



Assessing the techno-environmental performance of CO₂ utilization via dry reforming of methane for the production of dimethyl ether



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ABSTRACT

CO₂ utilization is gaining attention as a greenhouse gas abatement strategy complementary to CO₂ storage. This study explores the techno-environmental performance of CO₂ utilization through dry reforming of methane into syngas for the production of dimethyl ether (DME). The CO₂ source is a hydrogen production unit at a refinery, where solvent based CO₂ capture is applied. Aspen+ modelling and hybrid life cycle assessment (LCA) is used to assess the techno-environmental performance of this utilization option compared to a reference case without CO₂ capture and a case with CO₂ capture and storage. Results of the technical assessment show that although 94% of the captured CO₂ can be utilised for DME production, only 9% of CO₂ is avoided in the entire process as a result of direct CO₂ formation during DME synthesis and the combustion of syngas to provide the heat demanded by the dry reforming process. Besides, a substantial amount of electricity is required for syngas compression. Consequently, the LCA results indicate that climate change potential (CCP) is reduced by 8% while it is 37% higher than CCP when CO₂ is stored and DME is produced conventionally. Sensitivity analyses are performed on various process conditions. Overall, this study indicates that this utilization route lowers the CCP although the reduction is limited compared to CCS. While the techno-environmental analysis is a useful tool to gain better insights in the performance of CO₂ utilization options, the complex environmental trade-offs make it difficult to draw robust conclusions on the performance.

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1. Introduction

CO₂ capture and storage (CCS) is an essential technology to reduce the amount of greenhouse gas (GHG) emissions and mitigate climate change in the future [21,22]. CCS can be an attractive addition to other GHG reducing technologies as it can reduce GHG emissions without replacing fossil fuels, it can achieve net negative GHG emissions when combined with sustainable biomass and, it can be applied to industrial processes as well as to the power sector. Initially, CO₂ capture research has mostly focused on long term CO₂ storage, but CO₂ utilization options are gaining attention as alternative for CO₂ storage especially in scenarios where CO₂ storage is not feasible or economic incentives for CO₂ utilization are available. Potential CO₂ utilization options include enhanced oil recovery (EOR), biological conversion, mineralisation

and chemical conversion into chemicals, fuels or materials such as plastics [30,36].

Converting CO₂ into fuels or fuel additives is an interesting CO₂ utilization option as the transport sector has become a large contributor to GHG emissions. However, reforming CO₂ requires a large amount of additional energy due to the chemically non-reactive nature of CO₂. The potential of reforming CO₂ into fuels is considered limited, as the amount of energy required for the production of fuel can exceed the amount of energy that can be recovered, making it only a viable option when excess (renewable) energy is available [43]. CO₂ utilization into fuels is thus often referred to as an option to convert excess (renewable) energy into useable fuels [32,36,43].

Fig. 1 depicts the most common chemical conversion routes of CO₂ into fuels and fuel additives. Hydrogenation of CO₂ is extensively researched in literature [5,36] as it provides a direct route to methanol, a very useful chemical feedstock which can directly be used as a fuel (additive) or as an intermediate to produce more advanced fuels [5,32,36]. Other conversion routes,

