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Review

Review and perspective: Next generation DME synthesis technologies for the energy transition

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ABSTRACT

Renewable dimethyl ether (DME) is expected to contribute to the decarbonization of several sectors, including domestic heat supply and transport. The shift of the carbon source used for the production of DME from fossil to renewable, such as biomass, waste or captured CO_2, entails an industrial challenge in terms of reactors, operation regimes, catalysts and product purification, with strong technical and economic repercussions. In this work, we review the latest developments on this topic, focusing on the direct synthesis of DME, and especial attention has been paid to the separation-enhanced technologies for DME production, including the Sorption Enhanced DME Synthesis (SEDMES). We address other aspects that are often neglected, such as the impact of heat and mass transfer phenomena, which become increasingly relevant in processes in which several reaction and sorption stages occur in the same reactor. We also include a techno-economic section that gives insight in the feasibility of several renewable DME production processes. Finally, we review the most recently deployed installations for renewable DME production, at commercial or pilot scale, as a model of the near-future of the DME industry.

1. Introduction

Today's society is facing unprecedented energy and climate challenges. On the one hand, greenhouse gas emissions have increased again after the pandemic years. If urgent measures are not taken, the temperature increase is projected to reach 2.8 °C by the end of the century [1]. On the other hand, geopolitical tensions have caused a tremendous increase of energy prices, especially in Europe, which is strongly dependent on third countries. In order to deal with these issues, governments across the world have taken decisive actions to reduce their dependence on fossil fuels and to accelerate the path for the decarbonization of key sectors, including energy, production of chemicals etc. [2]. Along with electrification with renewables, advanced 2nd generation liquid biofuels will play a key role in the decarbonization of the energy system, especially in the transport sector [3]. The International Energy Agency (IEA) anticipates that liquid biofuel world consumption, which reached 4.3 EJ in 2021, will need to quadruple in the next decade to meet the 1.5 °C increase limit goal [4].

Renewable dimethyl ether (DME), either obtained from biomass-derived syngas or from non-biogenic CO_2 is among the biofuels or electro-fuels (e-fuels) considered by the IRENA to replace conventional fossil-based fuels [3]. DME, CH_3OCH_3, is the simplest ether and it contains no C-C bonds. At atmospheric conditions DME is a gas, but due to its vapour pressure of 5.1 bar at 20 °C, it can be easily liquefied [5,6]. Therefore, it can be easily stored and transported in pressurized tanks in liquid form. The first documented uses of DME are related to medicine/biology and engineering. Its presence in the chemical industry has been constant for decades, as it is a key intermediate to produce dimethyl sulphate [7,8]. This was in fact DME's main industrial application until 1980 s [6], when it started to replace chlorofluorocarbons as an aerosol propellant [9]. Other chemicals that can be derived from DME are methyl acetate [10], acetic acid [11] and olefins [12].

DME's role as an energy carrier has attracted a great deal of attention in the last years. Currently, the main global market of DME is as a blend with LPG for domestic energy applications [13,14]. Due to their similar properties, they are used as a blend with the existing infrastructure used for LPG, with compositions of up to 20 % in volume of DME [13–15]. This application has taken especial relevance in China [16], but also in

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other countries such as Indonesia [17], and expectedly will be adopted by other countries such as New Zealand [18]. DME can also be used as a diesel replacement, given its cetane number of 55–60, which overcomes that of fossil diesel, without producing NOx, CO or particulate matter during its combustion [19]. This enables its use in land transportation, as already proved by Volvo as partner of BioDME project [20] or Mack Trucks in collaboration with Oberon and New York City Department of Sanitation [21]. Other applications of DME in the energy system are its use in gas turbines to produce power [22] or as a hydrogen carrier [23] more conveniently stored and transported than hydrogen, and capable of showing the highest efficiencies along with methanol during steam reforming to H_2 [19,24]. Furthermore, DME will play an important role as a chemical intermediate or as feedstock for the production of materials in a future methanol-DME economy [25,26].

Initially, DME was obtained as the by-product of the high-pressure (300 bar) methanol synthesis process. With the emergence of low-pressure methanol synthesis from the 1960 s came the need for the development of dedicated processes for DME production [6,27]. Today, dedicated plants exist that dehydrate methanol to DME, at a current world market size of around 4 MTpa [14]. The demand for DME has continuously grown in the last years, with only a decline in 2020 due to economic downturn caused by the COVID-19 pandemic. In the coming years the DME market is expected to grow until reaching a production of 9.5 MTpa by 2027 [14].

The evolution of DME as fuel has been covered in several reviews since the year 1996. However, certain gaps have not been covered by the literature. For instance, until 2010, the reviews about DME neglected the role of biomass as the source for syngas production. Kaoru Takeishi introduced DME as an alternative fuel to mitigate environmental problems [28]. Despite many reviews addressed the chemistry of DME, it was not until 2017 that 3 reviews considered again the role of DME as a green fuel to reduce the carbon footprint [29–31]. Since then, a number of reviews have summarised the recent studies about the use of CO_2 as carbon source to produce DME directly [24,32–37], but the consequences of the new reacting gas compositions (CO_2-H_2 mixtures or syngas with high content in CO_2) in thermodynamics, kinetics and purification of the final products have not been adequately addressed in these reviews.

In this review, we address the current developments in DME production processes, including the direct production of DME and separation-enhanced processes, with special attention to the production of DME from CO_2 rich (or pure) syngas. We discuss the advantages of these new processes and the challenges they have to face, paying especial attention to the severe issues imposed by the high production of H_2O during the process. The deep insight in water separation enhancement that we offer in this review is a differential aspect that has not been included in the related publications before. We make a comprehensive review on the thermodynamics and kinetics of the different reactions involved in the production of DME, and present the most recent catalyst formulations for the novel processes of DME production. Finally, we include an insight on the techno-economic analyses performed so far, assessing the viability of several processes of DME production.

2. DME production: Indirect vs. Direct process

The current production process of DME, *i. e.*, the indirect process, is a well-established technology, both commercially and scientifically. It involves two individual steps in series: the production of methanol from syngas, a mixture of CO, H_2 and variable amounts of CO_2, over Cu/Zn-based catalysts and its subsequent dehydration to DME in the presence of acid catalysts. Before the dehydration step, methanol should be purified in order to remove unreacted gas and water. Downstream the dehydration reaction operation, the raw DME stream, which also contains methanol and water, undergoes separation and purification operations until the desired purity of DME is reached. For instance, for fuel applications, a DME purity of 98.5 % in weight is required [38].

The direct synthesis of DME entails the conversion of CO and/or CO_2 with hydrogen into DME in a single reactor. The interest in this novel process is driven by potential benefits in terms of an increase in equilibrium conversion led by continuous removal of one intermediate product (methanol) form the reacting medium, hence shifting the equilibrium towards the production of DME, allowing for simpler operation [31,39], higher reaction rates, and reduced recycle ratios. Although this process has not reached commercial status, it has attracted the interest of the major players in the DME production and notable technical developments have been reached, as summarised in Table 1.

2.1. Thermodynamics

Thermodynamically, the direct DME synthesis offers the advantage of higher syngas conversion per pass reaction. This is because the *in situ* methanol dehydration reaction to DME increases the overall COx conversion [39]. This effect becomes even more relevant if DME is produced from CO_2-rich feedstock, when the methanol production becomes more limited by the equilibrium [48–50]. Fig. 1 shows a comparison between the syngas conversion in the equilibrium in terms of total carbon conversion for the methanol synthesis and the direct DME synthesis for different syngas compositions (different CO/CO_2 ratios), all of them satisfying an M module (H_2-CO_2)/(CO + CO_2) of 2. Fig. 1 also displays the water partial pressure in the equilibrium corresponding to each point. All the calculations were carried out using the software Aspen Plus under pressure and temperature conditions relevant for these processes, *i. e.*, 250 °C and 50 bar.

Fig. 1 clearly shows that syngas (or CO_2) conversions in the equilibrium for the direct synthesis of DME are ca. 13 percent points higher in average in the whole compositions range than the ones that can be obtained for the synthesis of methanol. It also shows how the concentration of water is higher during the direct synthesis of DME. This issue, which becomes exacerbated when the inlet composition moves towards higher contents in CO_2, is a major concern for the implementation of this technology. Moreover, as the content in CO_2 in the inlet increases, the total C conversion in the equilibrium also decreases, which results in an extra challenge for the shift towards renewable sources for both DME and methanol synthesis.

2.2. Kinetics for the methanol and DME synthesis

DME synthesis from syngas involves in series methanol synthesis and dehydration processes that can be operated either in separated (indirect process) or in the same rector (direct process). This section first individually addresses the two processes involved in the indirect synthesis, and then reports on the kinetics of the direct synthesis of DME, which is the main focus of this article.

Table 1
Direct DME synthesis technical developments.

Technology provider	DME synthesis technology	Reactor	Pilot	Reference
Topsoe	TIGAS	1 t/d gasoline	1984–1987 Houston, Texas	[40,41]
Air Products & Chemicals	LPDME slurry process	10 t/d, slurry	1999, La Porte, Texas	[42]
JFE	Slurry process	100 t/d, slurry	2002–2006, Shiranuka-cho, Japan	[43,44]
KOGAS	Cooled fixed bed	10 t/d	2008, Incheon, Korea	[45]
KIT	Bioliq	600 t/a gasoline via DME	2014, Karsruhe, Germany	[46,47]

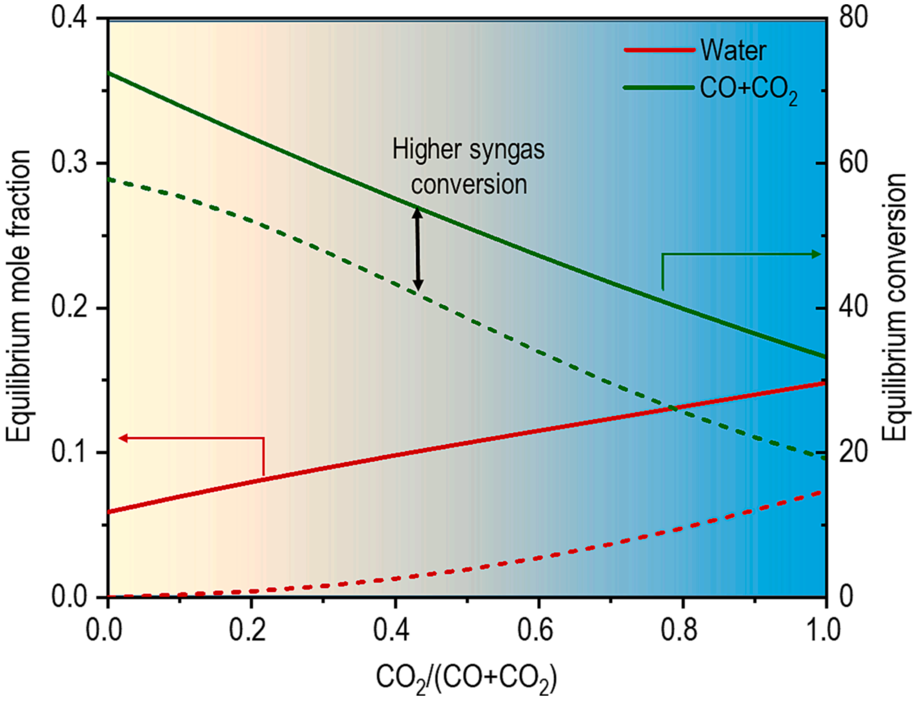

Fig. 1. Equilibrium CO + CO_2 conversion and water mole fraction for the methanol synthesis (dotted line) and direct DME synthesis (solid line) at different CO/CO_2 ratios. Conditions: 50 bar, 250 °C. Yellowish area: low H_2O production; blueish area: high H_2O production.

