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## PAPER



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## Economics & carbon dioxide avoidance cost of methanol production based on renewable hydrogen and recycled carbon dioxide – power-tomethanol

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The synthesis of sustainable methanol based on renewable electricity generation, sustainable hydrogen  $(H_2)$ and recycled carbon dioxide (CO<sub>2</sub>) represents an interesting sustainable solution to integrated renewable energy storage and platform chemical production. However, the business case for this electricity based product (denoted hereafter as eMeOH) under current market conditions (e.g. vs. conventional fossil methanol (fMeOH) production cost) and the appropriate implementation scenarios to increase platform attractiveness and adoption have to be highlighted. The aim of the following study was to perform a dynamic simulation and calculation of the cost of eMeOH production (where electricity is generated at a wind park in Germany), with comparison made to grid connected scenarios. Consideration of these scenarios is made with particular respect to the German energy market and potential for the reduction in fees/taxes (i.e. for electrolyser systems). This evaluation and indeed the results can be viewed in light of European Union efforts to support the implementation of such technologies. In this context, CO<sub>2</sub> is sourced from EU relevant sources, namely a biogas or ammonia plant, the latter profiting from the resulting credit arising from CO<sub>2</sub> certificate trading. Variation in electricity cost and the CO<sub>2</sub> certificate price (in the presented sensitivity study) demonstrate a high cost reduction potential. Under the energy market conditions of Germany it is found that eMeOH production costs vary between €608 and 1453 per tonne based on a purely grid driven scenario, whilst a purely wind park supplied scenario results in €1028–1067 per tonne. The reported results indicate that the eMeOH production cost in Germany is still above the present (although variable) market price, with the economical evaluation indicating that electrolyser and H<sub>2</sub> storage represent the lion share of investment and operational cost. Substitution of fMeOH results in CO<sub>2</sub> avoidance costs between €365 and 430 per tonne of CO<sub>2eg</sub> avoided for green methanol produced in Germany. The presented assessment indicates that the eMeOH production cost in Germany will reach market parity in ca. 2030-2035 with the price for the avoidance of CO<sub>2eq</sub> turning from a cost to a benefit at around the same time. Optimistically, the cost is predominantly influenced by rapidly reducing renewable electricity costs as is already the case in South American and Arabic countries offering the potential for methanol production at a cost of <€500 per tonne.

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## Introduction

With the steadily increasing contribution of renewable energy (RE) to the electrical grid, efficient and economic solutions to fluctuating energy supply storage are currently required. For example, the European Union (EU) aspires to reach

a contribution of renewables to primary energy supply >80% by 2050.<sup>1-3</sup> Currently storage at the TWh level is needed to avoid curtailing of RE power output (Germany: 4.7 TWh in 2015; 3.7 TWh in 2016)<sup>4</sup> during periods of high supply from solar and wind in combination with the continuous operation of large scale fossil and nuclear power plants. Stationary storage technologies need to provide large capacities whilst simultaneously being efficient and economically attractive. The conversion of electrical into chemical energy is one solution in this context that can also provide a route to clean synthetic fuels, potentially resulting in a reduction of greenhouse gas (GHG) emissions in the mobility sector. Future mobility, besides battery and fuel

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Fig. 1 The production of methanol based on renewable energy, water electrolysis and recycled carbon dioxide, commonly referred to as the "Power-to-Liquid" (PtL) process chain.

cell electric vehicles for private transport, will also be dependent on liquid fuels with energy densities suitable for heavy road freight, aviation and shipping. It would be an extremely attractive proposition if this could be achieved whilst generating suitable sustainable platform chemicals for the chemical industry and the decoupling of energy production from energy use.<sup>5,6</sup> Such a scheme, if based on the conversion of CO<sub>2</sub> will contribute to GHG emission reduction targets established through a number of national and international agreements (*e.g.* COP21).<sup>7</sup>

There has been much interest in the literature and at the industrial level regarding the interface between RE storage and chemical/fuel production schemes such as Carbon Capture & Utilisation (CCU) and Emissions-to-Liquids.<sup>8</sup> Currently in Germany, this concept is generally referred to as "Power-to-X" (PtX). X equals gas (H<sub>2</sub> or CH<sub>4</sub> – Power-to-Gas (PtG)), chemicals and liquid energy carriers (*e.g.* MeOH, Fischer–Tropsch diesel – Power-to-Liquid (PtL)). Regarding PtL, this scheme is based on the recycling of CO<sub>2</sub> from industrial exhaust gases or biomass plants and its hydrogenation (with H<sub>2</sub> produced from RE powered H<sub>2</sub>O electrolysis) to produce long lasting chemical molecules (Fig. 1). Taking MeOH as the desired liquid product, this C1 alcohol offers numerous potential benefits:<sup>9</sup>

(1) An industrially established synthesis under moderate conditions such as  $T \le 270$  °C and  $p \le 80$  bar.

(2) A relatively high energy density (at ambient conditions; 16.9 MJ  $L^{-1}$ ) and suitability as a storage molecule for RE (*i.e. via* 12.6 wt% (H<sub>2</sub>)).

(3) A highly versatile platform molecule (*e.g.* olefins and acetic acid) for higher fuel production.<sup>6,10</sup>

(4) High volume, existing market (*ca.* 75 Mt  $a^{-1}$ ; 2016) and a high ratio of market price to production cost in the case of conventional fossil production.<sup>11</sup>

However, the extremely low price of CH<sub>4</sub> (the main basis for current industrial MeOH production *via* reforming and syngas conversion<sup>6</sup>) makes adoption and market entry somewhat difficult for PtL.<sup>12</sup>

The option to recycle CO<sub>2</sub> is attractive as it could reduce industrial costs related to CO2-certification, whilst holistically elevating CO<sub>2</sub> from a liability to a potential commercial asset.<sup>5</sup> It is important to note that currently the capture of industrial CO<sub>2</sub> and its utilisation (CCU) in chemical processes is not included in the EU Emission Trading System (EU ETS)‡ and, for this reason, does not lead to CO<sub>2</sub> certificate savings (*i.e.* not as for Carbon Capture and Storage (CCS)).<sup>12,13</sup> For the current energy system, the regulatory context is extremely important to support the economical implementation of CCU.13-15 In January 2017 the European Court of Justice pronounced that in the case of CCU the transferred CO<sub>2</sub> is not to be seen as an emission, as it is not released into the atmosphere.16,17 Hereby the emitter (i.e. a lime producing company implementing CCU for the production of precipitated calcium carbonate) is not obliged to purchase CO<sub>2</sub> certificates. In this ruling, the court annulled the second sentence of Article 49(1) of the monitoring regulation with reference to the existence of sufficient means of monitoring for the avoidance of feared CO<sub>2</sub> loopholes. This case is foreseen as a critical legal precedent for any CCU project which, after careful assessment of its CO2 mitigation potential, is found to result in reduced CO<sub>2</sub> emissions. Therefore a comprehensive LCA is mandatory. Therefore, in this study it is assumed that imminent legislation will consider CCU as a part of the EU ETS market resulting in a credit due to the saving of CO2 certificates. For any large scale implementation of CO<sub>2</sub> converting PtL processes it is important to shift focus towards biomass based CO<sub>2</sub> sources. Only these (besides the still cost intensive direct air capture methods) enable the recycling of CO<sub>2</sub> from distributed emitters. For the following economic evaluation we consider an

 $<sup>\</sup>ddagger$  Annex I of the EU Directive 2003/87/EC underlines that "under the EU ETS rules for any other transfer" than in the case of long-term geological storage "of CO<sub>2</sub> out of the installation, no subtraction of CO<sub>2</sub> from the installation's emissions is allowed".

industrial/fossil and a biogenic source of CO<sub>2</sub>, namely an ammonia and a biogas plant.

