> products back-mixing,<sup>256</sup> and substituting MeOH feedstock by DME.<sup>218</sup>

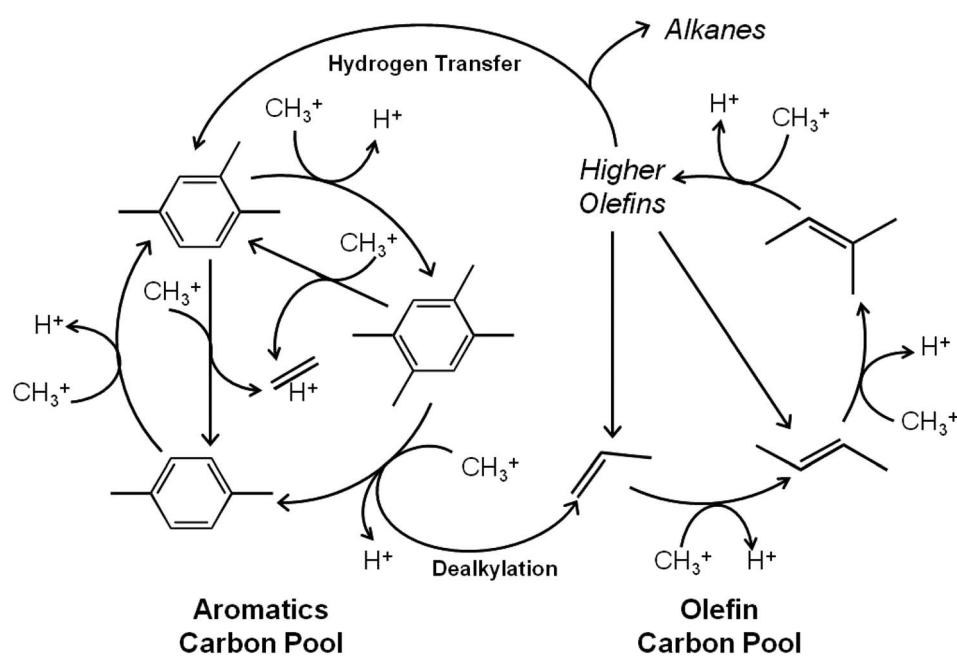


Fig. 5 Dual cycle mechanism of the MTO synthesis (reproduced from ref. 244 with permission from American Chemical Society, copyright 2013).

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.<sup>64,79,218,247–264</sup>

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.<sup>270</sup> 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.<sup>81</sup> 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).<sup>271</sup> 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.<sup>251</sup>