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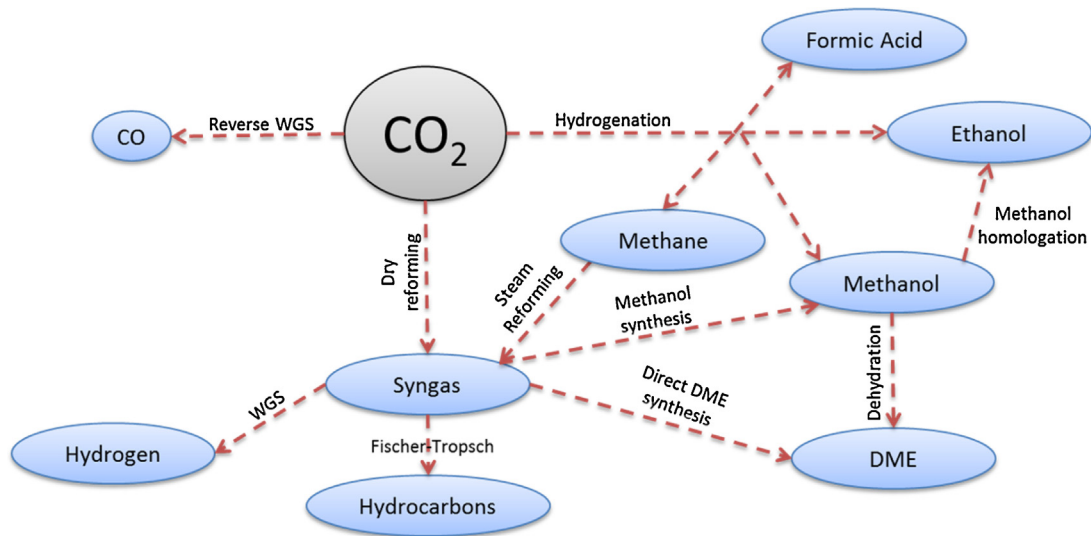
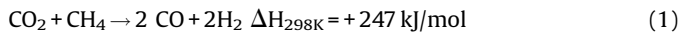


Fig. 1. Schematic representation of main production routes of CO₂ utilization into fuel.

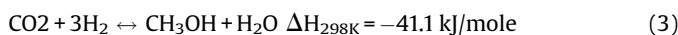
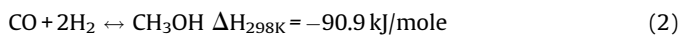
such as reversed water gas shift or dry reforming of methane can be used for the production of syngas [36].

Dry reforming of methane is a highly endothermic reaction of CO₂ and methane producing syngas:



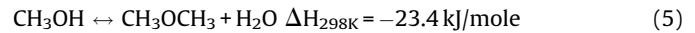
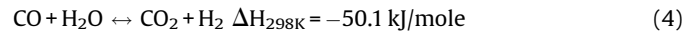
Dry reforming of methane is a well-studied process (e.g. [3,17,19,34,45]) and is often seen as an alternative for steam reforming of methane [17,18,31,34]. Combining dry reforming with steam reforming decreases the amount of steam required per unit of syngas produced and can potentially reduce the carbon footprint of syngas production [17]. Dry reforming of methane could also be a potential alternative for CO₂ hydrogenation if the produced syngas can be converted into a fuel, preferably methanol or dimethyl ether (DME), as these are best suited for the replacement of conventional fuels [24,32].

The efficiency of syngas conversion to methanol or DME strongly depends on the ratio H₂/CO present in the syngas. Syngas from dry reforming has a H₂/CO ratio of almost 1,¹ (see Eq. (1)), which is not sufficient for efficient conversion to methanol as the optimal syngas ratio for syngas conversion to methanol is close to 2² unless extra hydrogen is added [25,28,34]. However, syngas with a H₂/CO ratio close to 1 is sufficient for conversion to DME, when direct synthesis is considered. Studies have indicated that DME is a preferable fuel to methanol because DME can directly be used as a cleaner substitute for diesel [32,44] and the market is expected to grow [40]. Direct synthesis of syngas to methanol (Eqs. (2) and (3)), water gas shift (WGS) reaction (Eq. (4)) and dehydration of methanol (Eq. (5)) [24,25,28,29,35]:



¹ Occurrence of reverse water gas shift (RWGS) reaction tends to decrease the H₂/CO ratio [34].

² CO + 2H₂ → CH₃OH.



When these reactions occur simultaneously, the produced methanol is directly converted to DME. As a result, the equilibria of the remaining reactions are pulled towards additional methanol conversion and H₂ production from the WGS reaction, enabling a higher syngas conversion rate than when only methanol synthesis is considered [24,25]. Disadvantages of this process are CO₂ formation due to the WGS reaction and the requirement of a novel bifunctional catalyst which supports both methanol conversion and methanol dehydration to DME [16,24,25]. Direct synthesis of DME from syngas is a promising new technology to produce syngas and can be a more efficient alternative compared to the conventional dual-stage DME production from syngas [6,24,25]. A thorough analysis of the environmental and technical performance is however lacking. This study aims to assess the technical and environmental performance of utilizing CO₂ to produce DME through dry reforming of methane and direct synthesis. A key aspect of this study is not only to assess the technical feasibility of the process, but also the extent to which CO₂ emissions are actually reduced as well as the change in impact of other environmental indicators.