Regarding the synthesis of fossil based methanol (denoted hereafter as fMeOH), three key stoichiometric equations are important (eqn (1)-(3)). The reforming and gas cleaning involved in the syngas preparation give rise to high specific CO2 equivalent emissions. These range from 0.50 to 0.77  $t(CO_{2eq})$   $t(fMeOH)^{-1}$ , ref. 18 and 19 respectively, including direct specific CO<sub>2</sub> emissions of 0.24 t(CO<sub>2dir</sub>) t(fMeOH)<sup>-1</sup>.<sup>20</sup> These emissions are coupled with a very high environmental impact as a consequence of fossil fuel exploration and processing.21 Positively, the synthesis of electricity based methanol (denoted hereafter as eMeOH) based on the direct hydrogenation of a pure  $CO_2$  feed is also known (eqn (1)).<sup>22,23</sup> According to the equilibrium reaction, the production of 1 metric tonne of MeOH (CH<sub>3</sub>OH) requires 1.370 kg(CO<sub>2</sub>) and 188 kg(H<sub>2</sub>) are converted (producing 558 kg(H<sub>2</sub>O) as a side product) (N.B. this value ignores  $CO_2$  and  $H_2$  consumption via the Reverse Water Gas Shift reaction (eqn (3)) which becomes increasingly favoured with rising reaction temperature). This equilibrium reaction occurs under exothermal reaction conditions and as a consequence is favoured at low T and because the volume reducing reaction requires high p. Efficient compression of the feed stream(s) as well as integration of the exothermal reaction heat are important factors determining the overall process efficiency.

$$CO_2 + 3H_2 \rightleftharpoons$$

$$CH_3OH + H_2O, \Delta H_{R(298 \text{ K}, 50 \text{ bar})} = -40.9 \text{ kJ mol}^{-1} (1)$$

 $CO + 2H_2 \rightleftharpoons CH_3OH, \Delta H_{R(298 \text{ K}, 50 \text{ bar})} = -90.7 \text{ kJ mol}^{-1}$  (2)

 $CO_2 + H_2 \rightleftharpoons CO + H_2O$ ,  $\Delta H_{R(298 \text{ K}, 50 \text{ bar})} = +42.0 \text{ kJ mol}^{-1}(3)$ 

The commercial demonstration of PtL is exemplified by the George Olah Renewable Methanol Plant (Carbon Recycling International, Iceland), operating at 5 million litres per year production. Plant operation here is based on a very low electricity cost due to inexpensive renewable geothermal power and associated low cost  $H_2/CO_2$  sourcing.<sup>24</sup>

One significant distinction and possible advantage of developing CH<sub>3</sub>OH production based on direct CO<sub>2</sub> hydrogenation is the avoidance of the cost intensive syngas production step (e.g. CH<sub>4</sub> reforming at T > 700 °C). It typically accounts for ca. 60% of total plant investment.22 Whilst replacement of syngas production with CO2 and H2 sources can be relatively capital intensive, depending on the overall process conditions, investment in such a scheme can result in a "multi-benefit" system: MeOH production, recycling of CO<sub>2</sub> emissions, system services for the electrical power grid and indirect avoidance of fossil CO2 emissions. In this regard, a number of recent reports have sought to evaluate the costeffectiveness of PtL, focusing predominantly on evaluation of eMeOH synthesis with little consideration given to the preceding process steps in the process chain.3,11,25-34 Therefore, it is the aim of the following work to investigate different electricity and CO<sub>2</sub> purchase options, the fundamental

influence of total and partially dynamic system operation and, in turn, the impact on eMeOH production cost,  $H_2$  storage requirements and associated investment costs. Furthermore, a complementary parametric sensitivity study is presented, highlighting the most important factors concerning eMeOH production cost (*e.g.* in a future RE system). Concerning the environmental impacts of PtL-schemes, the economic evaluation presented is concluded with the CO<sub>2</sub> avoidance cost – *i.e.* an important key performance indicator when evaluating technologies for CO<sub>2</sub> emission mitigation.

# Power-to-liquid – MeOH production: a brief process description

The PtL scheme for eMeOH production, denoted hereafter as Power-to-Methanol (PtM), can be divided into six primary process steps (Fig. 1):

(I) Electricity as the main power source for the process is generated from renewables on-site or purchased from the grid.

(II)  $H_2$ , the first educt for eMeOH synthesis, is obtained *via*  $H_2O$  electrolysis or industrial streams providing high concentrations of  $H_2$  (*e.g.* coke oven gas from steel mills). The PtM process is investigated with the intent to minimise  $CO_2$  emissions. For this purpose,  $H_2$  used in hydrogenation should not be generated (in-)directly from fossil resources (*e.g.* steam reforming of CH<sub>4</sub> and H<sub>2</sub>O electrolysis powered by the electricity grid mix). Please note that a valuable by-product of  $H_2O$  electrolysis is high purity  $O_2$ , which will be discussed in the following evaluation.

(III) CO<sub>2</sub>, the second educt for eMeOH production, is captured from industrial processes, biogas or even ambient air.<sup>35–38</sup> Source dependent purification of the CO<sub>2</sub> is necessary.

(IV) Compression of the feed  $H_2$  and  $CO_2$  and the associated energy demand. This will be source dependent.

(V) Temporary storage, the size of which will be related to the fluctuation of the electricity production and the range of the systems' dynamics.

(VI) Catalytic conversion of  $H_2$  and  $CO_2$  to MeOH is based on established technology. Recent studies focus on higher efficiency and dynamic operation.<sup>23,31,39,40</sup>

(VII) Synthesis is followed by a purification step based here on distillation.

The PtM process steps that are varied within this study are marked in orange (*i.e.* power supply,  $CO_2$  source,  $H_2$  storage, and MeOH synthesis; Fig. 1). The non-variable components of the PtM process steps are marked in blue (*i.e.* polymer electrolyte membrane electrolysis (PEMEL), compression and pressure levels, and distillation).

# Technical analysis – general framework, examined PtM scenarios and process variables

A total of six different PtM production scenarios (each with two different  $CO_2$  sources) are considered (Fig. 2). In this study, two different electricity sources are considered: a constant grid

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supply (scenarios 1-4) and a local power supply (scenarios 5

and 6) from a 36 MW onshore wind park (which in turn provides

a dynamic, fluctuating electricity supply for this study). Grid

connected energy is further differentiated as a constant full load

power supply (scenarios 1 and 2) or a price dependent power

supply (scenarios 3 and 4), (i.e. dual tariff based on electricity

availability). Wind park electricity supplies a 100% dynamic

electrolyser and a MeOH reactor differentiated into a dynamic

(20% <  $P_{\rm RL}$  < 100%, scenario 5) and a stationary model ( $P_{\rm RL}$  =

100%, scenario 6;  $P_{\rm RL}$  = rated load). A dynamic MeOH synthesis

reactor is at present not realised at the industrial scale as

a consequence of the unknown effects on catalyst degradation/

behaviour and the challenges of efficient heat integration (i.e.

when operating under partial load). Dynamic simulation of

each system leads to H<sub>2</sub> storage capacities between 'zero H<sub>2</sub>

storage' and a '50 000 kg H2 storage' reflecting the synthesis

ability of flexible operation. The investigated scenarios are

additionally differentiated regarding the application of elec-

tricity fees. Finally, all six resulting scenarios are evaluated

based on the utilisation of two different CO<sub>2</sub> sources, namely

from a biogas treatment plant (biogenic CO<sub>2</sub>, indicated by 'B')

and from an ammonia production plant (fossil CO<sub>2</sub>, indicated

by 'A').  $CO_2$  from biomass offers, besides air capture methods,

the only possibility to close the global carbon-loop and offer

a long-term solution for a PtL-process independent from fossils.

Regarding ammonia plant-derived CO<sub>2</sub>, a high purity is

assumed and is considered an exemplary scenario for other

industrial processes (e.g. cement, steel or bioethanol produc-

tion). In the subsequent section a down-stream modular over-

view of the evaluated PtM process is provided. The various

parameters identified for the generated economic evaluation

are discussed and simulation results based on a combined

Matlab/Simulink-based analysis and previously reported data

Electricity purchase

Purchase from the German electricity market (scenarios 1–4): these scenarios refer to the spot market (*i.e.* short-term purchase, normally the next day) whereby the final purchase price is dependent on the actual spot market price plus taxation, fees and apportionments (electricity, grid and concession fee, the EEG, 'KWK' and offshore apportionment and the apportionment according to §19 'StromNEV' and §18 'AbLaV').

Low spot market prices are available in times of high production from RE (e.g. low or even negative residual load),43 or during periods of low energy demand (e.g. at night). Therefore, electricity purchase during such periods can aid in the reduction of the final production cost. The stock price is, however, not the biggest share since ca. 80% can be attributed to taxation and fees. Under certain circumstances (e.g. amount of energy consumed/total utilisation hours/specific electricity cost intensity), it is commonplace in Germany, as an industrial customer, to receive a tax reduction down to 15% (EEG 2017). For this study, electricity prices are calculated either with tax and fees (scenarios 1 and 3) or based on the aforementioned reduction of fees and taxes (scenarios 2 and 4). The respective reduction was calculated depending on the specific electric energy demand in the scenarios. Furthermore the calculation model differs between electric energy demand of the electrolyser and the 'rest' of the plant (i.e. compressors and eMeOH-plant). According to 'Energiewirtschaftsgesetz' (EnWG, §118 (6)) and 'Stromsteuergesetz' (StromStG, §9a), electrolysers are found to be exempt from the grid fee and electricity tax, respectively. The exemption from EEG apportionment for electrolysers and the energy demand of additional components in the PtM system takes effect after the first consumed GWh of electrical energy. After analysing the specific tax and fee reduction potential for each scenario, electricity prices are found to be between 3.11



Fig. 2 Overview of the six different "Power-to-Methanol" (PtM) scenarios (1-6) evaluated in this study; each differed in the sourced CO<sub>2</sub> either from an ammonia-plant (A) or from a biogas upgrading plant (B).

are used.41,42

and 3.28 ct  $\in$  per kWh with reduction, or 14.29–14.63 ct  $\in$  per kWh without the reduction. The partial reduction of EEG apportionment (6.88 ct  $\in$  per kWh full/0.18 ct  $\in$  per kWh reduced), grid fees (2.26–2.77 ct  $\in$  per kWh full/0.00 ct  $\in$  per kWh reduced) and electricity tax (2.05 ct  $\in$  per kWh full/0.00 ct  $\in$  per kWh reduced) is the most significant since they have the largest reduction potentials.