2.2.1. Methanol synthesis & WGS/rWGS kinetics

The mechanism and kinetics of the methanol synthesis on the low-pressure catalyst have been extensively investigated in the literature [51]. Within the scope of this review only lumped kinetics on commercial Cu/ZnO/Al_2O_3 (CZA) catalyst will be briefly illustrated with particular emphasis on the impact of CO_2 concentration in the feed syngas.

The reactions considered in the process are the CO and/or CO_2 hydrogenation to methanol (equations (1) and (2)) and, depending on process conditions, the direct or reverse-Water Gas Shift (WGS or rWGS) reactions (equations (3) and (4)). As shown in equations (1) and (2), the heat released by the process is determined by the carbon source for methanol production, being the path from CO_2 significantly less exothermic.

$$CO + 2H_2 \rightarrow CH_3OH, \Delta H^0 = -90.5\,\text{kJ/mol} \tag{1}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O, \Delta H^0 = -49.4\,\text{kJ/mol} \tag{2}$$

$$CO + H_2O \rightarrow CO_2 + H_2, \Delta H^0 = -41.4\,\text{kJ/mol} \tag{3}$$

$$CO_2 + H_2 \rightarrow CO + H_2O, \Delta H^0 = 41.1\,\text{kJ/mol} \tag{4}$$

Since the early 80′s, the effect of CO/CO_2 ratio has been investigated both to understand the methanol formation mechanism on Cu based catalyst and to identify the optimal operation conditions of the process. In one of the earliest papers on the topic, Klier *et al.* [52] found that the optimal H_2/CO/CO_2 ratio was 70/28/2. This observation is aligned with the industrial practice, which usually operates with a small amount (2–5.5 vol%) of CO_2 at the reactor inlet [51,53]. Klier *et al.* considered that the hydrogenation of CO was the main mechanism leading to methanol production, proposing that the direct CO_2 hydrogenation has minor role in the methanol formation through rWGS (Eq (4). At high concentrations of CO_2, its strong adsorption reduces the methanol formation rate; on the other hand, with low or null concentration of CO_2, the catalyst is deactivated by overreduction. The CO hydrogenation was considered as the main route for the methanol production in most of early works that studied the effects of the CO_x concentration [54,55].

In the late 80′s and subsequent years, the CO_2 hydrogenation also started to be considered. In particular, Graaf *et al.* [56] proposed a Langmuir-Hinshelwood-Hougen-Watson (LHHW) model in which methanol is formed by parallel hydrogenation of CO and CO_2 also including WGS. The CO hydrogenation path is still prevalent, being the rate of methanol formation from CO faster in the investigated range of operating conditions. The Graaf kinetics still performs well in describing the performances of industrial reactors. However, the original rate constants have to be increased in order to match the experimental data of the more modern catalyst formulations [57].

In the mid 90′s, the effect of CO_2 in the syngas feed became central in methanol kinetic studies: Skrzypek *et al.* [58,59] developed a kinetic model to specifically study the CO_2 hydrogenation to methanol. In the same years, Vanden Bussche and Froment [60], on the basis of literature and their own experimental data, proposed a model including rate equations for methanol synthesis from CO_2 and for reversible WGS/rWGS reaction. They showed that the model can reproduce the experimental data of Klier *et al.* at different CO_2 contents [60]. The hindering effect of adsorbed water, produced by reaction in Eq. (2) in presence of a syngas feed rich in CO_2, is particularly relevant to describing such a trend [61].

More recently, Seidel *et al.* [62] proposed a kinetics including CO, CO_2 hydrogenation and rWGS focusing on syngas obtained from renewable sources with widely variable CO/CO_2 ratios. The model was derived considering different active sites for CO and CO_2 activation. In a recent overall assessment, Nestler *et al.* [51] refitted the parameters in rate expressions of CO_2 hydrogenation and WGS of the Graaf kinetic model considering experimental data covering a wide range of M modules, CO_2/COx ratios (COR), pressures and temperatures. The refitted model was then compared with the most established literature models [56,60,63], showing superior performances in accounting for the effect of CO_2 concentration in the feed syngas with respect to both the original Graaf model, which is poorly sensitive, and Vanden Bussche and Froment kinetics, that overestimate the H_2O hindering effect on the catalytic activity (Fig. 2). Table S1 summarizes the proposed model equations for methanol synthesis kinetics over CZA catalyst at different reaction conditions.

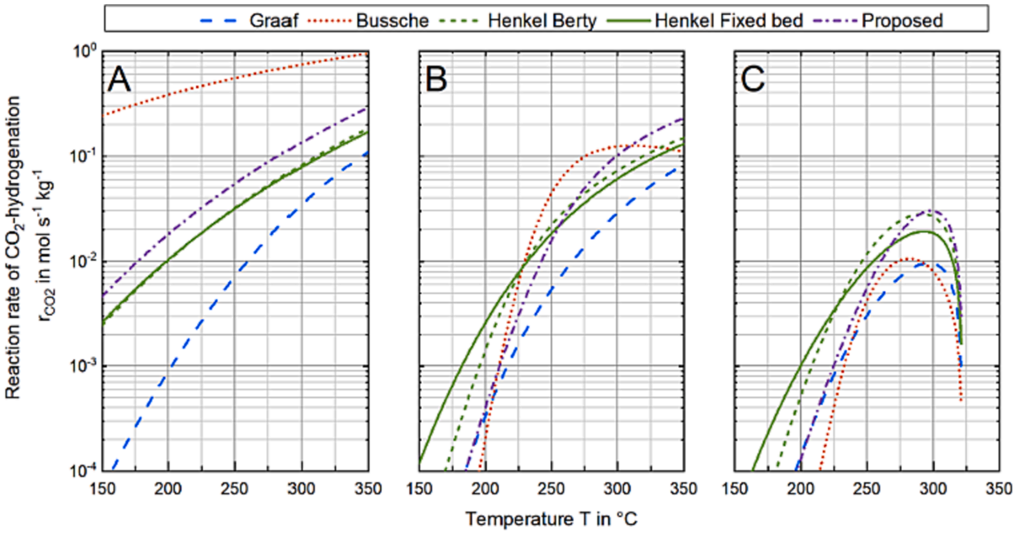

Fig. 2. Reaction rates of the kinetic models considered within this study at M = 2.0, COR = 1.0, P = 50 bar without product (A), with approx. 0.5 mol-% methanol and 1.7 mol-% water (B), and 1.6 mol-% methanol and 4.5 mol-% water (C). (Reproduced with permission from reference [51]).

2.2.2. *Methanol dehydration kinetics*

The kinetics of methanol dehydration to DME, represented in equation (5), has been investigated over different types of acid catalysts (Table S2).

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O,\ \Delta H^0 = -23.5\,\mathrm{kJ/mol} \qquad (5)$$

In the earliest works kinetics for ion exchange resins, operating at atmospheric pressure and low temperature (120–140 °C), have been developed using either Langmuir-Hinshelwood models, in which surface reaction between two adsorbed CH_3OH molecules is the rate determining step [64–66], or the Eley-Rideal mechanism [67,68]. All the models include an inhibiting effect of water due to its preferential adsorption on active sites. Noteworthy, since some of these works [67,68] were performed under catalytic distillation conditions with very low concentration of water in the vapor phase, the resulting kinetics could be described with a power law. In particular An *et al.* [67] reported a simple first order kinetic in methanol concentration.

Berčič and Levec [69,70] adapted a Langmuir-Hinshelwood model of methanol dehydration to a γ-Al_2O_3 catalyst in a study performed at low pressure (1.46 bar) and in the temperature range of 290–360 °C. In line with more recent studies [71,72] covering a wider range of pressure (1–16 bar), the kinetics exhibit an almost zero order for methanol and a strong negative order for water concentration.

Ha *et al.* [73], using the experimenal results obtained by co-feeding methanol and water in the temperature range of 220–345 °C, derived rate equations for two different modified ZSM-5 zeolites. The study showed that also in the case of zeolites the deydration reaction occurs between two methanol molecules non-dissociatively adsorbed, resulting in a zeroth reaction order for methanol and negative for water. This was further confirmed by Ortega *et al.* [74], who concluded that the same rate equation proposed by Klusáček and Schneider [65] for ion exchange resins is also suitable to describe the dehydration process on zeolites in a test the range of 140–190 °C at 1 bar pressure and different methanol partial pressures (0.3–1 bar). They also observed that in this low temperature range no side-products other than the desired DME are formed as long as the temperature remains below 200 °C. The mechanistic investigation of Jones and Iglesia [75] on methanol dehydration on zeolites confirms the zeroth order on methanol and water inhibition for the dehydration reaction on zeolites.

2.2.3. *Direct DME synthesis kinetics*

The DME direct synthesis is a combination of the two processes occurring in the indirect synthesis route. Therefore, the reaction network considered in the relevant kinetic models is a combination of the previously reported stoichiometries (1–5). The catalysts used in the development of the kinetics are usually a mixture of commercial CZA catalyst and an acid catalyst used for dehydration. As reported in the reviews of Ateka *et al.* [50] and Otalvaro *et al.* [76], most of the kinetics in literature (Table 2) for the direct DME synthesis are obtained starting from the models independently developed for methanol synthesis and dehydration processes. However, the kinetic parameters are usually refitted using experimental data obtained in the specific conditions of DME direct synthesis.

The first work on the topic was the one of Ng *et al.* [77] that combined and refitted the kinetics of Vanden Bussche and Froment [60] for methanol synthesis with that Berčič and Levec [69,70] for methanol dehydration. The study was related to a mixture of CZA and γ-alumina catalysts and analysed the effects of changing the inlet gas composition and the ratio of the two catalyst formulations at 250 °C and 50 bar. The analysis covered a wide range of feed composition, considering CO_2/CO_x ratios ranging from 0 to 100 %, which highlighted the impact of the inhibiting effect of water that becomes more significant at higher inlet CO_2 concentration. Identification of the best methanol/dehydration catalyst ratio is also addressed in this work, by varying the CZA: γ-Al_2O_3 ratio between 1:0 to 1:2 w/w.