2. Methodology

2.1. System boundaries

CO₂ utilization via dry reforming and direct DME synthesis can be considered an add-on utilization process, and therefore it could be applied to any CO₂ source. In this study a refinery was selected as the CO₂ source, because CO₂ utilization cases are well applicable to industrial processes and refineries already have the infrastructure in place for the use of natural gas for (steam) reforming processes. Within a refinery, a steam reforming H₂ production was specifically chosen as CO₂ source because H₂ units significantly contribute to the refineries' GHG emissions and efficient CO₂ capture from this process is possible [26]. In this study, a H₂ production unit of 59 kt/year with capture of 330 kt CO₂ per year

Table 1
Key characteristics of H₂ production plant assessed in this study.

Characteristic	
CO ₂ source	H ₂ production unit at refinery
Location	North West Europe
Temporal	2015
CO ₂ capture method	Solvent (MDEA)
Plant size	Hydrogen unit produces 59 kt/year H ₂ . 330 kt/year CO ₂ is captured [26]
Plant lifetime	20 years
Capacity factor	90%

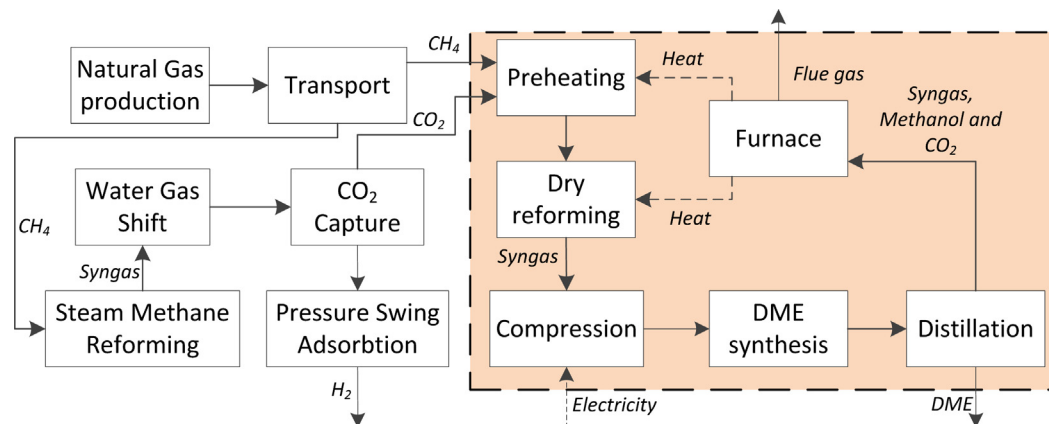


Fig. 2. Simplified process layout of the production of DME via dry reforming of methane. The area within the striped box represents the CO₂ utilization route which is the specific area of interest in this study.

Table 2
Overview of the applied cases in this study.

	Reference case	CCS case	Utilization case
Abbreviation	REF	CCS	CCU
H ₂ production	From H ₂ production unit at refinery	From H ₂ production unit at refinery	From H ₂ production unit at refinery
CO ₂ capture	–	MDEA	MDEA
CO ₂ usage	–	Underground storage	Utilised on site for production of DME via dry reforming
DME production	Conventional, via methanol synthesis	Conventional, via methanol synthesis	Direct synthesis of syngas produced via dry reforming

using methyl diethanolamine (MDEA)³ was selected. Key characteristics for this unit are presented in Table 1.

Fig. 2 schematically depicts the processes included in this study. The coloured area represents the proposed CO₂ utilization route, which is specifically targeted in the technical process modelling. Other processes assessed in the environmental analysis comprise natural gas production and transport and the H₂ production unit including CO₂ capture. H₂ is produced in the considered process via steam reforming of methane and water gas shift reaction and is separated via pressure swing adsorption. CO₂ capture is applied between the water gas shift (WGS) reactor and the pressure swing adsorption (PSA) unit as it has been shown this is the most efficient location for CO₂ capture for this configuration [26].