Another possibility for electricity purchase is based on participation in an operating reserve market (support of grid stability), where negative reserve (increase of load/H<sub>2</sub> production) and positive reserve (decrease of load/H<sub>2</sub> production) could both be provided. In our study, the German operating reserve market has been utilised as a model. Since market entry in this case is simplified (*e.g.* pooling is possible), there are more and more participants in the market, resulting in decreasing revenues. The exact economic benefit of participation in the control energy market, whilst an important global consideration, is not discussed in this study. Kopp *et al.* had a first evaluating insight into this topic in their work regarding the PtG plant in Mainz, Germany.<sup>44</sup>

It is important to note that PtM scenarios using grid electricity only produce eMeOH, if mainly RE is fed into the grid. The RE share will keep increasing following German/EU Climate Targets (>80% RE in 2050).<sup>44</sup>

Electricity purchase from a local onshore wind park with a rated power of 36 MW (scenarios 5 and 6): for the simulation, values at minute intervals have been applied. If insufficient wind electricity is available for  $H_2$  production (*i.e.* the amount required for eMeOH production), the difference is covered by either the flexible adaption of the eMeOH production rate (scenario 5) and/or an H<sub>2</sub> storage (scenarios 5 and 6). A limited flexible operation of eMeOH synthesis is a novelty, and therefore for the purposes of this study is assumed technically feasible. For the wind electricity driven scenarios 5 and 6 an additional grid connection to acquire electricity in periods of low wind supply is not considered for the purpose of a remote renewable scenario. The levelized cost of electricity (LCOE) from onshore wind energy is assumed to be 4.4 ct€ per kWh,45 without any additional fees or taxes since wind electricity is used for personal consumption and without grid connection (as defined by the "Renewable Energy Act" ("Erneuerbare Energiengesetz" EEG) of the German Government in 2014 (§61, subsection 2, sentence no. 2)).46

#### H<sub>2</sub> production and O<sub>2</sub> valorisation

A PEM electrolyser (PEMEL) is adopted in this study for  $H_2$  production as a consequence of its ability to operate under both dynamic and steady state conditions with only a marginal reduction in efficiency.<sup>1,47</sup> During dynamic operation, a PEMEL is capable of following fast load changes and load-ramp curves with high inclination (±138%  $P_{RL}$  per min).<sup>42</sup> Large-scale PEMELs with production capacities >10 N m<sup>3</sup>(H<sub>2</sub>) h<sup>-1</sup> do offer efficiencies as high as alkaline electrolysers (AELs) (PEMEL: <*ca.* 5.3 kWh<sub>el</sub> per Nm<sup>3</sup>(H<sub>2</sub>); AEL (pressurised): <*ca.* 5.0 kWh<sub>el</sub> per Nm<sup>3</sup>(H<sub>2</sub>); both system-related); a positive technical learning curve has been traversed over the last few years,

indicating that further efficiency improvements can be expected in the coming decade.<sup>48-50</sup> Additionally, PEMELs operate very well under variable loads, down to  $P_{\rm RL} = 0\%$  and an overload of up to  $P_{\rm RL} = 150\%$  (for up to 15 min).<sup>51,52</sup> The product purity from the PEMEL operation is high grade (*i.e.* H<sub>2</sub> purity > 99.9 vol%), whilst the operating temperature is typically low (50–100 °C), facilitating a faster start-up (*i.e.* in comparison to an alkaline electrolyser).<sup>52</sup> The operating PEMEL parameters evaluated in this study are displayed in Table 1.

Molecular O<sub>2</sub> is produced as a high purity by-product and as such is included in this study as a consequence of its valorisation potential. The selling price depends on purity, with O<sub>2</sub> purities > 99.99% (and without S or CO impurities) making it useful for many high-tech applications (*e.g.* medical use in hospitals, electronics industry, and oxy-fuel processing).<sup>53</sup> If possible, O<sub>2</sub> is utilised locally to avoid the associated energy intensive liquefaction and transport needs.<sup>3</sup> For these reasons, the use of O<sub>2</sub> from large electrolysers in nearby chemical/energy plants is considered the most appropriate option (*e.g.* in epoxide/polycarbonate production *via* oxidation of propylene and CO<sub>2</sub> addition).<sup>54</sup>

#### CO<sub>2</sub> sourcing

Technical processes for the capture of  $CO_2$  include both chemical and physical absorption processes (*e.g.* amine scrubbing, Rectisol®, Selexol®, cryogenic methods, *etc.*) based on the use of a variety of solvents, membranes and solid capture media.<sup>9,35,36,55–57</sup> Likewise, there are various  $CO_2$  sources, which can be distinguished on the basis of volumetric output,  $CO_2$ concentration, presence of impurities, pressure level,  $CO_2$ origin (biogenic/fossil), impact on up-stream processes due to carbon capture, and  $CO_2$ -price (prices from negative to positive possible).<sup>35,55</sup> Which  $CO_2$  source is captured by which method depends on the operating conditions of the emitting process. Concurrently, the downstream CCU process has its own requirements regarding required purity, tolerable impurities and volumetric demand.

In this study, two different  $CO_2$  sources are considered, namely a biogas treatment plant and an ammonia plant. In the case of biogas,  $CO_2$  is separated during a treatment process of the raw biogas. This is conventionally composed of  $CH_4$  (70– 50 vol%) and  $CO_2$  (30–50 vol%), with the exact composition influenced by the biomass or waste being converted, which also dictates the presence of other compounds and impurities (*e.g.*  $N_2$ ,  $H_2S$ ,  $H_2O$ , and organosulfur compounds). Taking Germany again as the example, the quality requirements for the feed-in of treated biogas to the gas grid are regulated.<sup>58,59</sup>  $CO_2$  sourced from biomass is designated as biogenic.

Table 1	PEM	electrolyser:	parameters	for o	dynamic	simulation
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Rated load, $P_{\rm RL}$ [MW]	12
Efficiency, $\eta_{\rm Elv}$ [kWh per Nm <sup>3</sup> ]	4.76
Output pressure, P <sub>H</sub> , [bar]	30
Grid connected scenario	P <sub>RL</sub> : 40% (day), 100% (night)
Wind electricity driven scenario	$0\% < P_{\rm RL} < 100\%$

For  $CO_2$  capture from an ammonia plant, it is assumed that  $CO_2$  is already a component of an existing ammonia production process and therefore is designated as fossil-based (from steam methane reforming as a process related step in ammonia production).<sup>60</sup>

#### H<sub>2</sub> storage

All process scenarios examined in this study, apart from the full-load power supply scenario, include H<sub>2</sub> storage facilities. In this study, the incorporated H<sub>2</sub> storage units consist of medium pressure vessels operating dependent on a load capacity in the range 30 bar  $< P_{H_2,storage} < 200$  bar. The required size and range of this storage has been identified, based on dynamic simulation *via* Matlab, to be in the range 100 kg(H<sub>2</sub>)  $< m_{H_2,storage} < 50 000$  kg(H<sub>2</sub>). It is important to mention that H<sub>2</sub> storage with a 50 tonne capacity would rather be realised as an underground cavern facility. However, due to a strict dependence on local conditions, the possibility of an environmentally sound disposal of the resulting brine, and socio-economic conditions in the case of underground cavern storage, and for a better comparability, the installation of storage vessels is assumed for all the evaluated scenarios in the present study.

In the first of the examined scenarios 1 and 2 (*i.e.* grid connected, constant supply), no storage is necessary as a consequence of a constant  $H_2$  production. The resulting  $H_2$  mass flow of 5.47 t( $H_2$ ) d<sup>-1</sup> is directly converted to MeOH. For the other scenarios,  $H_2$  storage requirements depend on the assumed dynamics of the MeOH synthesis reactor (Fig. 2). In wind powered scenarios, MeOH mass flow is a function of the actual wind power, the  $H_2$  storage pressure and the possible dynamics of the MeOH synthesis reactor (Fig. 3).

#### Compressor

Both  $H_2$  and  $CO_2$  streams require compression since MeOH synthesis is favoured under pressure (here designated at 40 bar). The output pressure of the PEMEL is 30 bar. In the case of direct feed *via* a by-pass to the MeOH synthesis reactor, a singlestage  $H_2$  compression step is deemed technically appropriate. If sourced from  $H_2$  storage, a maximum pressure of 200 bar is available. For the compression of the PEMEL  $H_2$  product stream for storage (*i.e.* 30 to 200 bar), a two-stage reciprocating compressor is considered. For the  $CO_2$  stream where a compression from ambient to 40 bar pressure is necessary, a two-stage reciprocating compressor is utilised. The compressor specifications are based on the manufacturer's operational details (*e.g.* in terms of energy demand).