Lu *et al.* [78] developed a kinetic model for a catalyst mixture using a zeolite as acid function. This kinetics is developed for a hybrid catalyst constituted by CZA + HZSM-5 in a fluidized bed reactor, using feeds containing only CO as carbon source, varying the H_2/CO ratio in the

Table 2
Kinetic studies for direct DME synthesis.

Temperature	Pressure	Feed composition	Catalyst	Reference
250 °C	50 bar	$CO_2/CO_x = 0–1$, $H_2/CO_x = 1–4$	CZA + γ-Al_2O_3	[77]
250–300 °C	20–40 bar	$H_2/CO = 0.75–2$	CZA + HZSM-5	[78]
225–325 °C	10–40 bar	$CO_2/CO_x = 0–1$, $H_2/CO_x = 4$	CZA + γ-Al_2O_3	[82–84]
210–270 °C	20–50 bar	$H_2/CO_2 = 3$	CZAZr + HZSM-5	[79]
250 °C	50 bar	H_2 66 %, CO 30 %, CO_2 3 %, inert 1 %	CZA + γ-Al_2O_3	[80]
250–270 °C	30 bar	$CO_2/CO_x = 0–0.289$, $H_2/CO = 0.67–1.5$	CZA + γ-Al_2O_3	[81]
220–280 °C	50 bar	$CO_2/CO_x = 0.063–0.8$, SN = 2.3–2.9	CZA + γ-Al_2O_3	[76,85]

range from 0.75 to 2. Also in this paper, a re-arranged Vanden Bussche and Froment kinetics (neglecting the effect of adsorbed water and methanol, considering the WGS instead rWGS) is used to simulate the CZA catalysed reactions. The methanol dehydration expression is instead developed ad-hoc. The catalyst ratio, understood as the ratio between the amounts of methanol synthesis catalyst and methanol dehydration catalyst, was investigated in the range of 4:1 to 6:1 (CZA: HZSM-5 w/w), showing a maximum in CO conversion at 5:1. The higher activity of HZSM-5 is the reason of the lower amount of acid catalyst necessary to reach an optimum performance.

Following a similar approach An *et al.* [79] proposed a kinetic model for the direct conversion of CO_2 to DME with a physical mixture of CuO/ZnO/Al_2O_3/ZrO_2 and HZSM-5. The model is based on a combination of the Graaf *et al.* kinetics (excluding the CO hydrogenation equation) with the kinetics of Tao et al. [66] for methanol dehydration. Pyatnitskii *et al.* [80] combined the kinetics of Vanden Bussche and Froment with that of Mollavali *et al.* [72] to fit results obtained with a 1:1 mixture of CZA and γ-alumina, while using data obtained on a similar mixture with variable CZA/γ-Al_2O_3 ratio. Pelaez *et al.* [81] re-elaborated the kinetics of Vanden Bussche for methanol synthesis and Berčič and Levec for the dehydration reaction.

Conversely, Aguayo *et al.*[82] developed from scratch a kinetic model for the direct DME synthesis. The experiments used for the kinetics were performed with a 2:1 CZA:γ-Al_2O_3 mixture accounting for a wide range of temperature (225–325 °C) and pressure (10–40 bar) conditions and covering the complete range of CO_2/CO_x ratio (0–100 %). The kinetic scheme included the synthesis of methanol from CO (CO_2 hydrogenation was reported to be negligible), the WGS and methanol dehydration. Moreover, differently from other models, the formation of hydrocarbons (HC) was also considered. The model was further improved in [83] by including a deactivation effect associated to coke formation, which in turn was attenuated by water formed in CO_2 rich streams [84].

Recently, to reconcile the vast array of data collected over CZA/γ-alumina catalyst mixtures, aiming at developing a lumped kinetics to be implemented in a mathematical model for optimization and design of fixed bed reactors for the direct DME synthesis from CO_2 rich syngas, Delgado Otalvaro *et al.* [85] re-evaluated parameters in the kinetic model of Lu *et al.* [78]. Their results further confirm the key role of the CZA/acid catalyst ratio and distribution as well as the negative impact on the performances of the process with high CO_2 content, mainly associated with the proportional amount of produced water. All in all, the excess of water generated as consequence of using CO_2-rich syngas in the feed is generally recognized in literature as a major hurdle for the implementation of the direct DME synthesis both for thermodynamic and kinetic reasons. In fact, Delgado Otalvaro *et al.* concluded that in-situ water removal could be a possible technical solution for the implementation of the direct synthesis of DME.

2.3. *Reactors for the direct DME synthesis*

The status and development of reactors for either indirect or direct processes, mostly consisting of fixed bed, fluidized bed or slurry reactors has been covered in a number of excellent reviews [33,34,114]. The industrial latest developments for the indirect process are related to the methanol reactor, attempting to increase the production capacity while taking advantage of economy of scale [86]. For this, this section will be brief and focus only on the direct DME synthesis, which, although it has not been commercially licensed yet, some companies have studied and developed to medium-large scale. Although at laboratory scale most studies on direct DME synthesis have been performed in fixed bed reactors, slurry reactors have been the first to be used in larger scale (100 t DME/day) demonstration plants for this process. The Japanese JFE first reported and patented a process for direct DME synthesis [44,87,88] using this type of reactor, in which an oil with the dispersed catalyst is loaded. It is important to choose an adequate liquid for the slurry, and this is because the reacting gas fed to the reactor has to dissolve properly into the reacting medium before contacting with the catalyst and being transformed into DME. A great advantage of this kind of reactors for this process is the good thermal conductivity of the liquid medium, which can absorb quickly the big amount of heat released by this reaction. The medium can also be recovered after deactivation and reactivated, and then recycled to the reactor to be used again.

Fixed bed technology has also been used for the direct DME synthesis at pilot scale, for instance, in that developed by KOGAS. This process counts with a multitubular reactor in which the catalyst is loaded in the tubes, and boiling water is fed through the shell to remove the reaction heat. To keep constant the temperature in the shell, the pressure of the boiling water is controlled. This reactor has been reported by KOGAS to obtain a DME yield of 55 % [89].

Lower scale demonstrations of the direct DME synthesis have been reported by Lu *et al.* [78] using a fluidized bed reactor with 24 cm if inner diameter and 2 m of length. In this type of reactor, fine particles of catalyst (150 μm) are loaded in a distribution board and the gas is driven through them, forming a bubble phase and fluidizing the bed. In order to avoid the loss of fine particles, an expansion zone is built in the reactor, with an inner diameter of 1 m, so the velocity of the gas is reduced. This kind of reactor has not been reported to be used at larger scale for this process, but interest has been shown in them, generating theoretical/mathematical studies [90].

2.4. *Heat and mass transfer in direct DME synthesis*

The direct synthesis of DME, combining the exothermic reactions for methanol synthesis and dehydration, carries a significant heat generation, as reported in equations (6) and (7). The equations show the overall process stoichiometry considering respectively CO and CO_2 as carbon source.

$$3\,CO + 3\,H_2 \leftrightarrow CH_3OCH_3 + CO_2,\ \ \Delta H^0 = -246\,kJ/molDME \tag{6}$$

$$2\,CO_2 + 6\,H_2 \leftrightarrow CH_3OCH_3 + 3\,H_2O,\ \ \Delta H^0 = -122\,kJ/molDME \tag{7}$$

The major reaction path is determined by the inlet syngas composition, being as in Eq (6) in case of traditional feedstocks (e.g. natural gas) or as in Eq (7) when CO_2-rich feeds (e.g. CO_2 from CCS, biomass gasification) are considered, in fact the pathways can be linked via (reverse) water–gas shift reaction. The path from CO_2 hydrogenation is significantly less exothermic than the one from CO, being less critical for the heat management. However, and regardless of the syngas composition, due to the high reaction enthalpy of the overall process, one of the main challenges of the reactor design is related to the heat transfer.

Multitubular shell-tube fixed bed reactors, externally cooled by boiling water, are due to their design simplicity one of the preferred options for managing the exothermicity of the direct DME synthesis. This reactor layout has been used since the early development of direct DME synthesis in the 90′s. The first significant experiments on pilot scale were carried out by Haldor Topsoe (see Table 1). Later, in the early 2000, during the development of KOGAS scale up of DME, different works were published by Lee *et al.* [91] and Song *et al.* [45,92]. These papers showed that despite the relatively small tube diameter (30 mm), compared to the standard for methanol synthesis (42 mm) [57], the hot-spot temperature exceeded 300 °C. Since the DME direct synthesis consists in coupling two catalytic functions in the same reactor, the KOGAS project also compared different catalyst distributions. The first one is a fixed bed filled by hybrid pellets made of intimately mixed powders of methanol synthesis and dehydration catalysts and the second one a mechanical mixture of single function catalyst pellets. They reported that the intraparticle diffusion limitations in the catalyst pellets, influences the actual performance resulting in a larger DME productivity but also in faster heat release and a more pronounced temperature hot spot. This effect is less relevant in the case of hybrid catalysts due to the direct contact between the two active phases, resulting in higher DME productivity and hot spot temperature.

The effect of the two catalyst functions layering was subsequently analysed by McBride *et al.* [93] who demonstrated that pellets of intimately mixed catalysts perform better than a series of separate layers thanks to the thermodynamic and kinetic synergy between methanol synthesis and dehydration processes. Bizon *et al.* [94,95] further investigated the problem of intraparticle diffusion extending this analysis also to the core@shell catalyst configurations. Core@shell pellets are obtained layering on the same pellet the two catalysts, with the methanol synthesis catalyst located in the pellet core and the dehydration catalyst located at the shell or vice versa (Fig. 3). These configurations allow a significant reduction of the diffusion length, reducing diffusion limitations, but at the same time reduces the contact surface between the two active phases, hence mitigating the possible detrimental interactions [96].

Guffanti *et al.* [98] reported on a model analysis focusing on heat exchange and diffusion limitation issues in direct DME synthesis in fixed bed, simulating an isothermal tubular reactor (25.65 mm tube diameter) using a 2D model. The different CZA/γ-Al_2O_3 catalyst pellet arrangements (hybrid pellets, mechanical mixture, core@shell pellets) have been considered. The work shows that the diffusion limitations, in the case of the mechanical mixture, hinder the performance in terms of DME yield (Fig. 4). The hybrid catalyst configuration, due to the synergy between the two active functions has the best DME yield but, on the other hand, the highest temperature peak ($>$290 °C with $CO/CO_2 = 1$ feed). The two core@shell configurations show intermediate performances, being the configuration with methanol synthesis catalyst in the core (MeOH@DME) particularly promising since it allows a proper temperature control while having DME yields comparable to the hybrid configuration.

2.5. *Novel production routes: Separation enhancement by membranes or sorption enhancement (SEDMES)*

The equilibrium for the direct synthesis of DME is already significantly improved compared to the indirect DME synthesis via methanol, yet further enhancements can be achieved by the *in situ* removal of water [49,99]. Both adsorbents and membranes have been investigated for the separation enhanced synthesis of DME. As deduced from the corresponding reactions, the equilibrium for the synthesis of DME from H_2 and CO_2 is strongly affected by the presence of water (Fig. 1).