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.<sup>272</sup> 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 <sup>-1</sup> )	Olefins yield	Objective of study	Reference
MeOH	500	Ca-modified ZSM-5	40	8	C <sub>2</sub> olefins = 14% C <sub>3</sub> + C <sub>4</sub> olefins = 82%	Aromatic cycle suppression in MTO reaction	231
MeOH	520	Ca-modified ZSM-5	89.8	4.2	C <sub>3</sub> olefins = 49%	Enhance catalytic stability & propylene selectivity	260
DME	400	ZSM-5	40.2	6	C <sub>2</sub> – C <sub>11</sub> olefins = 26%	Aromatic cycle suppression in DME to hydrocarbons reaction	261
		ZSM-48	73.5	1.5	C <sub>2</sub> – C <sub>11</sub> olefins = 90%		
		ZSM-22	50.4	0.3	C <sub>2</sub> – C <sub>11</sub> olefins = 50%		
MeOH	400–550	ZSM-5	25.4	5.8	C <sub>2</sub> –C <sub>4</sub> olefins	Kinetic modelling (seven lumps)	262
MeOH	300–450	ZSM-5	24	2.7–25	C <sub>2</sub> –C <sub>3</sub> olefins	Role of water on MTO kinetic modelling	263
MeOH	360–480	ZSM-5	200	—	C <sub>2</sub> –C <sub>8</sub> olefins	Single event kinetic modelling	264 and 265
MeOH	480	ZSM-5	200	5.3	C <sub>3</sub> olefins = 81.6%	MTP monolithic catalyst investigation/kinetic modelling	266
MeOH + C <sub>4</sub> H <sub>8</sub>							
MeOH	420–500	B-modified ZSM-5	180	2.0–9.4	C <sub>3</sub> olefins	Methanol and olefins co-feeding investigation/kinetic modelling	267
MeOH + C <sub>4</sub> H <sub>8</sub> C <sub>5</sub> H <sub>10</sub> /C <sub>6</sub> H <sub>12</sub>							
MeOH + C <sub>3</sub> H <sub>6</sub>	400–490	ZSM-5	200	—	C <sub>2</sub> –C <sub>7</sub> olefins	Methanol and olefins co-conversion/kinetic modelling	268
MeOH + C <sub>4</sub> H <sub>8</sub>							
MeOH + C <sub>5</sub> H <sub>10</sub>							
MeOH + C <sub>6</sub> H <sub>12</sub>							
MeOH + C <sub>3</sub> H <sub>6</sub>	400–490	ZSM-5	200	—	—	Paraffins and aromatics side reactions/kinetic modelling	269
MeOH + C <sub>4</sub> H <sub>8</sub>							
MeOH + C <sub>5</sub> H <sub>10</sub>							
MeOH + C <sub>6</sub> H <sub>12</sub>							



**Table 3** Comparison aspects between the industrial process of Lurgi MTP and UOP/INEOS MTO<sup>251</sup>

	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 <sub>4+</sub> , C <sub>2</sub>	DME
Products <sup>a</sup> , wt%		
Propylene	72	42
Ethylene	—	39
C <sub>5+</sub>	23	5

<sup>a</sup> Composition can vary.

540 °C and pressure between 1 bar and 3 bar.<sup>273</sup> 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.<sup>274–277</sup> 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.<sup>275</sup> The reactor temperature is crucial to adjust the propylene-to-ethylene ratio, as elevated temperatures favour higher propylene yields and coke formation.<sup>272</sup> 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.<sup>274</sup> Similar technologies have been developed in China by Dalian and Sinopec using catalysts containing SAPO-34 in a fluidized bed reactor.<sup>272,273,278</sup>

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.<sup>210,279</sup> 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.<sup>280</sup> However, the fixed-bed reactors are less effective in managing the heat generated by the highly exothermic reaction compared to the fluidized-bed reactor.<sup>281,282</sup> The MTP process produces propylene, and gasoline as a by-product, with a methanol + DME conversion of more than 99%.<sup>210</sup> 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.<sup>279</sup> Each reactor is equipped with five or six catalyst beds with feed injection between beds to control reaction temperature.<sup>279,283</sup> The process runs slightly above atmospheric pressure (1.3 to 1.6 bar), with steam added to the feed (0.5–1.0 kg<sub>steam</sub> kg<sub>methanol</sub><sup>-1</sup>), and at reactor inlet temperature between 400 °C and 470 °C.<sup>65,273</sup> Olefins such as C<sub>2</sub> and C<sub>4</sub>–C<sub>6</sub> are recycled to the reactor to maximize the propylene yield.<sup>284</sup> 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.<sup>285–287</sup>

In the context of the MTJ process, MTO aims to produce a mixture of C<sub>2+</sub> olefins,<sup>17,71,91</sup> 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,<sup>83,288–290</sup> 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,<sup>289</sup> and by zeolites with 3-D 10-ring pore structures, such as the MFI family.<sup>288</sup> The MTO subprocess outlined