### MeOH production and distillation

The hydrogenation of  $CO_2$  takes place under exothermal reaction conditions (eqn (1)–(3)). The final theoretical MeOH yield is based on a stationary simulation model generated using the ChemCAD® software platform. The selected reactor type is designated as an ideal adiabatic tube reactor with a reaction pressure of 40 bar.<sup>42</sup> For calculation of the  $CO_2$  amount needed for MeOH production, a per pass conversion efficiency of 90% is adopted resulting in 10% of the  $CO_2$  feed not being converted to



Fig. 3 Operating ranges for scenario 5: 'wind electricity driven, flexible' methanol production.

MeOH. Evaluation of the simulation is based on the results produced from the hydrogenation of  $CO_2$  on a lab scale MeOH production facility operated at Fraunhofer ISE. In this study, the total theoretical amount of MeOH produced varies between 4000 and 10 000  $t_{MeOH}$  a<sup>-1</sup>.

## Economic analysis – general framework

To establish a fair economic evaluation, the framework conditions for the study have to be defined (Table 2). Referring to the energy needed for eMeOH production, calculations include the electric energy demand. A large share of thermal energy demand results from distillation and is mainly covered by the exothermal MeOH synthesis. Cooling duties and advanced heat integration are not yet considered and will be addressed in a later report. Where possible, the economic evaluation is based on price data from manufacturers within the model market (*i.e.* Germany). Otherwise, values are taken from literature sources as indicated and adjusted accordingly for use with eqn (4).<sup>61</sup>

$$\operatorname{Co}_{1} = \operatorname{Co}_{2} \left( \frac{C_{1}}{C_{2}} \right)^{m} \tag{4}$$

Co<sub>1</sub>: plant costs new, Co<sub>2</sub>: plant costs old, C<sub>1</sub>: plant capacity new, C<sub>2</sub>: plant capacity old, and *m*: digression coefficient = 0.67.

If not included in the component's investment cost, additional costs for delivery and setup are added at a proportionate share of the total investment cost (TIC). Maintenance costs are either based on literature values for the specific component or comparable processes. Not considered in this economic evaluation are costs associated with land, buildings or employees. As mentioned earlier, alongside MeOH, the by-product of  $H_2O$ electrolysis, namely  $O_2$ , is also considered as a valuable product in the plant and its potential sales are also included. Credit for

#### Sustainable Energy & Fuels

Economic assumptions: plant investment & operating expenses Table 2

Recovery period	10 years	_
Interest rate	2.5% p.a.	Ref. 62
PEMEL specific investment	800€ kW <sup>-1</sup>	Ref. 48, 49, 63 and 64
PEMEL grid connection	$66 \in kW^{-1}$	Ref. 48
PEMEL stack life-time	50k hours	Ref. 64
PEMEL stack reconditioning cost	2.0% of spec. invest.	Ref. 64
PEMEL maintenance & insurance	2.0% of spec. invest.	Ref. 64
H <sub>2</sub> storage specific investment	Depending on storage size	Ref. 65
H <sub>2</sub> storage maintenance & insurance	2.0% of spec. invest.	Ref. 62
MeOH synthesis specific investment	$810 \in t^{-1} a^{-1}$	Ref. 66
MeOH synthesis maintenance & insurance	10.0% of spec. invest.	Ref. 66
Other installation maintenance & insurance	2.0% of spec. invest.	Ref. 62
Technical staff	14 h per week at 100€ $h^{-1}$	Own estimate
Plant buildings and facilities	7.0% of spec. invest.	Ref. 64
Engineering, planning, delivery, and setup	Inspired by internal experiences	—

 $O_2$  is considered at  $50 \in t(O_2)^{-1}$ ,<sup>67</sup> which is a relatively conservative value. Atsonios et al.29 and Matzen et al.30 considered a credit of *ca.*  $75 \in t(O_2)^{-1}$  for their calculations (see Table 5) (NB: any possible future increase of installed electrolysis capacity may act to decrease the impact of the O2 market value, unless a large increase in oxidation chemistry is anticipated).

The supply cost of CO<sub>2</sub> differs for different sources. From the considered biogas plant source, the CO<sub>2</sub> production cost is assumed to be  $0 \in t(CO_{2,capt.})^{-1}$ , as this is essentially a waste product from biogas cleaning and therefore, the cost for separating CO<sub>2</sub> is assigned to CH<sub>4</sub> production cost. Based on ammonia production, CO<sub>2</sub> capture costs are  $3 \in t(CO_{2,capt})^{-1}$ . Furthermore, assuming that avoided CO<sub>2</sub> emissions will also be considered within the European Emission Allowances (EUA) in the near future, a projected price of  $-10 \in t(CO_{2,emitt.})^{-1}$  is obtained. These allowances are tradable and the resulting CO<sub>2</sub> feedstock price is  $-7 \in t(CO_2)^{-1}$  (Table 3). Biogas treatment plants do not take part in the EUA trade, since the emitted CO2 is of biogenic origin.

The operating and full load hours of the PEMEL and the MeOH synthesis reactor differ for the different scenarios. For purely wind electricity driven scenarios, the PEMEL full load hours are in the range of 3585 to 3896 h  $a^{-1}$  and the operating hours (the period during which the PEMEL is operational at any load factor) at 7044 h  $a^{-1}$  (Table 4). The costs for maintenance and replacement of the PEMEL stacks do reflect the specific operating hours and a predicted stack life-time of 50 000 h. Furthermore, the yearly amortisation payments are calculated based on a linear depreciation over 10 years.

	Biogas treatment plant	Ammonia plant
Capture cost $[ \in t(CO_{2,capt.})^{-1} ]$	Excluded	3
CO <sub>2</sub> certificate price $[ \in t(CO_{2,emit.})^{-1} ]$	0	-10
CO <sub>2</sub> feedstock price $[ \in t(CO_2)^{-1} ]$	0	-7
Output pressure [bar]	Atmosph.	Atmosph.
Environmental burden	Biogenic origin	Fossil origin

## Results and discussion

## **Investment cost**

The TIC for every investigated scenario is found to be within the margin of 14.4–27.1 M€ (Fig. 4). The TIC is strongly influenced by the investment cost related to PEMEL use. The PEMEL is a necessary procurement, with an assumed cost of 800€ kW<sub>inst</sub><sup>-1</sup> without and 866€ kW<sub>inst</sub><sup>-1</sup> with grid connection related to installed capacity (kWinst). Considering that the midterm (for the year 2023-2030) cost of a PEMEL on the MW-scale ranges from 750 to  $1600 \in kW_{inst}^{-1}$ ,  $^{48,49,63,64}$  these values can be seen as an optimistic target value. The European Multi-Annual Implementation Plan of the Fuel Cells and Hydrogen Joint Undertaking (FCH JU) targets 720€ kW<sub>inst</sub><sup>-1</sup> for PEMEL systems with production capacities <1000 kg(H<sub>2</sub>) d<sup>-1.51</sup> Schmidt et al., based on interviews with experts from industry and academia, quantify PEMEL specific investment in 2030 between 850 and 1650€ kW<sub>inst</sub><sup>-1</sup> under the assumption of no changes in technology funding and without a production scale-up. Intensified R&D funding as well as a production scale-up could lead to a further 24% reduction in specific investment.52 Saba et al. reported even lower cost estimations of 397-955€ kW<sub>HHV</sub>-output<sup>-1</sup>.<sup>50</sup>

All scenarios take a PEMEL as a basis, even though the gridconnected scenarios would be able to function reasonably using an AEL electrolyser. As mentioned earlier, the TIC will likely decrease in the future as a consequence of further technology development, efficiency improvements, and more widespread use, with a target value of 440€ kW<sup>-1</sup> considered desirable for large water electrolysis systems >10 MW.67 The 12 MW PEMEL included in this investigation has a TIC of 9.6 M€ (without a grid connection) and 10.4 M€ (with grid connection), representing ca. 60-70% of the TIC of the overall process. An exception to this observation is the wind-driven scenario using a non-flexible MeOH reactor (scenario 6), since a large  $H_2$ storage is included, representing a significant expense in itself (*i.e.* TIC (PEMEL) = 35%; TIC (PEMEL +  $H_2$  storage) = 79%). Mignard et al. arrived at a similar conclusion in a previous report where the electrolyser's share of the TIC is within 65-82%, by far the biggest share, followed by the H<sub>2</sub> storage and