This section first discusses recent developments of the membrane-enhanced DME synthesis, followed by a discussion of the recently approach of sorption-enhanced DME synthesis.

Steam-selective membranes include important developments that combine the required functionalities: sufficient selectivity and high-temperature stability. Carbon membranes can reach up to 80 % water removal and increase DME production by 27 % [100]. Still selectivity issues remain and significant amounts of CO are produced. A technical solution for the incomplete selectivity is the combined permeation and condensation of water [101].

Zeolite membranes appear as a promising development with high selectivities, in particular LTA-based membranes [101]. Li *et al.* have demonstrated DME yields up to 54.5 % using a NaA zeolite-based membrane [102]. More recently, NaA membranes were tested in an experiment up to 300 °C [103], where the DME yield and CO_2 conversion were enhanced from 8.71 and 21.4 to 22.8 and 33.7 %, respectively. A DME production rate of up to 1.31 kg d^{-1} was achieved at 300 °C and a GHSV of 8400 mL g^{-1} h^{-1}. Yue *et al.* [104] demonstrated the integration of catalyst and membrane: a ceramic supported HZSM-5-membrane was further functionalised with copper, zinc oxide, and platinum to provide full functionality of methanol synthesis, methanol dehydration to DME, and water removal, leading to a CO_2 conversion up to 41.1 % and complete DME selectivity at 32.5 bar(a) and 280 °C. A diagram of a typical membrane catalytic reactor used in these experiments is shown in Fig. 5. In terms of process design for membrane reactors, De Falco *et al.* [104] have proposed a double recycling loop for the utilization of CO_2 as sweep gas. Sweep gas may also contribute to controlling the reactor temperature [104], where also microchannels have been proposed to manage heat and mass transfer resistances [105].

Steam-selective adsorbents are employed in industrial settings on a large scale, yet effective sorbents for DME synthesis need specific functionalities in terms of selectivity, sufficient capacity at relatively high temperatures, and fast regeneration. In general, rather conventional zeolite adsorbent materials appear to fulfill these conditions, in particular FAU- and Linde type A (LTA)-type zeolites [106]. Sorbents need to adsorb H_2O selectively over the other species present in the reactor. The selectivity can be based on size (Fig. 6 compares the kinetic diameter of relevant species with pore sizes of zeolite 3A and 4A) while affinity is also an important differentiator. Indeed, FAU-13X zeolite was shown to have a selectivity for H_2O over CO_2 at temperatures in the range of 100–250 °C, with results fitted to a double stretched exponential model, but the selectivity with respect to for example methanol needs to be confirmed. Good results have been reported with zeolite 3A based on size exclusion: Van Kampen *et al.* [107] have measured H_2O adsorption at 200–350 °C and 0.05–4.5 bar partial pressure which was fitted to a Generalized Statistical Thermodynamic Adsorption (GSTA) isotherm.

Owing to the deep dehydration that can be achieved using adsorbents, sorption-enhanced DME synthesis (SEDMES) has been able to demonstrate unsurpassed DME yields. Since the pioneering work of Kim *et al.* [108] who used $MgSO_4$, hydrophilic zeolites seem to provide a good performance for *in situ* water removal [106,107]. Reßler *et al.* [109] were the first to show a high DME yield, followed by developments at Laval University, Canada [110]. More recently, the technology has developed rapidly due to the successful demonstration of a SEDMES cycle, based on conventional methanol synthesis catalyst (copper-zinc-alumina) and dehydration catalyst (γ-alumina) and zeolite 3A (LTA) as an adsorbent [111,112].

Many applications require a temperature swing for regeneration, a process that is neither energy efficient nor fast, leading to relatively low productivities. In this context, the successful validation of pressure-swing adsorption cycles has been encouraging. Pressure swing regeneration has been demonstrated with over 80 % single-pass carbon selectivity to DME [112]. More recently, continuously operated multi-column sorption-enhanced production of DME using pressure swing regeneration was demonstrated at carbon selectivity to DME up to 95 % [113].

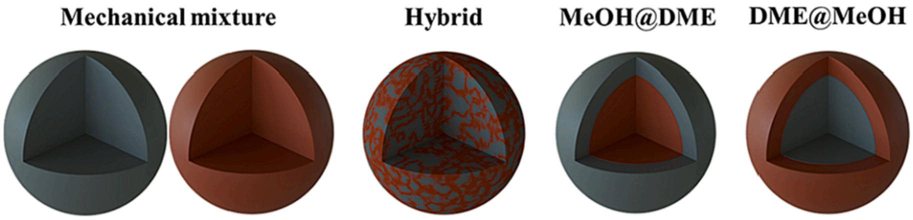

Fig. 3. Catalyst pellet configurations sketch. Brown, CZA (MeOH) catalyst; grey, γ-Al_2O_3 (DME) catalyst. (Reproduced with permission from reference [97]).

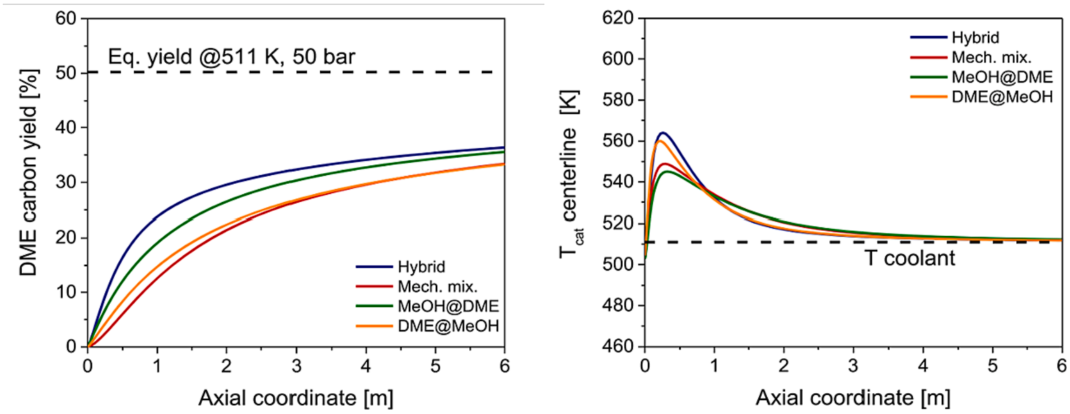

Fig. 4. DME carbon yield profiles and catalyst temperature profiles on the tube centerline with different catalyst configurations with different catalyst configurations with $CO/CO_2 = 1$. Reproduced with permission from reference [98]).

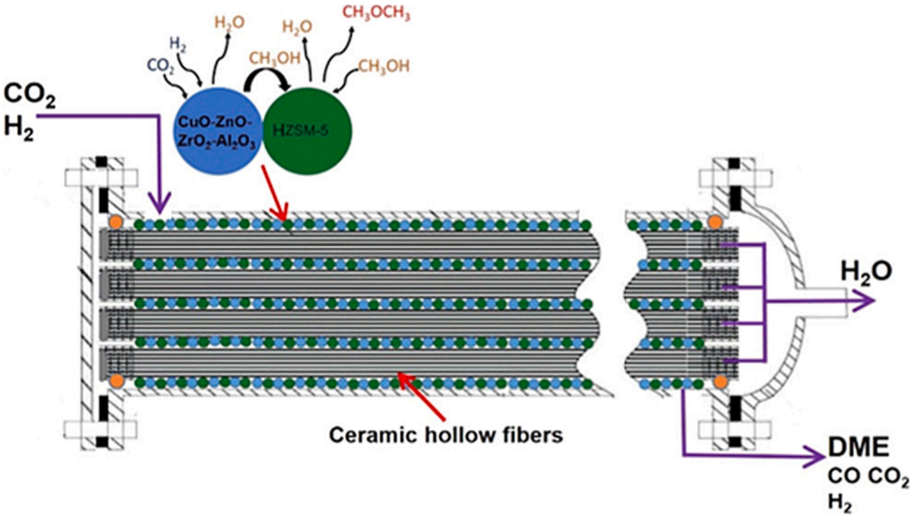

Fig. 5. Catalytic membrane reactor for SEDMES process. Reproduced with permission from reference [103].

As shown in Fig. 7, further intensification by means of shorter cycle times has been demonstrated to allow for optimisation of the DME productivity while maintaining the high single-pass yield typical for SEDMES.

An essential advantage of SEDMES is the ability to deal with various feed gas compositions. In fact, Van Kampen *et al.* [112,113] have recently demonstrated that it is possible to convert H_2-CO as well as H_2-CO_2 (and intermediate ratios) to DME, provided a stoichiometric amount of hydrogen is fed, see Figure S2. The difference in the amount of water that is produced (when feeding more CO_2) can be accommodated by modification of the cycle time. Liuzzi *et al.* [114] also demonstrated experimentally the SEDMES process at laboratory scale parting from CO_2-rich syngas, and compared it with the methanol and direct DME synthesis processes. The results, shown in Fig. 8, show the higher performance of SEDMES than that of the direct DME synthesis, and also minimized the CO_2 concentration at the outlet of the reactor, in contrast to both methanol synthesis and direct DME synthesis. This feature is very advantageous for the operation at higher scales as it simplifies the subsequent separation section. Provided that the methanol catalyst is highly selective for the methanol formation, the production of DME achieved is very high for SEDMES in comparison to the direct synthesis of DME. If the catalyst presents higher selectivity for the r-WGS reaction, an almost total conversion of CO_2 is also achieved by SEDMES, but the main product obtained is CO.

The largest dedicated SEDMES installation was built at TNO Petten, the Netherlands, and commissioned in 2023 (Fig. 9) [115]. It employs three parallel shell and tube reactors with an internal (tube side) volume of 150 L each. Heat management, consisting of cooling the heat of reaction and the heat of adsorption, and supplying the heat for the endothermic water desorption, is done by thermal oil in the reactor shell. The three-column design allows continuous DME production of 3 kg/h in one of the columns starting from CO_2 and H_2, while allowing for sufficient regeneration time in the other two.