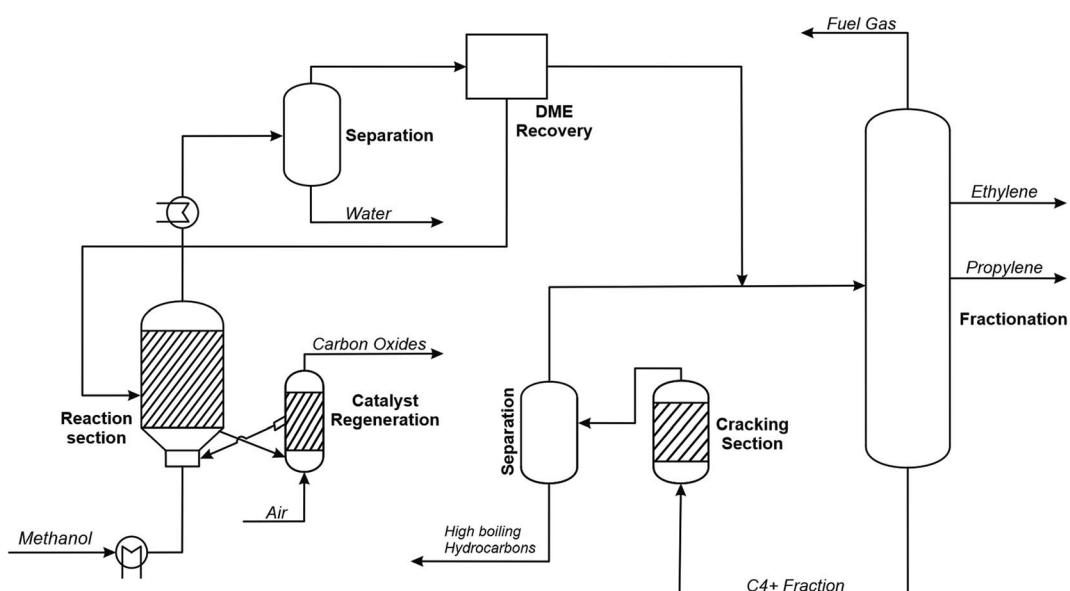


Fig. 6 Simplified process flow diagram of the UOP/INEOS MTO process.<sup>243,258</sup>



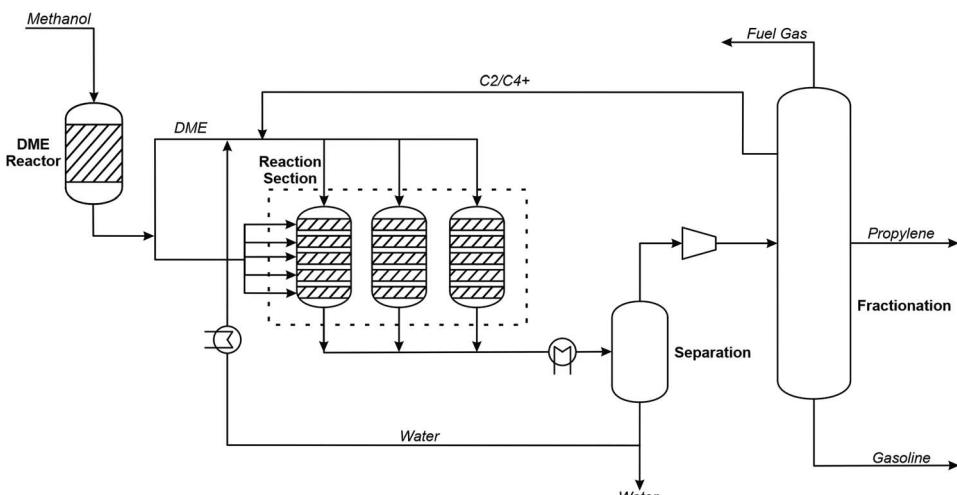


Fig. 7 Simplified process flow diagram of the Lurgi MTP Process.<sup>184,243</sup>