	Grid connected constant supply	Grid connected electricity price driven	Wind electricity driven flexible	Wind electricity driven non-flexible
PFM-electrolysis – production capacity [t $a^{-1}$ ]	1906	992	791	1210
PEM-electrolysis – energy demand [GWh $a^{-1}$ ]	100.80	55.44	43.02	46.75
PEM-electrolysis - operating/full load hours [h]	8400/8400	8400/4620	7044/3585	7044/3896
Hydrogen storage – volume [m <sup>3</sup> ]	_	6	345	2840
Carbon capture – capturing capacity $[t a^{-1}]$	15 225	7765	6392	9780
Methanol reactor – production capacity [t $a^{-1}$ ]	10 031	5139	4188	6408



Fig. 4 Investment cost (CAPEX) of the different plant scenarios in M€.

compression cost, with a share of 9-16%.27 The impact of investment in the MeOH reactor depends on the annually produced MeOH, which is assumed in this study to be  $810 \in t^{-1}$  $a^{-1}$ .<sup>66</sup> Therefore, the grid connected scenario without H<sub>2</sub> storage (scenario 1) has the highest MeOH reactor cost (3.3 M€), since this scenario produces the greatest amount of product. The potential of additional cost for a flexible reactor is not considered in detail. Excluding this mentioned scenario, the MeOH synthesis reactor's influence is comparatively low. For future assessments a detailed investigation of the cost incurred by a dynamic reactor design should be included. Additionally, since methanol from syngas with high CO<sub>2</sub> content and H<sub>2</sub> potentially offers higher purity (free of most ketones, paraffins and other by-products) compared to methanol from syngas, a reduced demand for distillation could have a cost decreasing effect.23,69

### **Operational & annual costs**

Each scenario has a different operational mode with different resulting operating costs, ranging between 4.00 and 12.93 M€

 $a^{-1}$  (Fig. 5). It can be seen that the main factor is electricity cost, as long as a reduction in taxation/fees is not possible (left bar of each scenario). In that case, the operational cost (OPEX) is ca. 2.5 times higher than in scenarios including a reduction, which results in a share of electricity cost of ca. 70-81% of the OPEX (with 45-59% reduction). Wind energy-based scenarios however indicate that the electricity cost share lies approximately between 42 and 44% and therefore represents a reduction relative to grid-connected scenarios. Due to the high electricity demand of the PEMEL, slight changes in the electricity price have significant impacts on the electricity cost. A similar observation was made by Atsonios et al.29 Although this report assumed a low electricity price of 2.9-5.0 ct€ per kWh, electricity still represents the largest share of the OPEX. The CO<sub>2</sub> feedstock costs by comparison (e.g. for ammonia plant scenarios) are very low (*i.e.* 19 000–46 000  $\in a^{-1}$ ). As mentioned earlier, the trade of the EUA in the amount of recycled CO<sub>2</sub> is assumed to be possible in the near future. Since this generates a negative value, it may even lead to positive revenues (Table 3). However, the assumed certificate price is very low at the current time (ca.  $10 \in t(CO_2)^{-1}$ ) and the revenue, based on current values, is accordingly small. It is important to consider that the EUA value is increasing and a rise to just  $30 \in t(CO_2)^{-1}$  would lower the OPEX by between 1.7 and 5.0% (or 0.17–0.3 M $\in$  a<sup>-1</sup>).

### Methanol production cost

The eMeOH production cost (MPC) is calculated using eqn (5).

$$C_{\rm spec.} = \frac{A + C_{\rm total}}{M_{\rm total}} \tag{5}$$

 $C_{\text{spec.}}$ : specific production cost, *A*: annuity,  $C_{\text{total}}$ : annual operational cost, and  $M_{\text{total}}$ : total amount of produced methanol.

Currently, the MPC of all considered scenarios (Fig. 6) is above the actual market price (*i.e.* Methanex average 2017 (Jan to June):<sup>70</sup> 410 $\in$  t(eMeOH)<sup>-1</sup>), which has featured a low-level upward trend of +3.20 $\in$  per month over the last 2.5 years. The scenario with the lowest MPC (scenario 2B, grid connected with constant supply, fee reduction, without H<sub>2</sub> storage, CO<sub>2</sub> from biogas, 608 $\in$  t(eMeOH)<sup>-1</sup>) costs 1.5 times the possible market revenues, whereas the most uneconomical scenario (scenario 3A, electricity price driven, without fee reduction, with H<sub>2</sub> storage, ammonia, 1453 $\in$  t(eMeOH)<sup>-1</sup>) is 254% above the 2017 market price level. The electricity price has a huge impact on the MPC: where a fee reduction is not possible, MPCs are in the



range of 1284 to  $1453 \in t(eMeOH)^{-1}$ . If taxation and fees do not have to be paid in full, the MPC will decrease to  $608-782 \in$  $t(eMeOH)^{-1}$ . The wind driven scenarios feature MPCs in the range of  $1028-1067 \in t(eMeOH)^{-1}$ , which are characterised by large H<sub>2</sub> storage capacities and associated high investment costs.

In this study, a positive value of  $50 \in t(O_2)^{-1}$  for selling the electrolyser by-product was used. Previously Atsonios et al. considered an O<sub>2</sub> revenue of  $87 \in t(O_2)^{-1}$  reflected in a decrease in eMeOH production cost (ca. 10% reduction as a consequence of O<sub>2</sub> sales).<sup>29</sup> Matzen et al. also included O<sub>2</sub> sales in their process evaluation and concluded that a price of  $75 \in t(O_2)^{-1}$ had a positive impact on the economic feasibility of their process.<sup>30</sup> Likewise, Rivarolo et al. assumed a much higher market value of  $150 \in t(O_2)^{-1}$ .<sup>34</sup> Compared to the  $50 \in t(O_2)^{-1}$ used in this study, this results in a difference of 150€  $t(eMeOH)^{-1}$  (1.5  $t(O_2)$   $t(eMeOH)^{-1}$  produced). For further analysis a detailed evaluation of the necessary process steps for pressurizing, bottling and transportation of O2 has to be included as well as a discussion of the development of the O2 market price in the case of increasing market penetration for electrolyser technology.

#### Sensitivity study

The economic feasibility of PtM is influenced by a number of parameters, and it is essential to know which parameters, besides the obvious electricity price, have a high impact on the process economy. Therefore, a sensitivity study was performed for the wind-powered, flexible MeOH synthesis based on biogas-

derived CO<sub>2</sub> (scenario 5B). Based on a biogenic CO<sub>2</sub> source and a local supply of wind power the chosen scenario represents the most preferable option up to now regarding the establishment of a sustainable eMeOH production route. Only one parameter has been varied at a time; the unchanged parameters are based on the one set for the economic evaluation of scenario 5B (see also Table 2). Displayed are the costs (negative slope) and benefits (positive slope); the steeper the slope the stronger the influence of the parameter on the process economy (Fig. 7). The most important factor is identified to be the MeOH selling price, since it has a direct impact on the specific profit. Increasing MeOH selling prices are consequently directly visible in the process economics. The electrolyser investment is another important impact factor. At 12 MW, a reduction of the specific investment has a large impact on the TIC. A specific investment reduction of only -10% leads to an investment decrease of 1 M $\in$  (-6.2% of the TIC). If an investment target value of  $440 \in kW^{-1}$  for water electrolysis systems could be reached, the TIC would decrease by an amount of *ca.* 4.3 M€ (-27% of the TIC). Regarding the expected price decrease of the PEMEL, eMeOH production costs should decrease in the long term. Thirdly, as already discussed in the context of operational cost, the electricity price has a strong impact on the overall process economy. Marginal changes in electricity price are directly visible in the eMeOH production cost. Therefore, the availability of green but inexpensive electricity (e.g. in periods of excess or over-production and regions with significantly lower RE generation costs) is a basic prerequisite for an economic elaboration of PtM. Although the investment in the methanol synthesis reactor is not a key indicator for the TIC, scaling-up of



the methanol reactor will also have a decreasing effect on the reactor specific investment cost and hence on the TIC of the PtL systems. Hence, to improve the economic viability of PtM and decrease the difference between the current market price level and the production cost, the above-mentioned parameters are important starting points to be considered and in turn optimised.

### Evaluation

To provide an overview and classification of the results generated from this study, in comparison with previously reported studies and data, Table 5 has been compiled. In this comparison, monetary values that were not given in  $\in$  were calculated based on a time-dependent currency exchange rate (the average exchange rate in the year of the study). For a better comparability of the values, eMeOH production costs were also converted based on the current currency exchange rate (average 2017). For the calculation of production capacity, 350 days per annum were assumed if no value for working h  $a^{-1}$  was available. All values not directly stated in the studies were calculated on the basis of the available values (where possible).

Due to the different parameter assumptions used in the calculation of eMeOH production costs, the results vary considerably from study to study. Therefore selection of system boundaries, system components and framework conditions is critical as they have a significant impact on the final results and as a consequence, different studies should be compared carefully.



Fig. 7 Sensitivity study for the wind powered, flexible synthesis based on biogas-derived CO<sub>2</sub> (scenario 5B).