Kinetic models for direct DME synthesis fail to represent faithfully the SEDMES reacting system, for which specific models must be developed. As shown by Van Kampen *et al.* [116] in a comparison model vs. experimental data of SEDMES, using the Vanden Bussche and Froment model to simulate the methanol synthesis led to an overestimation of the process performance. This is due to the strong inhibiting effect of water that makes this kinetics suitable for normal methanol or direct DME synthesis conditions, but makes the model failing under water depleted SEDMES conditions. The kinetic model of Graaf, which exhibits a less significant effect of water, was shown instead to be more suitable to be adapted to the SEDMES conditions. However, as reported in the previous section focused on methanol kinetics, the Graaf kinetic is not fast enough to predict the experimental results. Guffanti *et al.* [117] used a combination of Graaf and Ng kinetics to simulate the performance of a SEDMES pilot reactor showing that an activity factor of 5 for the CO and CO_2 hydrogenation to methanol and 7.5 for the rWGS kinetics were necessary to obtain a reasonable agreement between the model and the

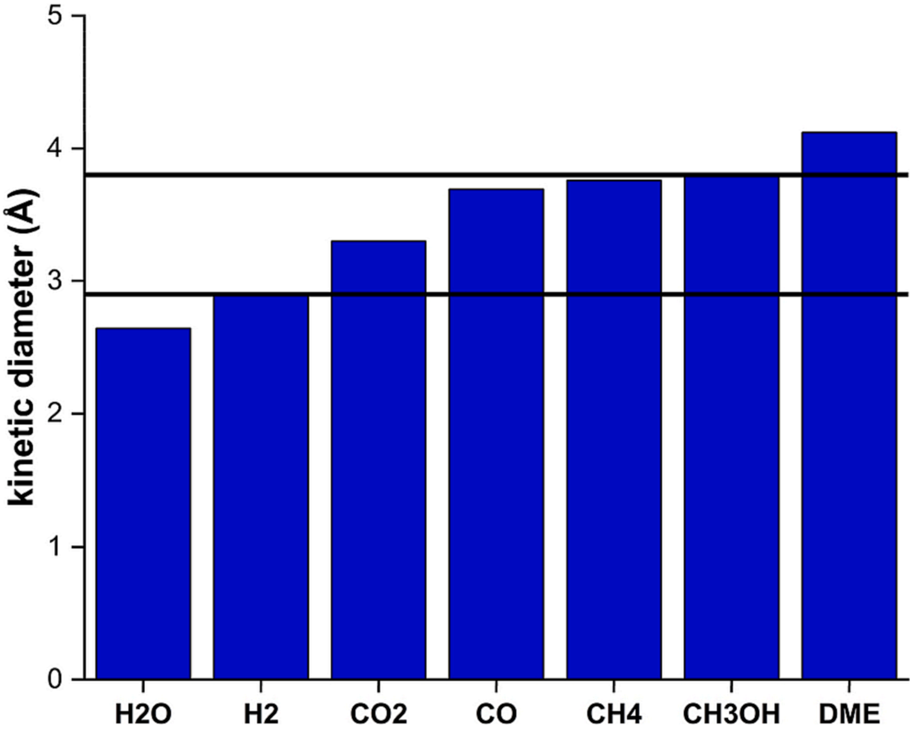

Fig. 6. Kinetic diameter of various components present in sorption enhanced reactions, compared to the pore sizes of zeolites 3A (2.9 Å) and 4A (3.8 Å) respectively. Reproduced with permission from reference [107].

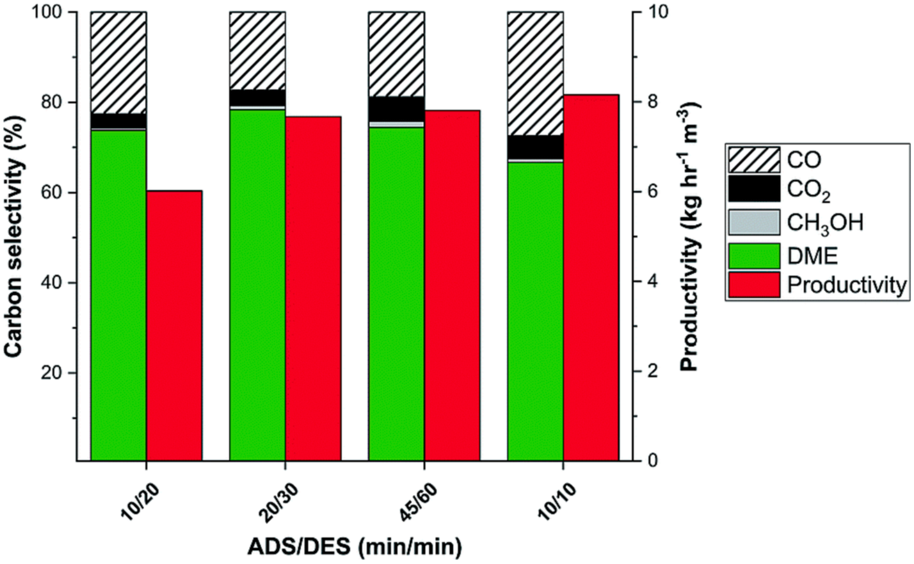

Fig. 7. Experimental carbon selectivity and the productivity for the minimum number of columns (adsorption + purge time; red bars) as function of ADS/DES ratio; conditions: 250 °C and 25 bar(a) for a CO_2:CO = 2:1 feed with stoichiometric hydrogen and CH_4 tracer.
Reproduced with permission from [111]

experiments. Such preliminary results clearly highlight the need for kinetic data and models developed under specific SEDMES conditions.

Regarding the heat transfer phenomena, the heat released per mole of DME produced in SEDMES process is significantly higher than the conventional synthesis due to the additional heat released by water adsorption [118]. The overall heat released by the process, considering both CO and CO_2 as carbon source, is reported in equations (8) and (9):

$$2\,CO + 4\,H_2 \leftrightarrow CH_3OCH_3 + H_2O{\downarrow}_{ads},\ \ \Delta H_r^0 = -250\,\mathrm{kJ/mol_{DME}} \tag{8}$$

$$2\,CO_2 + 6\,H_2 \leftrightarrow CH_3OCH_3 + 3\,H_2O\downarrow_{ads},\ \ \Delta H_r^0 = -260\,\mathrm{kJ/mol_{DME}} \tag{9}$$

The energy released in SEDMES process considering CO as feedstock is similar to the one obtained from the standard process (Eq. (6). This because the heat released by the water adsorption is balanced by the rWGS reaction, occurring in SEDMES as combined effect of CO_2 generation and equilibrium shift as effect of water removal. The heat of reaction in SEDMES, considering instead carbon dioxide as carbon feed, is more than double with respect to the conventional case (Eq. (7) as a consequence of the high amount of water produced (3 mol per 1 DME

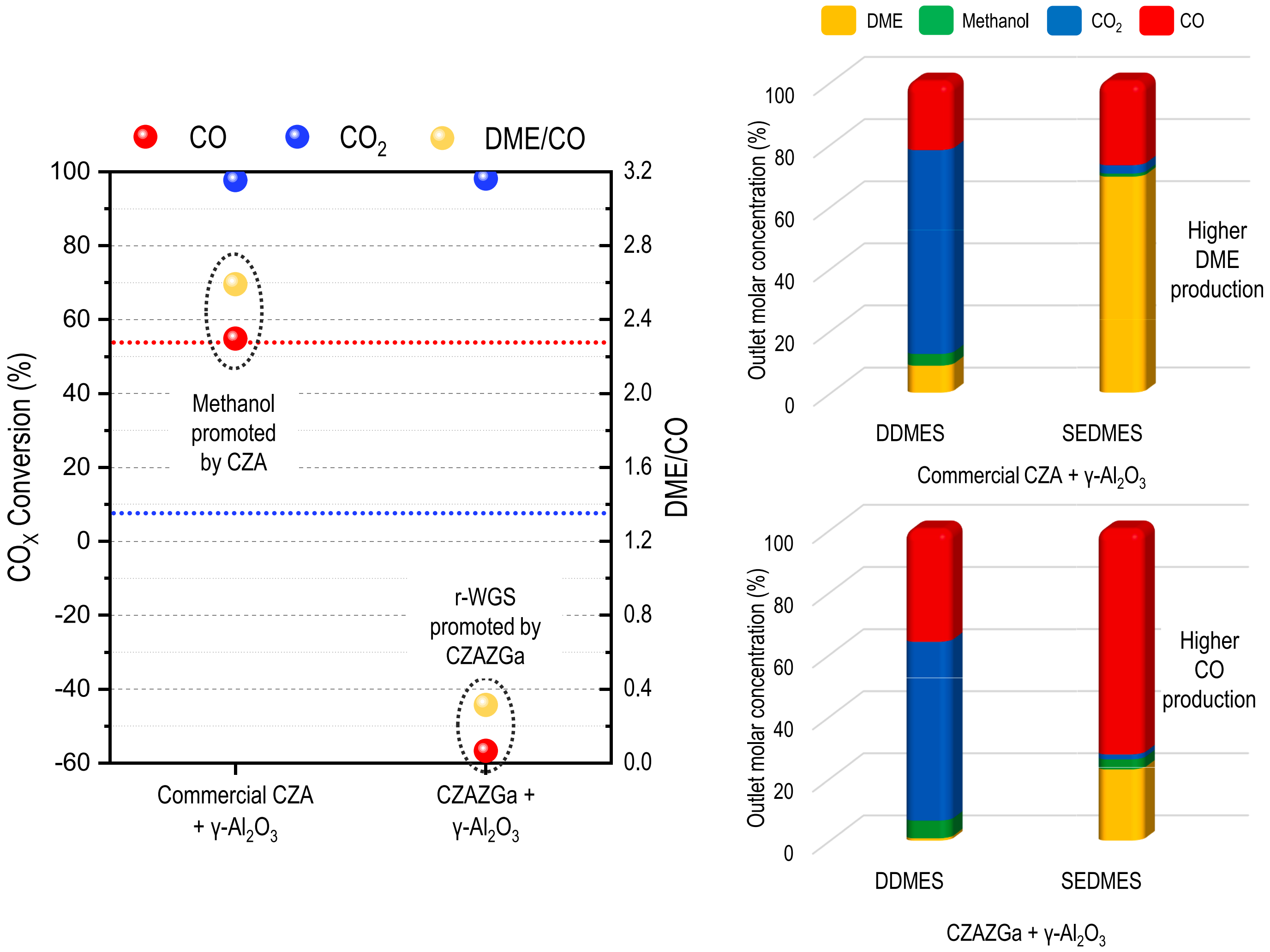

Fig. 8. CO_2 and CO conversions (equilibrium conversions in dotted lines), and DME/CO-ratios for SEDMES (left) and outlet mole concentrations for direct DME synthesis (DDMES) or SEDMES (right) for two different mixtures of methanol catalyst and γ-Al_2O_3. 275 °C, 25 bar, 1080 h^{-1}, $CO_2/CO = 2$. Adapted from reference [114].

mole) and adsorbed.

On the other hand, in the work of Guffanti *et al.* [117] it was demonstrated through a 2D tubular reactor modelling, validated in pilot scale experiments, that despite the higher exothermicity, the maximum temperatures reached during SEDMES process are more moderate than in the case of the conventional synthesis. This is the result of the thermal dilution provided by the adsorbent material that helps moderating the temperature, and thanks to that, tubes diameter larger than in conventional direct synthesis can be used. Moreover, the authors showed that the maximum temperature profile is mildly influenced by the inlet CO/CO_2 ratio, being slightly higher in the case of CO rich feed for kinetic reasons. In a subsequent work [97] the model was upgraded considering different CZA/alumina catalyst arrangements (mechanical mixture, hybrid, core@shell) and then used to analyse the effects of heat and mass transfer on the SEDMES process. Similarly to the previous work on conventional direct DME synthesis [98] it was concluded that the catalyst configuration has an influence on the DME yield as well as on temperature profiles due to the internal diffusion limitations.