The captured CO₂ is preheated before entering the dry reforming reactor, which requires a continuous supply of heat due to the endothermic nature of the process. The produced syngas is compressed to enable direct synthesis of DME. After this synthesis step, a mixture of DME, methanol, CO₂ and remaining

syngas is formed. Two distillation steps are applied to separate the components: in the first step, the mixture of DME and methanol are separated from the syngas and CO₂ and, in the second step the ultimate product DME is purified by separating it from the methanol. Heat required for the dry reforming process is produced by a furnace via combustion of remaining syngas, methanol and, if required, natural gas. Electricity required for the compression of syngas is assumed to be delivered by the grid.

The dry reforming case is compared with two other cases, namely a reference case (REF) and a CO₂ storage (CCS) case (see Table 2). In the reference case, no CO₂ capture is applied in the H₂ production unit and DME is assumed to be produced conventionally via direct synthesis of methanol. In the storage case, CO₂ is captured from the H₂ production unit and is transported and stored in a geological reservoir. Similarly to the reference case, DME is produced via conventional synthesis of methanol. Conventional synthesis of methanol is also technically assessed by process modelling, in which natural gas is considered an input stream. In all cases, the total amount of produced H₂ and DME is set equal to the utilization case to enable comparison between the cases. Schematic diagrams of the main processes and system boundaries for each case are presented in Appendix II in Supplementary material.

³ Although other solvents such as ADIP-X and MDEA with piperazine showed improved performance [26], MDEA was selected as CO₂ capture solvent because more data is available on production processes and degradation products of this solvent.

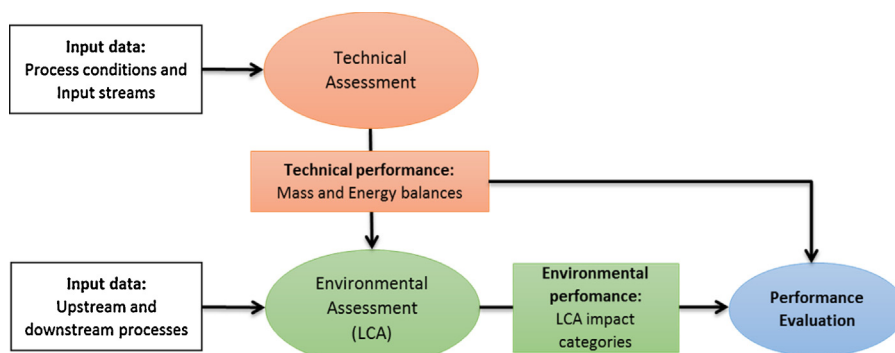


Fig. 3. Schematic overview of general approach.

2.2. General approach

The general approach applied in this study is presented in Fig. 3. The technical assessment (see Section 2.3) was carried out by developing a process model for which process conditions of the dry reforming process and direct DME synthesis and input streams for these processes served as input data. The technical performance together with input data of up- and downstream processes (e.g. natural gas production and H₂ production) was used to carry out a life cycle assessment (LCA) to determine the environmental performance of the full chain (see Section 2.4).

2.3. Technical assessment

2.3.1. Method selection

The main goal of the technical modelling was to explore the performance of this utilization route and to provide input in the form of mass and energy balances for the environmental assessment. In order to provide a conservative scenario, the dry reforming process and DME synthesis have not been optimised or integrated with other refinery processes. Aspen+ software was selected for the modelling and the Peng–Robinson equation of state was selected as thermodynamic model, as it is well-known to be suitable for hydrocarbon systems.

2.3.2. Process conditions

Table 3 presents the key assumptions regarding the process conditions for the dry reforming process and direct DME synthesis. Both dry reforming and direct DME synthesis were modelled using a Gibbs free energy reactor in Aspen+. Catalysts and corresponding process conditions were selected from literature (Table 3). Carbon deposition reactions⁴ were also included in the dry reforming reactor.

Conventional DME production via methanol dehydration was also modelled using a Gibbs free energy reactor in Aspen+ to support a fair comparison with the novel DME production route. Methanol dehydration can be performed at relatively low temperature and pressure [23,49]. An inlet temperature⁵ of 160 °C and pressure of 15 bar were selected after some model test runs. The selected catalyst for this process was γ -Al₂O₃ as this is the most commonly used catalyst for conventional DME production [2,49].