Electricity		Electrolyse	r		$CO_2$		Storage		Methanol r	eactor + dist	illation			
Source	Price [ct€ per kWh]	Type	Spec. invest [€ kW <sup>-1</sup> ]	${ m O}_2$ price $[\in { m t}_{{ m O}_2}^{-1}]$	Source	Spec. $\operatorname{cost}^a$ $[\in t_{\operatorname{CO}_2}^{-1}]$ $\mathrm{a}^{-1}]$	$H_2$	CO <sub>2</sub>	Spec. invest <sup>b</sup> [ $\in$ t <sub>MeOH</sub> <sup>-1</sup> ]	Plant capacity [t d <sup>-1</sup> ]	Pressure level [bar]	Plant depreciation time [a]	Methanol production cost $[\in t_{MeOH}^{-1}]$	Source
Grid	3.74-	PEM 12	800	50	Biogas/	0/3	No	No	1514	29	40	10	608-1615	This
Grid	13.43 3.67- 1112	MW PEM 12	800	50	ammonia Biogas/	0/3	6 m <sup>3</sup>	No	2745	15	40	10	816–1969	study This
Wind	14.13 4.4	MW PEM 12	800	50	ammonia Biogas/	0/3	345 m <sup>3</sup>	No	3830	12	40	10	1040-1051	study This
onsnore Wind	4.4	MW PEM 12 MW	800	50	ammonia Biogas/	0/3	2840 m <sup>3</sup>	No	4144	19	40	10	956–967	study This study
Hydro	1.3		I	I	Flue gas/ atmosphere	I	I	I	I	200	I	15	258/387	1999- Specht
Hydro power	2.5	Ι	Ι	I	CPP/ atmosphere	I	I	I	Ι	200	Ι	15/20	529/717	and Bandi 1999- Specht
RES	1.5 - 2.2	AEL 100/ 500 MW	422-1409	102	Flue gas (CPP)	I	Floating head/ pressurised	I	1299- 2420	178-372	50	15	$498-711^{c}$ $429-613^{d}$	et al. 2003- Mignard et al.
Grid/RES	4	AEL 2 MW	200	Sold/used	Flue gas (CHP)	15	100–900 t <sub>H2</sub> underground	No	I	890	144	I	555	2010- Clausen
Grid/CPP	2.9–5	AEL 140 MW	376	87	Flue gas (CPP)	44	gas storage Partially	I	I	318	65	25	870-913	et al. 2015- Atsonios
Wind	6.3	AEL 41 MW <sup>e</sup>	440	75	Ethanol plant	I	Pressurised storage	Liquid storage	850	97	50	10	$324{-}781^c$ $389{-}938^d$	et al. 2015- Matzen
CPP	9.5-12.1	fsg	٦	٣	Flue gas (CPP)	0	I	I	497	1320	76	20	724	<i>et al.</i> 2015- Perez- Fortes
٦	9.3	u'f	٣	٦	Purchased	50	Yes <sup>f</sup>	No	1329	138	75	10	980	<i>et al.</i> 2015- Tremel
RES	2.6/3.3	SOEC 50 MW	I	Used	Flue gas (CPP)	20	I	Buffer storage	1000	96/235	I	20	450/484	et al. 2015- Varone et al.

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Table 5 Comparison of different PtM studies

Electricity		Electrolyser	τ.		$CO_2$		Storage		Methanol r	eactor + dist	illation			
Source	Price [ct€ per kWh]	Type	Spec. invest [€ kW <sup>-1</sup> ]	$O_2$ price [ $\in t_{O_2}^{-1}$ ]	Source	Spec. $\operatorname{cost}^{a}$ $\left[ \in \operatorname{t}_{\operatorname{CO}_{2}}^{-1} \right]$	$\mathrm{H}_2$	$CO_2$	Spec. invest <sup>b</sup> [ $\in$ t <sub>MeOH</sub> <sup>-1</sup> ]	Plant capacity [t d <sup>-1</sup> ]	Pressure level [bar]	Plant depreciation time [a]	Methanol production $\cos t$ $[\in t_{MeOH}^{-1}]$	Source
Ι	ى ا	SOEC 20 MW	1469– 5785	Sold		3-10	I	Ι	6115 (SOEC)	58 (SOEC)	78	20	5459 (SOEC)	2016- Rivera-
		PEM 24	(SOEC) 600 (PEM)						883 (PEM)	49 (PEM)			891 (PEM)	Tinoco et al.
RES	$1^{-5}$	PEM 2190 MW	700	40	Flue gas	40	I	I	1247– 2495	5003	I	15	$400-2775^{i}$	2016- Bertau
RES + grid	3-5	AEL 1 MW	I	150	Biogas/ purchase	10	I	I	I	I	80	10	I	et al. 2016- Rivarolo et al.
<sup>a</sup> Without daily need <sup>i</sup> Conversio	including CC ed hydrogen m with low <u>F</u>	)2 certificate amount for neating value	revenues. <sup>b</sup> V methanol pr (LHV), RES	Whole meth <i>i</i> oduction. <sup>f</sup> = renewabl	anol plant. <sup>c</sup> Cu Outside system e energy source	irrency exchai i boundaries. es, CPP = coi	nge rate in the ye <sup>g</sup> Assumed purc al power plant, a	ar of the s hase price nd CHP =	tudy (averag tor hydroge combined	e). <sup>d</sup> Currenc en: 3090€ t <sup>−</sup> heat and pov	y exchange  -1 h Assume wer plant.	rate of 2017 (ave) d purchase price	rage). <sup>e</sup> Calculat e for hydrogen:	ed with the 3000€ t <sup>−1</sup> .

In this context, CO<sub>2</sub> sourcing differs from study to study. Typically, flue gas of a Coal Power Plant (CPP) is used. Varone et al. evaluated an integrated oxy-fuel/co-electrolysis process, where the oxy-fuel coal plant delivers the CO<sub>2</sub> and the O<sub>2</sub> byproduct from the electrolysis is used for the oxy-fuel process.<sup>32</sup> Such combined processes are indeed logical but have not been considered thus far by other studies. Besides CO<sub>2</sub> captured from coal fired power plants is of fossil origin and should therefore not be part of a future energy system with the intention to provide sustainable fuels. The use of CO2 from the atmosphere has been considered by Specht et al.,25,26 and was recently revisited by the German-Swiss initiative of Audi, Sunfire and Climeworks.71 More recent studies have considered this possibility but assess the acquisition cost to be still too high (e.g. Bertau et al.<sup>3</sup>). The EUA has, except for this study, so far not been considered by other authors. Depending on the source, the assumed costs to provide CO<sub>2</sub> lie between 0 and  $50 \in t(CO_2)^{-1}$ .

Compared to the actual MeOH market price of 410€ t(MeOH)<sup>-1</sup> (Methanex, average 2017),<sup>70</sup> almost all reported production costs are above the market price and the production via H<sub>2</sub> and CO<sub>2</sub> is as such not considered economical (when excluding additional O2 sales). The cost of producing fMeOH from conventional processes via natural gas or coal varies depending on the geographical location of the production site between  $51 \in t(fMeOH)^{-1}$  and  $408 \in t(fMeOH)^{-1}$ . They are therefore less expensive than any process based on RE, H2 and CO2.6 If legislation or regulation regarding either RE or CO2 conversion is established (e.g. within the EU), it remains to be seen how long these relatively low prices will be maintained. The smallest difference compared to the actual price level was reported in 1999, by Specht and Bandi (i.e. an eMeOH production cost of 258-387€ t(eMeOH)<sup>-1</sup>).<sup>25</sup> This report was based on an unrealistically low electricity price of 1.3 ct€ per kWh (in 1999), leading in turn to low eMeOH production costs. However, recent reports demonstrate the rapid reduction in renewable electricity costs (e.g. solar power in Dubai<sup>72,73</sup> or Chile<sup>74,75</sup> with prices <3 ct€ per kWh).