2.6. Separation and purification of DME

In contrast to the reaction section, the information on the separation operations downstream the reactor is somewhat scattered in bibliography. In this section, we address the status of the separation and purification of DME. Regarding the indirect process, the outlet products of a methanol-to-DME reactor are separated in a first step by removing the water in a first distillation column. The distillate containing methanol and DME is then loaded into a second column and separated into a methanol stream (bottom) and a DME (distillate) stream. If there are still non-condensable gases in the DME stream, it is routed to a scrubber to recover residual DME [119]. Dividing wall column distillation allows to reduce both CAPEX and OPEX for the separation process itself [120], recovering in a single column purified DME, methanol and water [120,121]. A joint optimisation of methanol dehydration reactor, with multiple feed/quench points, and diving wall column distillation has shown an optimal performance in terms of system energy efficiency [121].

Reactive distillation, integrating the methanol dehydration reaction with the separation of the DME product, offers further process intensification and consequently cost reduction [120,122]. A recent catalyst screening study has indicated that ion exchange resins could outperform more traditional catalysts (zeolites) in reactive distillation of methanol to DME [121] (Fig. 10); interestingly, a novel kinetic mechanism was introduced to account for the highly non-linear inhibition by water (related to swelling of the ion exchange resin) [199]. The operation pressure can be increased in order to enhance reaction rates and reduce energy penalty for separation: the optimal conditions are around 11 bar (a) and 130–150 °C [122].

Fig. 9. SEDMES pilot reactor installation for the production of 3 kg/h of DME via SEDMES at TNO, the Netherlands.

The purification of DME in the direct process is different compared to the purification of DME downstream the reaction sections in the two-step DME synthesis because the raw DME of the direct process is mixed with unconverted feed (CO, H_2, CO_2), and side products (H_2O, methanol, CO_2). In particular, the separation of CO_2 from DME is cumbersome due to the high affinity between DME and CO_2. Indeed, DME is a major constituent of absorbent in the Selexol process for CO_2 absorption as CO_2 dissolves very well in liquid DME [124]. As a matter of fact, some of the direct DME existing installations and patents propose a mixture of DME and methanol as an absorbent solution for one of the unit operations of the separation train, as described below.

Several approaches for the DME purification section for direct synthesis plants can be found in the literature. The first decision to be taken is whether the CO_2 and DME, the affinity between which hinders their separation in a first stage, will be part of the vapor or the liquid fraction in the first separation unit. This first separation takes place either at cryogenic temperature or at high pressure. JFE and KOGAS processes opt for a cryogenic separation in which a liquid fraction comprising DME, CO_2, methanol and water is obtained, while the vapor phase (mainly unreacted syngas) is recycled to the reactor. The liquid fraction is then driven to two separation columns, the first of which operates at 35 bar to remove CO_2 from the stream, and the second one operates at 18 bar, from which pure DME is recovered [86]. A similar scheme has been proposed by other authors [125]. A recent patent proposes an alternative configuration, where the hydrogen from the DME synthesis feed can be used as a stripping gas in the distillation column, strongly improving the separation between CO_2 and DME [126]. In other proposals found in patents, DME and CO_2 are part of the gas phase leaving the first separation unit, consisting of a flash unit, along with unreacted syngas, while a liquid phase is obtained at the bottom. The gas phase is then treated in a scrubber unit, in which DME and CO_2 are separated from the syngas by absorption with a mixture of DME and methanol, as stated above. Once the solvent is regenerated and DME and CO_2 are removed from it, these two components are fed to a DME-CO_2 distillation column, where pure DME is obtained as bottoms [127].

A third option can be found in bibliography, where the outlet of the DME reactor, containing syngas, DME, methanol, water and CO_2 is directly fed to an absorption unit in which CO_2 is removed from the stream using an aqueous solution of K_2CO_3. Then, the CO_2 lean stream is distilled, obtaining a top product comprising DME and syngas, and a bottom product consisting in water and methanol. The top product is

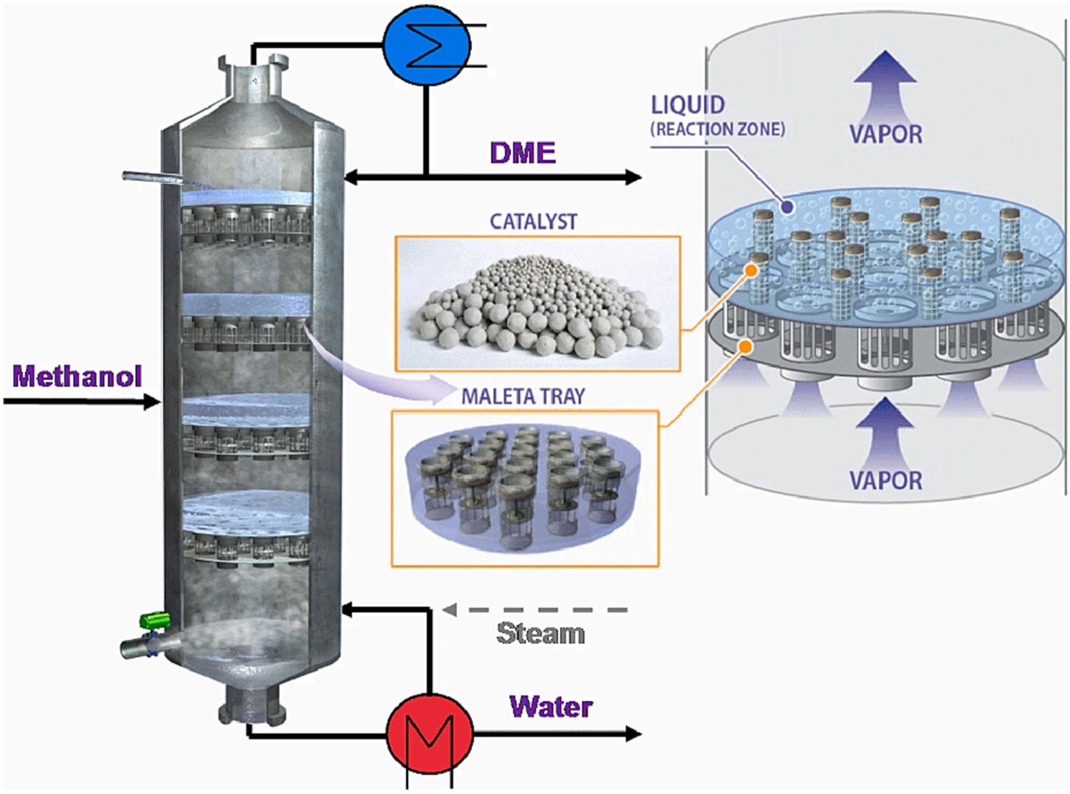

Fig. 10. Reactive distillation process for DME production. Reproduced with permission from reference [123].

then introduced to a condenser, where pure DME is obtained as liquid and syngas is recycled to the reactor [128].

3. Catalysts for the synthesis of DME

We have structured this section regarding the three catalytic needs for the reacting systems relevant for the two DME production processes: methanol synthesis catalysts, methanol dehydration catalysts and catalysts for direct synthesis of methanol, which requires the active sites present in the two former types of catalysts.

3.1. Methanol synthesis catalysts

Throughout the history of methanol production, there have been two predominant catalysts at industrial level. The formulation of the current catalyst, $Cu/ZnO/Al_2O_3$ has not suffered major changes for decades, although the research on the enhancement of its activity is still a recurrent topic in the literature. In addition, the shift of the source of syngas from fossil to renewable and the development of the methanol synthesis process from captured CO_2 and green H_2 may bring about the necessity of modifications in the catalyst, or the development of new ones.

3.1.1. Catalysts for methanol synthesis from syngas

$Cu/ZnO/Al_2O_3$ (CZA) is the state-of-the-art catalyst for the synthesis of methanol from syngas. CZA enables the production of methanol at low temperature 230–260 °C and pressure of 50–100 bar, thus allowing relatively high CO/CO_2 conversions and very high selectivity of ca. 99.9 % to methanol. In this multiphase catalyst, Cu act as the active site for the synthesis of methanol [129,130], ZnO is a textural promoter that, among other features, promotes Cu dispersion and prevents its agglomeration during operation. Al_2O_3 is a structural promoter that stabilizes ZnO and Cu against sintering. Cu catalysts are poisoned by heteroatoms such as sulphur or chlorine. However, the major source of deactivation is Cu sintering due to high temperature, overreduction (high concentration of CO) or by a high concentration of water (steam) typically occurring when CO_2-rich syngas is used. Commercial catalyst providers state that conventional CZA materials for methanol synthesis have demonstrated lives of around four years under conditions of high CO_2 concentrations. This suggests that the life of these catalysts is even higher when an ideal, CO_2-lean feed is used [131].

Since the beginning of the modern methanol synthesis process, there have been attempts to improve the formulation of the CZA catalyst by adding of other components [132]. The promoting effect of many additives (B, Ag, Ce…) has been studied [133], the most remarkable of which are MgO, ZrO_2 and Ga_2O_3. MgO provides stability to the CZA material, avoiding Cu sintering, and was incorporated to the commercial formulation of some CZA catalysts [134]. A number of studies suggests that ZrO_2 and Ga_2O_3 promote methanol productivity from CO_2-rich syngas or from H_2/CO_2 mixtures [135–139].

Palladium was studied for the synthesis of methanol for the first time in the 1920 s, and in the 1980 s a renewed interest in developing Pd-based catalysts emerged [140]. Supported Pd catalysts were proposed for the production of methanol from sulphur-containing syngas [141–143], and CeO_2-supported ones demonstrated superior performance due to the ability of ceria to protect Pd phase from sulphur-poisoning [142,143]. Many other rare earth oxides were used as Pd support for syngas conversion to methanol, for instance, La_2O_3 and Pr_6O_{11}, but rare earths have been also studied as promotors in Cu, Zr-Cu alloys and Pd catalysts. Among these, Pr-promoted Pd/SiO_2 catalysts showed a 10-fold improvement in comparison with its unpromoted homologous, while La stood out among other rare earths as a promoter in Cu catalysts, but their activity was never found to be higher than that of the CZA [144].

Raney catalysts have been studied as well for the methanol synthesis from syngas, and a summary of those studied until 1988 can be consulted elsewhere [133]. Raney materials, especially Raney Cu ones, remained a topic of interest for some years, but no improvement in comparison to co-precipitated CZA were found in these catalysts [145–147]. Recently, some studies on 3D printed Raney Cu based catalysts report that these materials could present activities comparable to that of traditional CZA catalysts at 75 bar and 250 °C, but still, the development of the preparation method of the different catalysts make difficult for any other material to compete with the current commercial one [148,149].