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.<sup>288</sup>

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.<sup>83,288–290</sup> 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%.<sup>83,288–290</sup> Furthermore, the relatively mild reaction temperature may suppress monomolecular cracking of higher olefins.<sup>291</sup> 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<sup>-1</sup>.<sup>83,288–290</sup> 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.<sup>83,288–290</sup>

**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.<sup>249,250</sup>

### 2.3 Oligomerization

The oligomerization process involves increasing the olefin chain length by coupling of light olefin monomers.<sup>292</sup> 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.<sup>293–295</sup> 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 ( $C_{10}$ – $C_{20}$ ).<sup>296,297</sup> 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.<sup>294</sup> 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.<sup>293,298–301</sup> 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.<sup>19,297,302–309</sup> 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).<sup>297</sup> 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 <sup>-1</sup> )	Target olefins products	Reference
C <sub>2</sub> H <sub>4</sub>	120	50	Ni/SiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub>	0.6	8	C <sub>6</sub> –C <sub>12</sub>	302
C <sub>3</sub> H <sub>6</sub>	270	40	Ni/H-ZSM-5	25	4.03	C <sub>6</sub> –C <sub>18+</sub>	303
C <sub>3</sub> H <sub>6</sub>	200–274	1	H-ZSM-5	12–140	—	C <sub>6</sub> –C <sub>12+</sub>	304
C <sub>3</sub> H <sub>6</sub>	210–250	2.2	H-ZSM-5	13	—	C <sub>4</sub> –C <sub>9+</sub>	305
C <sub>4</sub> H <sub>8</sub>	175–325	1.5	H-ZSM-5	30–180	5.6–112	C <sub>8</sub> –C <sub>12</sub>	306
C <sub>2</sub> H <sub>4</sub>	200–450	1	H-ZSM-5	30	—	C <sub>2</sub> –C <sub>8</sub>	307
C <sub>3</sub> H <sub>6</sub>			H-Na-ZSM-5				
C <sub>4</sub> H <sub>8</sub>							
C <sub>2</sub> H <sub>4</sub>	120	16–32	Ni/SiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub>	—	4	C <sub>6</sub> –C <sub>13+</sub>	308
C <sub>3</sub> H <sub>6</sub>							
C <sub>4</sub> H <sub>8</sub>							
C <sub>3</sub> H <sub>6</sub>	200–250	40	Pristine ZSM-5	18	1–8	C <sub>3</sub> –C <sub>12+</sub>	309
C <sub>6</sub> H <sub>12</sub>			Meso-ZSM-5	12.8			
C <sub>3</sub> H <sub>6</sub> /C <sub>3</sub> H <sub>8</sub>	100–200	20–40	Meso-SiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub>	—	1–20	—	297
C <sub>3</sub> H <sub>6</sub> /C <sub>4</sub> H <sub>8</sub>	140–260	13.8	H-ZSM-5	23	1.1	C <sub>6</sub> –C <sub>12+</sub>	19
			H-Y	5.2			
			H-beta	20			
			Amberlyst-36	—			
			Purolite-CT275	—			
				—			

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

(1) Ethylene oligomerization over transition metal catalysts.<sup>293,311</sup>

(2) Oligomerization of higher olefins such as propylene and butylene over acidic catalysts.<sup>294,312,313</sup>

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.<sup>294</sup> Ethylene oligomerization is not favourable over solid acid catalysts due to an unstable primary carbenium intermediate.<sup>69</sup> 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.<sup>295,314–318</sup> 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.<sup>295</sup> 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.<sup>293,317</sup> As discussed by Olivier-Bourbigou *et al.*,<sup>293</sup> 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.<sup>319–321</sup> Reviews by Finiels *et al.* and Olivier-Bourbigou *et al.* provide detailed discussions on the

dimerization and oligomerization mechanisms over nickel-based catalysts.<sup>293,317</sup> 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.<sup>302,311,316,322</sup> For example, Betz *et al.* demonstrated that ethylene oligomerization over Ni/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalysts predominantly produces C<sub>6</sub>, C<sub>8</sub>, C<sub>10</sub> and C<sub>12</sub> fractions under conditions of 120 °C and 50 bar ethylene partial pressure, and a space velocity of 8 h<sup>-1</sup>.<sup>302</sup>