The highest eMeOH production costs (excluding the production *via* High Temperature Solid Oxide Electrolysis)<sup>33</sup> with >2000 $\in$  t(eMeOH)<sup>-1</sup> were reported by Bertau *et al.*<sup>6</sup> In this work, eMeOH production costs depended on the electricity price and operating hours per year. With less than 2000 h a<sup>-1</sup>, the MeOH production costs rise sharply, reaching values up to 2800 $\in$  t(eMeOH)<sup>-1</sup>. Their calculations show clearly that the maximisation of operation is desirable regarding an economical production. A comprehensive PtL-overview focussing on electrofuels for the transport sector is provided by Brynolf *et al.*(2018).<sup>76</sup>

## CO<sub>2</sub> avoidance cost

The economic inefficiency of the evaluated PtM scenarios on the one hand results from the energy and capital intensive structure of the PtM process itself. On the other hand cheap production conditions in the case of fossil based methanol production are reflected in a low market price. The lack of performing legislation taking into account the environmental burdens resulting from the production and provision of fossil based syngas leads to a 'free-lunch' for coal and methane based production of

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Table 5 (Contd.

methanol. The internalization of direct and indirect environmental damage would mean further expenses for (up-stream) production processes which are very intense in terms of, for example, CO<sub>2</sub>-, CFC-11- and SO<sub>2</sub>-equivalents (eq)§ and can result in thorough land-occupation and -change. In terms of climate change and curtailing global warming CO<sub>2eq</sub>-emissions are in the focus of scientific and political discussions. We evaluated the global warming potential (besides other impact categories) in a profound life-cycle-assessment (LCA) for the 'green' methanol production. In the frame of the present study we establish a first interconnection between the higher production costs and the possibly lower CO<sub>2eq</sub>-footprint of the green methanol pathway compared to the fossil reference¶ by calculating the CO<sub>2</sub> avoidance cost:

$$CO_{2,AC} = \frac{PC_{eMeOH} - PC_{fMeOH}}{GWP_{fMeOH,C2G} - GWP_{eMeOH,C2G}}; \quad \left[ \in t_{CO_{2eq}}^{-1} \right] \quad (6)$$

The CO<sub>2</sub> avoidance cost (CO<sub>2,AC</sub>) (eqn (6)) is expressed as the ratio of the differences between the production cost (PC) of green ('electricity based') and fossil based methanol (PC<sub>eMeOH</sub> and PC<sub>fMeOH</sub> respectively) and their respective global warming potentials (GWPs).

The  $CO_{2,AC}$  can be seen as a key performance indicator when discussing the future of CCU processes and the establishment of an economy covering the majority of its C-demand with recycled carbon. It is important to note that the  $CO_2$  avoidance cost is an indicator for the connection of economic and ecological efficiency besides many other ecological parameters such as water demand and indirect land use change or occupation. For a holistic evaluation of PtM and other CCU processes and their comparison to fossil based references a multitude of economic and, even more importantly, ecological parameters have to be included in a process' evaluation.

For the production cost of green methanol the results obtained in scenarios 5B and 6B with production cost of 1028 and  $1062 \in t(eMeOH)^{-1}$ , respectively, have been used. The production costs for fossil methanol depend on geographical location, ranging from  $51 \in t(fMeOH)^{-1}$  (Saudi Arabia) to  $408 \in$  $t(fMeOH)^{-1}$  (Europe) and are dominated by the cost for the syngas feedstocks.<sup>77</sup> In order to put a price on the amount of avoided CO<sub>2eq</sub> not emitted within the European region we decided to compare 'our' green methanol pathway (mainly dominated by the German electricity prices) with any fossilbased methanol production facility located within European borders. Therefore for this evaluation the production costs for fossil methanol are set to a 'European level' of  $400 \in$  $t(fMeOH)^{-1}$ .|| It could be argued that for other regions featuring significantly lower production costs for fossil methanol such as Saudi Arabia or China the difference between cheap fossil and cost-expensive green methanol production would increase. But likewise a lower levelised cost of renewable electricity would have a clear decreasing effect on green methanol production cost and would partly balance the cheap market conditions for the fossil production.

Regarding the GWP for the green methanol production the values are based on a life cycle assessment based on hydrogen from a wind-powered PEM electrolyser in combination with CO<sub>2</sub> from a biogas upgrading plant\*\* (representing scenarios 5B and 6B). The LCA was performed using the Umberto NXT Universal software with the Ecoinvent-v3.3 database. With a GWP of 506 kg( $CO_{2eq}$ ) t(eMeOH)<sup>-1</sup> during the production phase and an uptake ('molecular binding') of 1374 kg( $CO_2$ ) t(eMeOH)<sup>-1</sup><sup>††</sup> the PtM process can be seen as 'netto-negative'  $(506-1347 = -868 \text{ kg}(\text{CO}_{2eq}) \text{ t}(\text{eMeOH})^{-1})$  in terms of  $\text{CO}_{2eq}$ emissions when evaluated by a cradle-to-gate approach. Expanding the system boundaries by containing also the utilisation of the produced methanol (cradle-to-grave, C2G),<sup>‡‡</sup> all C-content will be oxygenated (1388 kg( $CO_{2eg}$ ) t(MeOH)<sup>-1</sup>) again and released into the environment. Utilisation could be in the MeOH-form as a partial fuel substitute or further processed to downstream derivatives such as DME or OME<sub>3-5</sub>. In this case the resulting cradle-to-grave emissions would add up to 520  $kg(CO_{2eq}) t(eMeOH)^{-1}$ .§§

As a reference for the GWP of a European based fossil methanol production process we used the Ecoinvent process 'methanol production [GLO] from natural gas'. ¶ Where possible the contained activities have been adjusted to an assumed methanol production in Europe. This accounted for the supply of natural gas for syngas production and the market for electricity as well as the provision of tap water. The adjusted EU-based fossil methanol production results in slightly higher specific CO<sub>2eq</sub>-emissions (cradle-to-gate: 526 kg(CO<sub>2eq</sub>)  $t(fMeOH)^{-1}$  (global) vs. 623 kg(CO<sub>2eq</sub>)  $t(fMeOH)^{-1}$  (EU-based)) which mainly arise due to the transport intensive provision for the syngas production with natural gas/process heat in Europe (GWP<sub>100a</sub>: +18.3 and +33.4% resp.). Concurrently the electricity supply shows a lower GWP (GWP<sub>100a</sub>: -36.0%) presumably due to higher efficiencies in fossil electricity production and higher shares of renewables within the EU. For fMeOH also a complete oxygenation of the C-content is assumed for the utilization phase (1388 kg( $CO_{2eq}$ ) t(fMeOH)<sup>-1</sup>) resulting in cradle-to-grave- $CO_{2eq}$ -emissions of 2011 kg( $CO_{2eq}$ ) t(fMeOH)<sup>-1</sup>.

Based on these values the  $CO_2$  avoidance costs are  $421 \in t(CO_2)^{-1}$  (scenario 5B) and  $444 \in t(CO_{2eq})^{-1}$  (scenario 6B) giving

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 $<sup>\</sup>P$  In this evaluation: methanol production based on syngas from steam-reforming of natural gas.

<sup>||</sup> In the case of assuming lower fossil MPC for example for any production facility in Saudi Arabia or China, the green MPC would also decrease presumably because of lower renewable electricity generation cost (PV electricity in Abu Dhabi @ 2.45 ct€ per kWh; in Chile @ 2.91 ct€ per kWh; and levelised cost of electricity for large PV plants within the G20 states below 4.10 ct€ per kWh).

<sup>\*\*</sup> To be reported in a forthcoming article.

<sup>†† 41</sup> kg of CO<sub>2</sub> are vented during the synthesis step. Therefore 1388-41 = 1347 kg of CO<sub>2</sub> per t(eMeOH) are 'bound' in the product.

<sup>&</sup>lt;sup>‡‡</sup> The cradle-to-grave assessment does not consider impacts resulting from transportation of the produced methanol and any recycling of the infrastructure. However it is assumed that impacts resulting from these phases in the eMeOH and the fMeOH are in a comparable range.

<sup>§§</sup> GWP100a, method CML 2001, allocation cut-off.

 $<sup>\</sup>P$  Original ecoinvent activity methanol production [GLO]: GWP<sub>100a</sub>: 52 545 kg(CO<sub>2eq</sub>); method CML 2001, allocation cut-off.



Fig. 8 Estimation for the future development of green methanol production cost and CO<sub>2</sub> avoidance cost in the case of fossil methanol substitution.

emitted CO<sub>2</sub> significantly higher prices than the recent prices envisioned by the European Emission Trading Scheme (EU-ETS) with CO<sub>2</sub>-certificate prices of *ca.*  $5 \in t(CO_{2eq})^{-1}$  for the last 12 months (Sept 16 to Aug 17).

# Future development of methanol production cost & the corresponding CO<sub>2</sub> avoidance cost

For future development of the parameters until 2035 we assumed the development of some central sensitive parameters. The initial point for this assessment sets scenario 5A. Parameters are set considering in-house studies for the decrease of large-scale PEMEL specific cost (2035 (a)  $300 \in kW_{inst}^{-1}$ ), a significant increase in CO<sub>2</sub> certificate prices (2035 (a)  $80 \in t(CO_2)^{-1}$ ),<sup>78</sup> and a further decrease in the levelised cost of renewable electricity in general and PV-electricity in particular (2035 (a)  $1.8 \text{ ct} \in \text{per kWh}_{el}$ ).<sup>72-75</sup> The resulting predictions in green methanol production costs and the corresponding CO<sub>2</sub> avoidance costs are compared with a constant (business as usual, 'bau') and the exponential forward projection of the methanol market prices ('exp') based on the Methanex European posted contract price for the last 15 years.<sup>70</sup>

Fig. 8 contrasts the resulting development of eMeOH with an increasing methanol market price, demonstrating a prediction for market parity in *ca.* the year 2032. At around the same time the  $CO_2$  avoidance cost will turn negative (based on the assumptions made regarding investment and operational costs) which can be interpreted as the market offering an economic incentive to the industry for utilising their  $CO_2$  emissions instead of emitting them. These points of time fit the published results for the development of the market demand for electrolyser technology showing a clear market launch from the year

2032.<sup>78,79</sup> Furthermore a future increase of the GWP for fMeOH production could be assumed due to the necessity of a more intensive exploration of fossil resources and longer transport distances. This would have an additional lowering effect on  $CO_2$  avoidance cost, which was not considered here.