3.1.2. Catalysts for methanol synthesis from CO_2

Although there are similarities between the reacting systems for the production of methanol from CO-rich or CO_2-rich syngas, it has been demonstrated that the composition strongly affects the performance of CZA [150,151]. This topic has been addressed in a number of recent papers [32,36,152]. Two groups of catalysts can be identified. The first includes copper-based catalysts, for which researchers tend to avoid the incorporation of hydrophilic γ-Al_2O_3 to their formulation. In contrast, these Cu-ZnO systems have been modified with different components such as ZrO_2, La_2O_3 or Ga_2O_3, CeO_2, Pd or SiO_2 [153]. The best results obtained for the CO_2 hydrogenation to methanol with copper catalysts require operation pressures as high as 360 bar, at which CO_2 conversion and methanol selectivity reached 23 % and 77 %, respectively [153]. Interestingly, this catalyst actually contains Al_2O_3, but the conditions at which it shows this high activity may prevent the process at large scale to be economically feasible. The second group includes catalysts based upon precious metal-based catalysts such as Au, Ag, or, more recently, Pd. These catalysts usually combine the precious metal with different functions, such as Zn-, Zr-, or In-oxides phases, among others. Rui *et al.* synthesized a Pd/In_2O_3 catalyst that reached a CO_2 conversion above 15 % and a selectivity towards methanol over 80 % at 275 °C and 50 bar, which make it very competitive with the above mentioned Cu catalyst in terms of conversion. Nonetheless, the space time yield obtained by Rui *et al.* was substantially lower than that obtained with the Cu catalyst at the mentioned conditions (0.9 vs. 7.7 g of methanol per g of catalyst) [154].

3.2. Methanol dehydration catalysts

The most important characteristics that these catalysts must have are the presence of Brönsted and/or Lewis acid sites, and a certain hydrophobic character [155], since water is the most abundant by-product in the production of DME from syngas. Among the many reviews dealing with this topic, [32,36,156], that written by Bateni and Able in 2019 made a comprehensive compilation of the catalysts used for this reaction [157], and we will only mention the most important ones, indicating their respective characteristics.

Due to its weak and medium-strength Lewis acidity and good properties, γ-Al_2O_3 is the most commonly used catalyst to produce DME from methanol [32]. The structure of γ-Al_2O_3 is that of a typical $MgAlO_4$ spinel-type, in which Mg^{2+} ions are replaced by Al^{3+} ones [158]. The structure of the unit cell is depicted in Fig. 11a. Despite its high activity, the high hydrophilic properties of γ-Al_2O_3 can play a negative role in its catalytic performance, since water, produced in the dehydration reaction, not only reduces the acidity, but also competes with methanol to be adsorbed on γ-Al_2O_3 surface sites [36]. Deactivation can also be caused by the adsorption of alcohol-water clusters, which is in competition with the desired adsorption of alcohol dimers for the formation of ether [159,160], while similar phenomena have been reported in dehydration over H-ZSM-5 [160]. Nevertheless, the deactivation by water has been proven to be reversible, and γ-Al_2O_3 can be recovered by thermal treatment [71,161]. Mitsubishi has reported an expected life of 4–6 years or more for the γ-Al_2O_3 in their process for methanol dehydration [86]. The use of different materials intended to modify the properties of γ-Al_2O_3, by either reducing the hydrophilicity or increasing the acidity, has been reported in many publications. Other Al-containing catalysts

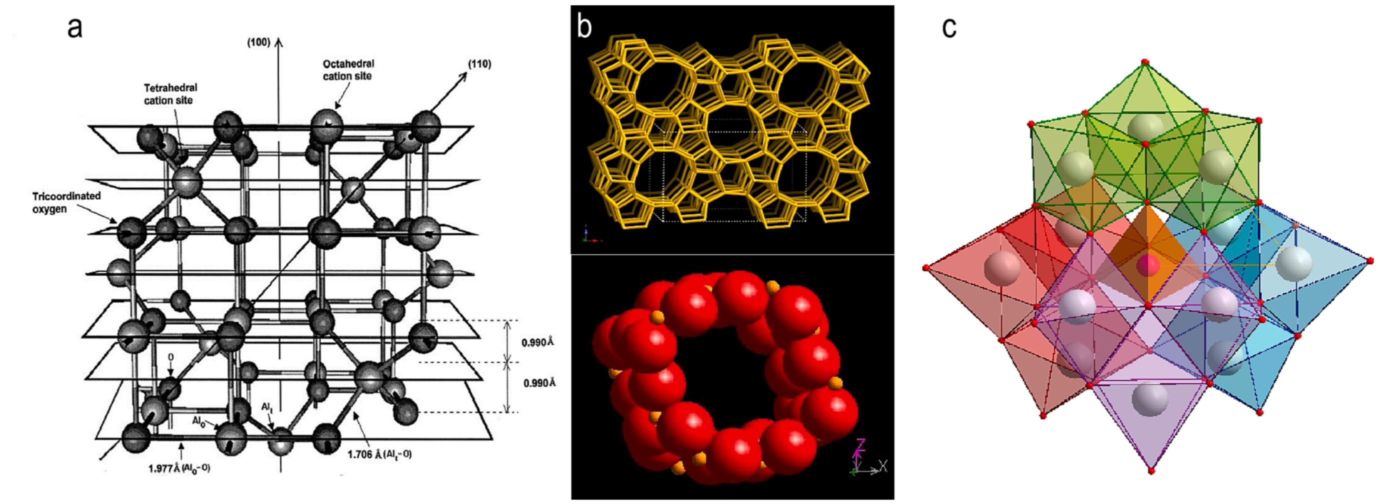

Fig. 11. (a) Experimental cubic γ-Al_2O_3 spinel-type unit cell, reproduced with permission from reference [158]; (b) Framework Type MFI (ZSM-5) viewed along [0 1 0] (top) and complex of 10 rings viewed along [0 1 0] (bottom). From Structure Commission of the International Zeolite Association (IZA-SC); (c) polyhedron representation of the Keggin unit (orange: XO4, green, blue, red and purple: MO8).

such as silica-alumina, aluminium phosphates or SAPOs have been also used for methanol dehydration [157]. Nevertheless, silica-alumina has been reported to last only 24 months in the operation of a two-step production plant, showing a lower life than γ-Al_2O_3 [86].

Zeolites are also used for the production of DME. Zeolites with high content in Si, and a Si/Al ratio of at least 5, are the most used ones for methanol dehydration; among them, the protonated HZSM-5 is the most studied catalyst (Fig. 11b). The Brønsted acidity they present makes them very active for the dehydration of methanol [157].

In contrast to γ-Al_2O_3, water does not deactivate zeolites as strongly during DME production. However, due to the strong acid sites on their surface, they shift the reaction toward the formation of hydrocarbons. This has led to studies that try to cope with this drawback, for instance, Fei *et al.* showed that a suitable amount of AlF_3-modified HZSM-5 exhibited a much higher activity and better stability than bare HZSM-5, by eliminating a fraction of the strong acid sites of the zeolites and leading to the reduction of undesirable by-products of the DME synthesis [162].

Heteropoly acid-based catalysts (HPA), especially those with the Keggin structure, see Fig. 11c, have also drawn attention of researchers on the DME synthesis process. Due to their high Brønsted acidity display very high activity for the dehydration of methanol, reaching equilibrium conversion of methanol at temperatures as low as 180 °C with 100 % selectivity towards DME [163–165]. The high activity of HPA stems for the combination of surface catalysis and bulk catalysis. This kind of catalysis, usually referred to as pseudo-liquid catalysis accounts to ability of HPA to absorb water or alcohol molecules between the polyanions that form their structure, hence resulting in higher catalytic activity [166]. In addition to displaying high activity and durability, HPA are not negatively affected by the presence of water the synthesis of DME [167]. Moreover, due to their high activity, they can operate under mild conditions, hence avoiding the formation of by-products, thus constituting a very promising family of acid catalysts for the direct synthesis of DME from CO_2-rich syngas.

3.3. Catalysts for direct DME synthesis

The first catalyst for the direct DME synthesis tested in a pilot plant in 2000 was a CuO-ZnO-Al_2O_3-containing material conceived for a slurry reactor [44]. Before that, some syngas to DME processes, with the reaction taking place in the gas phase, were patented, and they used Cu-Zr catalysts admixed with an acid solid, but all these proposed mixtures showed a very limited lifetime [168]. Ever since, the search for an active, selective and durable catalyst for the direct synthesis of DME has been a constant topic in scientific literature.

The materials involved in the direct synthesis of DME need to combine two catalytic functions; metallic sites for the synthesis of methanol from syngas and acid sites for the dehydration of methanol. The first catalytic beds for this reaction were prepared by pressing together powders of a copper-containing catalyst and an acid catalyst to form pellets [168], which could be denoted as physical mixtures at the particle level (PM-PL), or hybrid particles. This kind of catalytic beds usually suffer from a drastic deactivation due to the interaction of both materials caused by the close contact between them [169,170]. Later studies [171] proposed the mixture of both catalysts after they were sieved to form the catalytic bed, which some authors have called physical mixtures at reactor level (PM-RL) [169], and others have denoted them as mechanical mixtures [98]. Regarding this method, especial attention must be paid during the preparation of the bed so that segregation of the different catalyst particles does not occur [171]. Alternatively, to avoid segregation and deactivation observed in PM-RL and PM-PL approaches, the synthesis of bifunctional materials which include both kind of active sites in a single catalyst has been studied by many authors for the direct DME synthesis [169]. This strategy usually consists in a core–shell material, in which the methanol synthesis takes place in the core and the dehydration step occurs as the methanol leaves the material through the acid shell [172–174]. Other kind of materials, for instance based on GaN, have been also reported for the direct synthesis of DME from CO_2 [175]. Hybrid catalysts tested at pilot scale for the direct DME synthesis have demonstrated lives of 1–1.5 years when using a CO_2-lean syngas [86]. The different approaches to prepare catalysts for this reaction are represented in Fig. 3.