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<sub>3+</sub> olefins to jet fuel range olefins in a second reactor.<sup>319,323,324</sup>

(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.<sup>325</sup>

Oligomerization of C<sub>3</sub>–C<sub>6</sub> olefins has been investigated in literature over various heterogenous solid acid catalysts, including zeolites (*e.g.*, H-ZSM-5, H-beta),<sup>299,326</sup> amorphous silica–alumina (ASA, SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>),<sup>327</sup> sulfonic acid polymeric resins (*e.g.*, Amberlyst),<sup>302,328</sup> and SPA.<sup>294,329</sup> Among these, zeolites and sulfonic resins have been extensively studied for converting olefins to fuel-range hydrocarbons.<sup>19</sup> Zeolites are favoured for operations at increased temperatures of about 250 °C, facilitating multiple reaction types including oligomerization, disproportionation, cracking, and isomerization.<sup>19</sup> 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.<sup>292,328</sup> 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.<sup>19</sup> Saavedra Lopez *et al.* investigated the oligomerization of propylene/isobutylene over H-Beta zeolite at a temperature range of 140–260 °C.<sup>19</sup> 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.<sup>305,330</sup> 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.<sup>331,332</sup> Oligomerization extends the carbenium ion chain. In contrast,  $\beta$ -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.<sup>333</sup>

The shape selectivity and acid properties of the H-ZSM-5 zeolite catalyst enable a high activity for transforming C<sub>3</sub>–C<sub>6</sub> olefins into gasoline, jet fuel and diesel fractions, while exhibiting a low deactivation rate.<sup>334</sup> 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.<sup>309</sup> 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.<sup>309,335</sup> Thus, mesoporosity not only facilitates the diffusion of reactants and products, but also promotes the formation of longer chain hydrocarbons and extends catalyst lifetime.<sup>309,336,337</sup> 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.<sup>338</sup>

Modification of the oligomerization catalyst, by alteration in composition, structure, and acidity, can impact the catalyst performance.<sup>339–341</sup> 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.<sup>303</sup> 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.<sup>325</sup>