## Conclusions

The presented evaluation shows that the economic feasibility of a specific PtL process (*i.e.* for eMeOH) strongly depends on electricity and  $H_2$  production cost,  $CO_2$  cost (also reflecting any introduced carbon taxes), specific electrolyser cost and the possible dynamics of the methanol reactor (having an impact on the necessity and size of  $H_2$  storage). Furthermore, indirect parameters such as carbon taxes will have an impact on the willingness of the market to pay for eMeOH (and derived sustainable chemicals) and as such can be considered desirable.

Under the evaluated process conditions in this study, the production of eMeOH in Germany is currently not economically competitive, if one presupposes the competition with fossil based large capacity methanol production and its current low price. The investment and operational costs are currently inhibitory and therefore, the eMeOH production price exceeds the expected revenues. Currently, conventional large scale methanol production based on  $CH_4$  reforming has a very low price due to very inexpensive fossil supply (*e.g.* from increased fracking in the USA and increased production of fMeOH from coal in China). A high degree of capacity utilisation is advantageous and favourable for low eMeOH production cost. Therefore maximised plant operation (*e.g.* in terms of hours) is also to be highlighted as an important factor in achieving eMeOH economic feasibility.

 $<sup>\|||</sup>$  EU CO $_2$  Emission Allowances (Sept 16 to Aug 17) according to the European Energy Exchange.

The presented sensitivity study demonstrates that a decrease in the specific investment costs of the PEMEL leads to a major economic efficiency improvement for the described PtM process. Heading towards the target value for specific electrolyser investment (target value:  $440 \in kW^{-1}$ ) is in general an important step towards the economic feasibility of PtL-systems. The low-emission eMeOH production scenario (wind energy driven) had a higher production cost due to the additional requirement for H<sub>2</sub> storage (*i.e.* 2<sup>nd</sup> largest share of investment costs). A reduction in specific H<sub>2</sub> storage size and costs would therefore be beneficial. The possibility of underground  $H_2$ storage in salt caverns (e.g. in northern Germany) depends on local conditions but offers a promising way for mitigating the strong interlinkage between H2 storage volume and its associated investment costs.64 In the long-term it will be necessary to offer possibilities for a more dynamic operation of the synthesis step to reduce the storage demand for H<sub>2</sub>.

To successfully introduce any PtL process, it is initially important to think of potential synergies: the methanol production of Carbon Recycling International is underpinned by low-cost geothermal electricity and CO<sub>2</sub> from a geothermal power plant (located adjacent to the plant). Thyssenkrupp AG is aiming to significantly cut their CO<sub>2</sub> emissions by utilising the waste gases from steel production (coupled with additional H<sub>2</sub> production) to generate side streams of fuels and chemicals.<sup>80</sup> The presented PtL scenarios are all on a small-scale compared to fossil based plants on the Mt-scale. Future large-scale PtLplants, coupled with existing chemical or heavy industry, would also have a number of advantages: instant access to low-cost grid electricity, availability of (highly concentrated) CO<sub>2</sub> streams (which still need purification) or unused  $H_2$  in off-gases, if necessary access to HT-process heat/steam and last but not least, the vast cost-reducing effect of a PtL plant scale-up.

Regarding policy instruments to support the introduction of economically viable PtL schemes, amendment of general policy frameworks and taxation systems (e.g. special grid fees for energy storage and grid-supporting technologies, and an improved European Emission Trading System) would be beneficial. A modified taxation system for CO2 emissions could generate a CO<sub>2</sub> certificate price and market conditions appropriate for an industrial business case for CCU. Another approach could be a tax reduction for "renewable fuels". The gradual reduction of fossil fuel subsidies would also aid in the long term attractiveness of PtM schemes, particularly as the amount of the RE share in the electric grid increases. The proposed 'double counting'\*\*\* of 2<sup>nd</sup> generation biofuels according to the revision (iLUC Directive 2015/1513/EC<sup>81</sup>) of the RE directive RED (2009/28/EC<sup>82</sup>) is a first step when also including CO2-based fuels. Regarding fossil-based production, environmental costs and impacts are generally not internalised and therefore factoring environmental burdens would lead to

a higher price of fMeOH. One example is the introduced foundation for climate protection and  $CO_2$ -compensation (Foundation for Climate Protection and Carbon Offset (Stiftung Klimaschutz und  $CO_2$ -Kompensation, Klik)),<sup>83</sup> following the revision of Swiss  $CO_2$ -law. It commits producers and distributors of fossil fuels to provide compensation for the environmental impacts of their products and in turn provides investment in funding programs focusing on Swiss GHG emission reduction.

The presented analysis highlights that the CO<sub>2</sub> avoidance costs for the evaluated wind electricity based scenarios are currently in the range of 421-444€ t(CO<sub>2eq</sub>)<sup>-1</sup> avoided and strongly depend on the process and market conditions within the selected scenarios. The process conditions (electrolyser efficiency, synthesis pressure, source of CO<sub>2</sub>, etc.) not only influence eMeOH production cost but also the results for the  $CO_{2eq}$  footprint and thus the  $CO_2$  avoidance cost. It has been shown that for future technological optimisation of some CCU key components (resulting in the improvement of central economic process parameters) even for cost intensive 100% RE based set-ups the green methanol production cost can be strongly decreased (543  $\in$  t(eMeOH)<sup>-1</sup>, -47%, scenario 5A) within the next two decades bringing market competitiveness with fossil based methanol within the realms of possibility. In the same time frame the CO<sub>2</sub> avoidance cost will feature a clear drop (-124%) resulting in negative values and through this provide an incentive for industries to reinterpret their CO<sub>2</sub> emissions from waste to feedstock.

It is important to consider that the CO2 avoidance cost should be used only as one key-criterion for the selection among the variety of possible CCU processes.84 In combination with the specific CO<sub>2</sub> avoidance potential of each PtL-/CCU-technology, the most cost- and eco-efficient routes should therefore be selected. In this context, a detailed Life Cycle Assessment (LCA) is mandatory to identify the specific CO<sub>2</sub> avoidance cost and potential. Positively, the analysed technology will be supported by (and also support) the rapidly growing and intended expansion of RE (e.g. in Germany and the EU in general) over the next few decades. This growth will necessitate consideration of technologies such as PtL, further supported in terms of economic readiness by the ever reducing RE price per ct€ per kWh. PtX technologies will be one important pillar of the integrated-energy concept ('sector-coupling') within the European markets of electricity, heat and mobility. Further postponement of integrating renewable energies in the mobility sector and chemical industries will further impede the climate protection programs.79

Our results demonstrate that off-grid wind electricity is promising for eMeOH production, but in the case of an isolated wind energy system and without large  $H_2$  storage it cannot ensure a high degree of capacity utilisation. For realisation of an off-grid renewable PtL process, the coupling of wind power with photovoltaic or solar thermal electricity generation and/or additional baseload supplies (*e.g.* biogas plants or combined heat and power plants based on biomass, offering also a biogenic CO<sub>2</sub> point source) would lead to higher capacity utilisation and a reduced storage demand. Thinking globally,

<sup>\*\*\*</sup> Double counting of advanced/second generation biofuels: regarding the extension of the Renewable Energy Directive (RED) 2009/28/EC (28.04.2015) member States must ensure that 10% of the final energy consumption in the transport sector is provided by renewable sources. The share provided with advanced/second and/or third generation biofuels is double weighted.

relocation to regions with higher solar irradiance (e.g. the Maghreb region, Australia or south western parts of North America) and/or reliable wind power (e.g. Chile, Peru, South Africa, or Scandinavia) offers the possibility of a low cost RE supply. Low cost RE electricity of around 2.5 ct€ per kWh<sub>el</sub> (reflecting recent price bids for PV electricity<sup>72-75</sup>) and a higher degree of capacity utilisation due to a less fluctuating RE potential MPC of  $\sim 500 \in t(eMeOH)^{-1}$  and below are in a realistic range. Regions with a current and prospectively low RE production cost provide opportunities for the further development of a business case for PtL (and PtX) technology within the coming decade. Further installation of pilot plants and the associated operational experiences, coupled with expected economies of scale, will lay a path to improved PtL economics, even in countries where RE electricity costs are currently prohibitive.

## Conflicts of interest

There are no conflicts to declare.

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