Distillation columns were required in the novel process as well as the conventional process to purify the DME. Aspen+ 2 phase

Table 3

Overview of key assumptions dry reforming and direct DME synthesis processes.

Process	Dry reforming	DME synthesis
Selected catalyst	Ni/Rh/Al ₂ O ₃	Pd/ZnO/Al ₂ O ₃
Temperature	800 °C	250 °C
Pressure	1 bar	79 bar
Stream input	330 kt CO ₂ /year 120 kt CH ₄ /year	Syngas produced in dry reforming process

1) Selected because this catalyst showed promising results at selected process conditions [17].

2) Based on Lebarbier et al. [24].

3) Typically, values between 600 and 1000 °C are reported [17,33,34,37]. The selected temperature of 800 °C is high enough to enable a high CO₂ conversion rate [17] but low enough to limit carbon deposition [34].

4) Shown to give the highest syngas conversion in the reported temperature range 250–380 °C for the selected catalyst [24].

5) Assumed to be optimal pressure for this process [17,33,34], as at higher pressure the RWGS reaction starts to dominate which decreases the CO₂ conversion rate [33].

6) Pressure at which selected catalyst showed optimal syngas conversion rates [24].

7) Matching the amount of CO₂ assumed to be captured in H₂ production unit.

8) Assuming a CH₄:CO₂ ratio of 1:1 (CH₄+CO₂ ↔ 2 CO+2H₂).

rigorous fractionation single columns were used to model the distillation steps and a minimum purity of DME of 99.5% was set as distillation target. In the dry reforming case, the first distillation column separates the methanol, DME and water mixture from the remaining syngas and CO₂, with DME as the heavy key component (boiling point of –23 °C) and CO₂ as the light key component (boiling point of –57 °C). The second distillation column purifies the DME by separating it from the remaining water, with methanol as the heavy key component and DME as the light key component. In the reference cases, in the first distillation column the DME is separated from the methanol and water and in the second column the methanol is separated from the remaining water before being recycled to the DME synthesis process. Cooling water inlet temperature was set at 12 °C (average North Sea water temperature).

2.3.3. Process line-ups

Fig. 4 presents the Aspen+ process line-up for the novel CO₂ utilization route via dry reforming and direct DME synthesis. Complete details of all flows can be found in Appendix I in Supplementary material. CO₂ (S1) and methane (S2) are mixed (B1) and fed into pre-heating station (H1) where the mix is heated to 800 °C. After preheating, the CO₂ and methane (S4) enters the dry reforming reactor (DRYREF) where at constant temperature of 800 °C the mix is reformed into syngas (S5).

The syngas is cooled down (H2) before three-stage compression (COMP1, COMP2 and COMP3) with intermediate cooling (H3 and H4) and water knock-out vessels (DRUM1 and DRUM2) is applied to increase the pressure to the required pressure of 79 bar. Water

⁴ Most prevalent: CH₄ ↔ C(s)+2H₂, ΔH_{298K}=+75 kJ/mole and 2CO ↔ C(s)+CO₂, ΔH_{298K}=–171 kJ/mole.

⁵ Due to the exothermic nature of methanol dehydration, actual reaction and outlet temperature are higher.