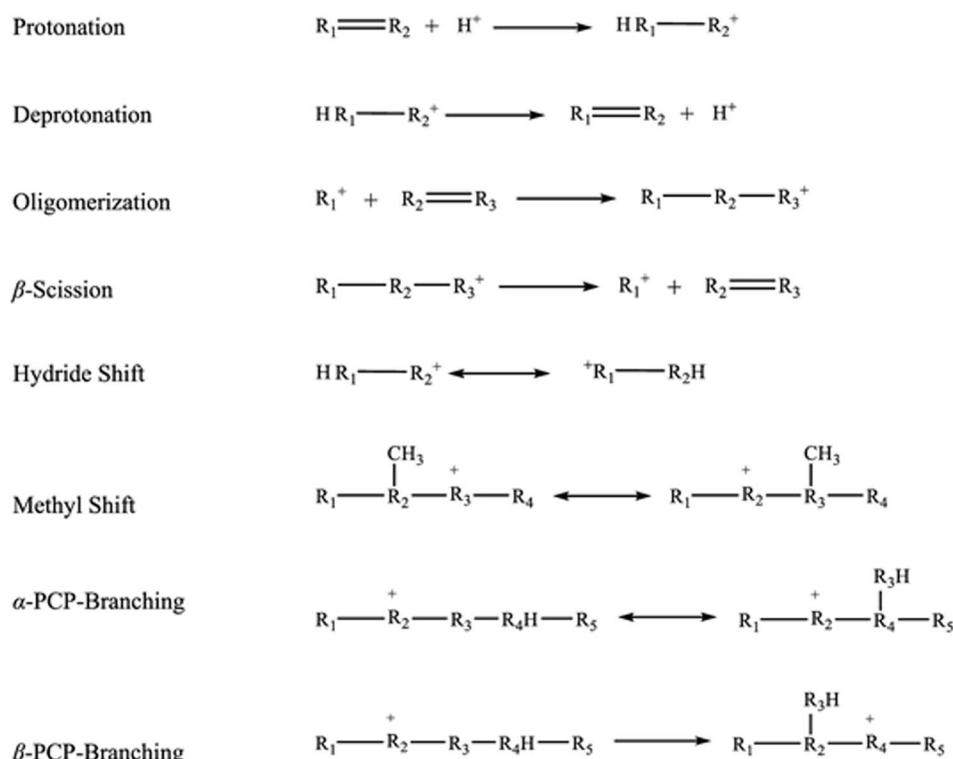


Fig. 8 Proposed reactions for propylene oligomerization on acid zeolites (reproduced from ref. 330 with permission from John Wiley and Sons, copyright 2019).



Research by Mlinar *et al.* indicated that a lower Si/Al ratio in catalysts enhances selectivity towards dimer formation rather than cracking products.<sup>304</sup> 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.<sup>304,342</sup>

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.<sup>343</sup> 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.<sup>344</sup> 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  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$ , Díaz *et al.* demonstrated that increasing the space time (0.5–10 g<sub>catalyst</sub> h mol<sub>c</sub><sup>-1</sup>) results in higher butylene conversion, associated with higher selectivity for C<sub>5</sub>–C<sub>7</sub> and lower selectivity for C<sub>8</sub>–C<sub>12</sub>.<sup>306</sup> This can be attributed to the cracking of C<sub>8</sub>–C<sub>12</sub> 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<sub>8</sub>–C<sub>16</sub>) 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.<sup>307,345–348</sup> Integrated with ExxonMobil's MTO process, the MOGD process can convert light olefins in the C<sub>3</sub>–C<sub>6</sub> 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.<sup>80,270,349</sup> 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.<sup>270,350</sup> The integration of the MTO and MOGD processes therefore also demonstrates the potential of producing jet fuel out of methanol.<sup>69,349</sup>

The conversion of olefins to distillate (COD) process, developed by PetroSA in South Africa, converts C<sub>3</sub>–C<sub>6</sub> olefins produced in FT synthesis into higher olefins, with the purpose of producing fuels such as gasoline and diesel.<sup>327,351</sup> The COD process was investigated over ASA, SPA and H-ZSM-5 catalysts.<sup>327,352,353</sup> Among those, H-ZSM-5 is notable for producing a higher cetane number post hydrogenation reaction.<sup>69</sup> 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<sup>-1</sup>.<sup>353</sup> 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%.<sup>354</sup> 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<sub>3</sub>–C<sub>6</sub> 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<sub>8</sub>–C<sub>16</sub> while minimizing the formation of