While the catalyst of choice for the synthesis of methanol is almost exclusively limited to metallic copper, normally combined with ZnO and other oxides, a wider range of acid catalysts have been tested. Table S3 shows a chronologic summary of the catalytic beds for the syngas to DME reaction reported in the literature. γ-Al_2O_3 and ZSM-5 materials have been the most studied type of acid components in this reaction. It should be noted that a proper comparison between the performances obtained for catalytic beds with different composition is not straightforward. This is because the direct synthesis of DME not only depends on the nature of the catalysts but also on other features such as pressure, temperature and space velocity conditions; composition of the feed gas; preparation method of the catalytic bed; and composition of the bed, i.e., the ratio between the metallic and the acid components, and their natures. With this respect, one of the most recent studies on CZA-γ-Al_2O_3

catalytic beds includes a thorough investigation on the effects of the bed and the feed gas composition, concluding that the CZA/γ-Al_2O_3 weight ratio which maximizes carbon oxides conversion is 2 for a PM-RL for every syngas composition tested [76]. A previous study indicated that for a PM-PL bed with similar components, higher contents in CZA resulted in higher conversion of carbon oxides [176]. Regarding zeolite-containing catalytic systems, latest studies have shown the dependence of the DME selectivity on the pore diameter of those. Zeolites with smaller pores appear to show weaker acidity than those with large pores, avoiding the production of higher hydrocarbons and thus reducing deactivation of the catalyst [177]. HPAs are starting to receive attention for this topic, and most authors that have compared them with other acid materials for the direct synthesis of DME in the same conditions have observed superior activity with the HPA-containing systems [178–180].

Another important aspect in this process is the composition of the starting gas. As shown by Delgado *et al.*, an increase in the content in CO_2 in the syngas is detrimental for the performance of CZA-γ-Al_2O_3 mixtures [76]. In addition, although the direct synthesis of DME mitigates the restricting CO equilibrium conversion for the methanol synthesis reaction system, this effect is much less relevant for CO_2-rich syngas, since its equilibrium conversion is less affected. This is in fact a serious challenge for the use of pure CO_2 or CO_2-rich syngas such as that obtained from renewable sources. Consequently, while the early research on the direct synthesis of DME was limited to the use of CO_2-lean or free syngas, the studies emerging in the last 10 years report a variety of compositions in the starting syngas with CO_2/CO ratios of up to 4 [76,179]. Additionally, the new carbon source provided by CO_2-capture technologies has opened a new route for the production of DME, for which some especial considerations must be taken into account in terms of catalysts development.

A very recent review by Ateka *et al.* [48] points out the aspects that must be regarded when designing catalysts for the CO_2 to DME reaction. Similar to methanol synthesis from CO_2, direct DME synthesis from CO_2 is characterized by a higher partial pressure of water in the reactor, which, as discussed above, is detrimental for copper catalysts and γ-Al_2O_3. Thus, the higher concentration of CO_2 also hampers the stabilization of the appropriate Cu oxidation state for the methanol formation. In other recent review on direct DME synthesis from CO_2, a representative selection of catalytic beds for this reaction can be consulted [32]. From this selection, an overview of the trends in the development of these catalysts can be deduced. One of these trends is that, while CZA materials are the preferred ones for syngas conversion, for CO_2/H_2 feeds ZrO_2, La_2O_3 or Ga_2O_3-doped copper materials are more frequently used [181]. This is in line with the bibliography on methanol synthesis catalysts from CO_2. However, a recent work clearly shows that addition of dopants such as Ga_2O_3, which promote the r-WGS reaction, lead to lower DME productions than non-promoted CZA catalysts [182]. Other general impression is that γ-Al_2O_3 has been discarded for the dehydration step, presumably due to its high hydrophilic character. Conversions and yields reported for these beds suggest that there is still room for improvement in the catalysts for this reaction.

4. Techno-economics of DME synthesis

Estimation of sustainable DME production costs using relevant assumptions plays an important role in determining a business case, technology competitiveness and likelihood of its implementation. Identification of the main cost drivers and sensitivity of the costs towards a certain parameter can indicate priorities for development of innovative scientific basis, creating infrastructural capacities and shaping policies.

Skorikova *et al.* have recently reported the costs for e-DME produced via Power-to-DME technology of 1300 €/t_{DME} [183]. In the core of the plant there is an energy efficient sorption-enhanced DME synthesis (SEDMES) technology operated on green hydrogen and captured CO_2 with a capacity of 23 kt_{DME}/y. The authors point out that the costs associated with green hydrogen i.e. electricity price, electrolyser efficiency and capital cost are the main concerns for technology implementation at the moment. This message is supported by other studies and is common for e-fuels in general. Another cost driver was identified to be CO_2 price (or CO_2 capture costs). Break-even cost, which is required to make the process economically viable is – 310 €/t_{CO2} meaning that carbon taxes should be raised above this value. Another recent techno-economic assessment of e-DME production via CO_2 hydrogenation was done by Poto *et al* [184]. The authors studied operation of another innovative separation-enhanced technology using membrane-assisted reactor. The study mentions that the minimum DME selling price (i.e., 1739 €/t_{DME} and 1960 €/t_{DME} for the MR-assisted and the conventional process, respectively) is over 3 times greater than the current (fossil) DME market price.

Earlier Michailos *et al.* assessed the costs of a bigger plant producing 250kt/y of e-DME. The calculated range of a minimum DME selling price of 1828–2322 €/t_{DME} considering 95 % confidence was calculated using Monte Carlo simulations [184]. The authors agree that green hydrogen is driving the costs and predict increased competitiveness of the new Power-to-DME technologies by 2050. Muazzam *et al.* found out that e-DME production costs via conventional indirect route are sensitive to the connected type of an electrolyzer with the price increasing in the following order: solid-oxide (1043 €/t_{DME}), proton exchange membrane (1125 €/t_{DME}) and alkaline water (1345 €/t_{DME}) electrolysers [185].

Another way to produce sustainable DME is from residual biomass as feedstock. Martín *et al.* compared biomass with the captured CO_2 as feedstock for DME synthesis for the plant sizes 82–197 kt_{DME}/y. The results show the cost benefits of utilizing biomass which is 250 €/t for bioDME vs. 1400 €/t for e-DME [125]. Fornell *et al.* studied bioDME (164 kt_{DME}/y) and bioethanol co-production from softwood via black liquor at a conceptual biorefinery based on repurposed kraft pulp mill [186]. The study shows that a typical annuity below 0.15 can provide a positive business case considering DME selling price of 600 €/t_{DME}. The authors also point out that carbon taxes should be just higher than 20 €/t_{CO2} to make a business case of bioDME production profitable. Clausen *et al.* modelled the bioDME production costs for torrefied wood pellets gasification followed by a DME synthesis [187]. The costs were found to be \$11.9/GJ_{LHV} (320 €/t_{DME}) for recycle conversion and \$12.9/GJ_{LHV} (347 €/t_{DME}) for once through conversion. Baena-Moreno *et al.* used 363 €/t_{DME} as production costs for DME suggested that profitable scenarios would be reached by setting prohibitive DME prices (1983–5566 €/t_{DME}) or very high feed-in tariffs subsidies (95.22 €/MWh in the best case scenario [188]).

Additionally, as mentioned earlier DME is an important commodity for production of jet fuel, diesel and plastics. Trippe *et al.* have compared the costs of biokerosene and biodiesel production from residual wood or straw via DME synthesis and Fisher-Tropsh synthesis. DME demonstrated lower expenses against syngas as an intermediate – 1.15 €/L vs. 1.23 €/L [189].

5. The future in DME production

In order to reduce its carbon footprint, the source of DME is likely to swift from natural gas and coal feed to more sustainable feedstocks such as biomass, waste or CO_2 captured from the waste streams of industrial processes or even atmosphere. On the one hand, biomass and waste, after proper preparation, can be transformed into syngas through a gasification process, which, after purification, can be converted to bio-DME in the same way than fossil-derived DME is produced. Bio-DME production steps have been demonstrated individually, as well as in combination with each other demonstrating the full chain of DME production from biomass, at various scales.

Although the use of palm oil waste as a feedstock for bioDME production is a controversial issue from a sustainability perspective, papers were published on this option [190–192]. Im-orb *et al.* determined that the gasification-DME process from palm oil waste is more economically feasible than the gasification to MeOH. Concerning practice developments, BioDME project [193] in Sweden represents a successful pilot project that demonstrated the full chain of bioDME by integrating biomass gasification and the DME synthesis process. The pilot-scale gasification plant converted Chemrec's black liquor (a byproduct of pulp and paper production), into syngas, which was then purified and converted into DME using a catalyst developed by Haldor Topsoe [194]. The DME was then used as a fuel for Volvo's heavy-duty trucks, which were modified to run on DME. The project demonstrated the technical and economic feasibility of using renewable feedstocks to produce DME as a clean-burning fuel for transportation, with lower greenhouse gas emissions compared to diesel fuel.

European Horizon 2020 project FLEDGED [195], with consortium members Politecnico di Milano, TNO, CSIC, University of Stuttgart, LUT, QUANTIS, INERIS, and SHI-FW, developed advanced technologies for producing DME from biomass with an improved efficiency and economy. The main results are related with evaluation and demonstration of Sorption-Enhanced Gasification (SEG), for flexible production of syngas from biomass, and Sorption-Enhanced DME Synthesis (SEDMES), for improved single-passage conversion from syngas to DME. Additional objectives of the project are demonstration of plant flexibility to different feedstocks (from woody biomass to waste organic fraction) and to the injection of hydrogen from electrolysis (Power-to-X). The possibility of pure CO_2 separation for storage purposes is also considered (Bio-CCS) with the goal of a negative-emissions fuel.

The first company that produces DME from renewable sources commercially is Oberon Fuels. The production process involves gasification of a variety of organic wastes, including from biomass, agriculture, municipal, and cellulosic sources, to produce syngas, which is then converted into DME using a catalyst. The company's commercial-scale production plant, located in California, has a capacity of 3,000 metric tons of renewable DME per year [196].

Another promising feedstock for DME production is carbon dioxide. CO_2 can be captured from industrial processes, and used as a feedstock for DME production. This process involves combining carbon dioxide with hydrogen produced from renewable sources, such as solar or wind power. This mixture could be fed either to an indirect or an direct DME production facility, although some theoretical studies state that the indirect route would be preferred due to the complexity of the CO_2-DME separation in the direct route (cf. discussion in Section 2.5). Nevertheless, these studies do not include the water sorption approach [197]. A well-to-wheel study that integrated SEDMES for the production of CO_2-derived DME states that, provided that renewable energy is used for the capture of CO_2 and proper heat integration is achieved, this process can would mean a reduction of about 90 % of carbon emissions in transportation in comparison to the use of current fossil fuels [198].

Few examples of demonstration plants of CO_2-to-DME can be found in the literature. Recently, a pilot plant for CO_2-based DME has been developed in the frame of the European Project ALIGN-CCUS. The whole process captures 180 kg of CO_2 per day from a lignite-fired power plant and transforms it to DME in a two-step process, producing 50 kg of crude DME per day [198].

Finally, producing DME from industrial waste streams is another promising approach to reduce greenhouse gas emissions and promote a circular economy. Industrial waste streams can include waste gases, such as carbon dioxide and carbon monoxide, which are produced as byproducts of various industrial processes. Several research institutions are actively working on developing this route and it is an emerging route with the potential to reduce greenhouse gas emissions and promote a circular economy technology.

Overall, the future of DME production is likely to involve a combination of feedstocks, including biomass, waste, and carbon dioxide, as well as continued technological advancements to improve efficiency and reduce costs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2023.147494.

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