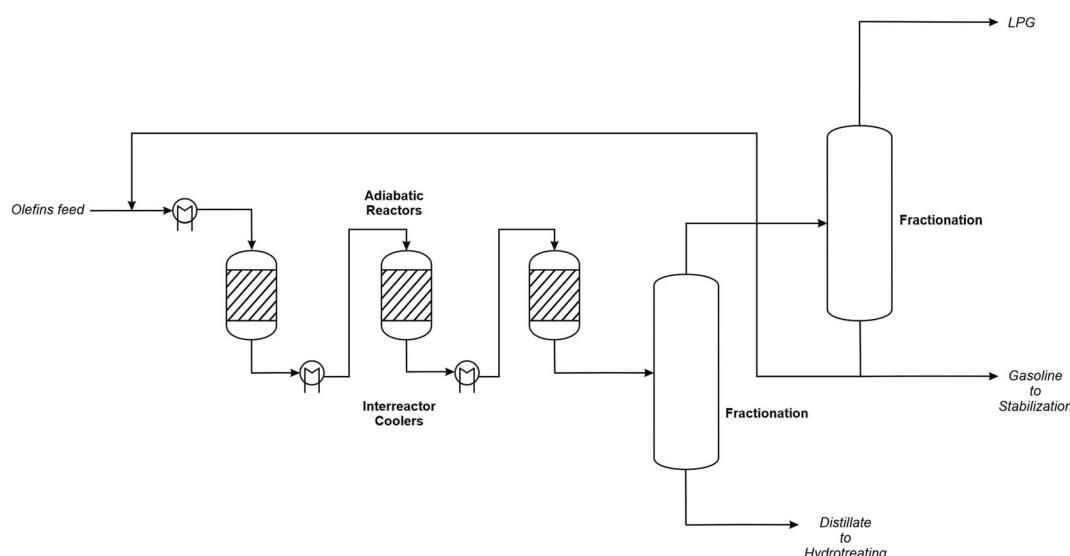


Fig. 9 Simplified process flow diagram of the MOGD process.<sup>278</sup>



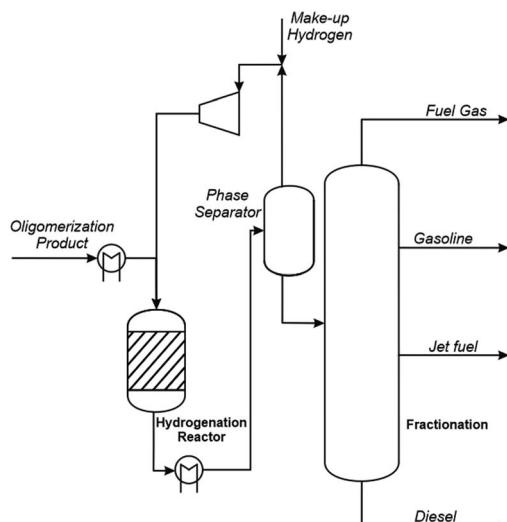
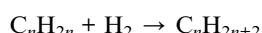


Fig. 10 Simplified process flow diagram of the hydrogenation of the oligomerization products.<sup>341</sup>

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.<sup>71</sup> 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.<sup>355–357</sup> The hydrogenation process involves the addition of H<sub>2</sub> to unsaturated olefins:



The reaction is catalysed by reduced metals, such as Ni, Pd or Pt supported on alumina or activated carbon.<sup>358–360</sup> 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.<sup>69,70,357,361</sup> Specific hydrogenation conditions depend on the active metal, feedstock and targeted product. The H<sub>2</sub> gas is fed in stoichiometric excess to achieve an approximately complete conversion of olefins to paraffins. Excess H<sub>2</sub> is recovered downstream the reactor by a gas/liquid separator and recycled to the reactor inlet (see Fig. 10).<sup>24,358</sup> Downstream the separator, hydrocarbons are fractionated to segregate light hydrocarbons (<C<sub>8</sub>), jet fuel range hydrocarbons (approximately C<sub>8</sub>–C<sub>16</sub>), and heavier hydrocarbons. An isomerization unit is not required, as acid-catalysed olefin oligomerization within the MTJ process produces branched olefins.<sup>71</sup> 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.<sup>20</sup>

## 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.<sup>362–364</sup> 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.<sup>365,366</sup> Therefore, directly using crude methanol as feedstock for the MTO process can save energy and costs associated with distillation.<sup>71</sup> 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.<sup>367</sup> 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<sub>2</sub> and C<sub>3</sub>–C<sub>6</sub> 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.<sup>218,219</sup> 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.<sup>368–370</sup> 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



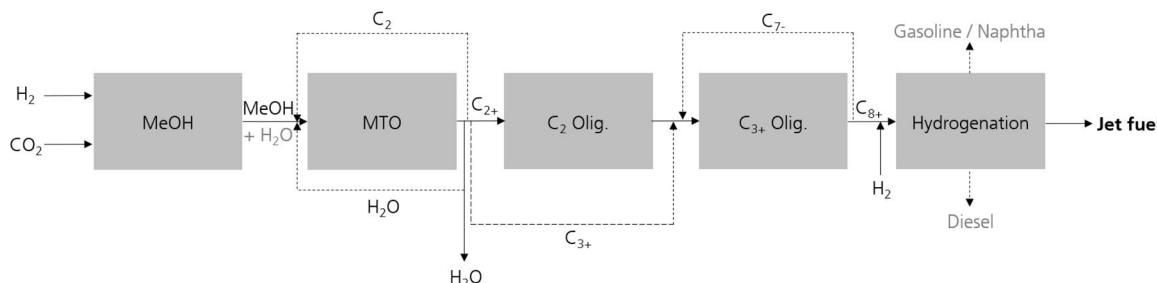


Fig. 11 A simplified block diagram illustrating various recycle options and process configuration discussed in Section 3 regarding the potential for process integration and intensification starting from  $\text{CO}_2$  and  $\text{H}_2$ .

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,<sup>251</sup> 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.<sup>294</sup> Literature discusses three main approaches for the further conversion of ethylene within the MTJ process:

- (1) Recycling ethylene back into the MTO reactor<sup>213</sup>
- (2) Direct ethylene oligomerization<sup>325</sup>
- (3) Two-step oligomerization<sup>319,323,324</sup>

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.<sup>319,324,325</sup> 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.<sup>325</sup> This method involves oligomerizing the ethylene fraction in a separate reactor with transition metal catalysts to produce higher olefins (primarily in the  $\text{C}_4$  and  $\text{C}_6$  range).<sup>319</sup> 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  $\text{C}_{3+}$ .<sup>242,249,250</sup> 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.<sup>19,308</sup> This enables multiple options for recycling light olefins ( $\text{C}_2$ – $\text{C}_7$ ) 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.<sup>83</sup> 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  $\text{C}_8$ – $\text{C}_{16}$  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.<sup>357</sup> 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  $\text{CO}_2$  to olefins.<sup>371</sup> The direct conversion of  $\text{CO}_2$  and  $\text{H}_2$  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.<sup>372,373</sup> This method can be implemented *via* two primary pathways:

- (1) The combination of the RWGS reaction with FT synthesis ( $\text{CO}_2$ -FT route)
- (2) The integration of the methanol synthesis with the MTO synthesis (MeOH-mediated route)

While the limitations and potentials of the  $\text{CO}_2$ -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.<sup>374</sup> This route is capable of producing light olefins with a high selectivity due to the metal/zeolite composite catalysts used.<sup>375</sup> 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.<sup>372,376</sup> Moreover, the direct CO<sub>2</sub> to olefins conversion suffers from lower conversion compared to the established two-step methanol synthesis and MTO processes.<sup>211,377</sup> Given the currently low TRL for the direct CO<sub>2</sub> 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<sub>2</sub> and H<sub>2</sub> 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<sub>2</sub> and H<sub>2</sub> 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 MTO 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.<sup>73–76,378</sup> Furthermore, scenario-specific techno-economic 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<sub>2</sub> and CO<sub>x</sub> 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<sub>3</sub>–C<sub>6</sub> 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<sub>2</sub>–C<sub>6</sub>) into longer-chain olefins (C<sub>8</sub>–C<sub>16</sub>). Available scientific literature mainly targets ethylene oligomerization over transition metal catalysts and C<sub>3</sub>–C<sub>6</sub> 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<sub>2</sub> and C<sub>3</sub>–C<sub>6</sub> olefins needs special consideration regarding catalyst and process design. The oligomerization of C<sub>3</sub>–C<sub>6</sub> 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<sub>2</sub>–C<sub>7</sub> 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
NO <sub>x</sub>	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 Elwally: 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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