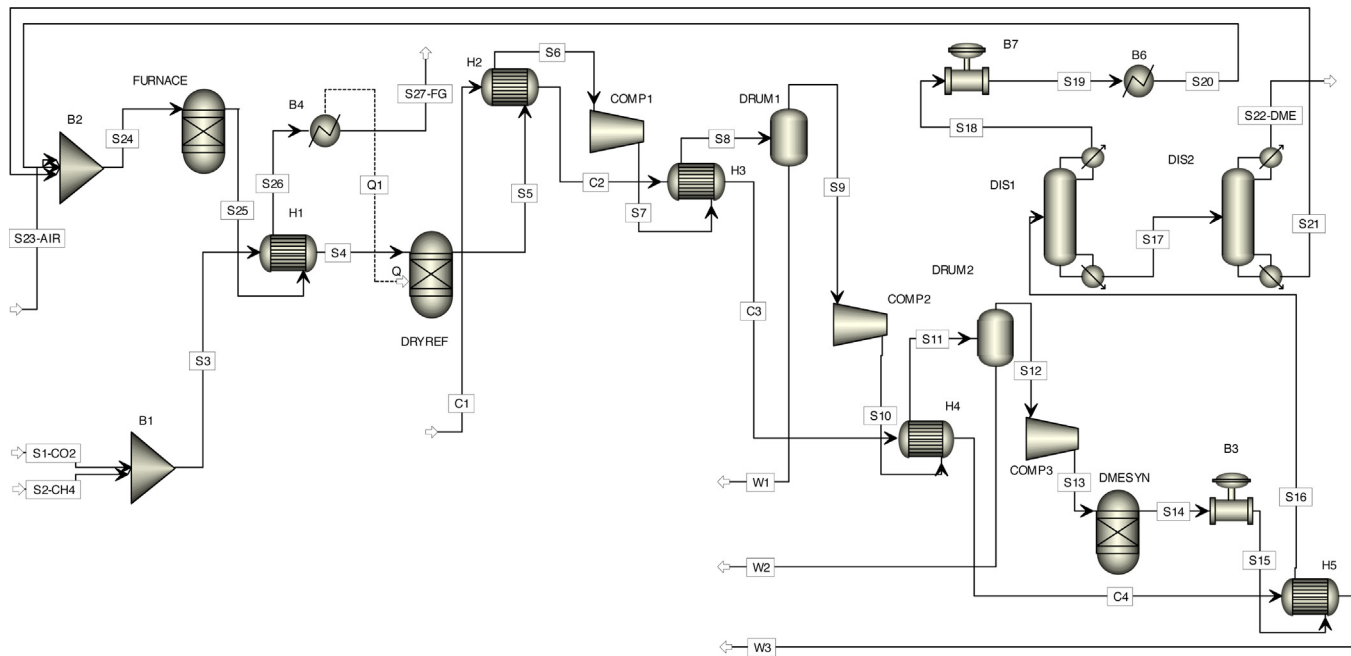


Fig. 4. Process flowsheet of CO₂ utilization via dry reforming and direct DME synthesis. Characteristics of each flow can be found in Appendix I in Supplementary material.

knocked out of the mix is discharged to the environment (W1 and W2). Cooling water (C1) is used for cooling the syngas between compression steps and is discharged into the environment after use (W3). After the final compression step, the temperature of the syngas is 250 °C and therefore suitable for direct DME synthesis. In the direct DME synthesis reactor (DMESYN), the syngas is converted to DME without additional heat supply. Because the outlet stream of this reactor (S14) also contains methanol, syngas, water, CO₂ and methane further steps to purify the DME are necessary.

The DME mix (S14) is first depressurized (B3) and cooled down (H5) before the mix (S16) is fed into the first distillation column (DIS1). In this column, the lighter components (CO₂, CH₄, CO and H₂) are separated from the heavier components (DME, methanol and water) at a pressure of 10 bar. Because the boiling point of the key heavy component DME is very low, −23 °C, the condenser at the top of the column is operated at very low temperature. As such, a refrigerator cycle is required to enable this condenser to work at this temperature. Calculations for this refrigerator cycle are done apart from the Aspen+ model assuming an ideal Carnot-cycle. Refrigerant consumption is calculated combining the cooling demand of the Carnot cycle with an assumed cycle time of 100 s [1] and a lifetime of 20 years. The selected refrigerant for this cycle is Freon-22, which characteristics, e.g. boiling point = −40.8 °C [12], are well suited for this purpose. The DME mixed with methanol and water (S17) leaves the column at the bottom and enters the second distillation column (DIS2), where the DME is separated from the methanol and water. DME with high purity (>99.5%) leaves the column at the top (S22).

The gas mix containing syngas, methane and CO₂ that exits the first distillation column (DIS1) at the top, is depressurized (B7) and heated (B6) before the stream (S20) is mixed (B2) with the methanol and water mixture (S21) exiting at the bottom of the second distillation column (DIS2) and an inlet air stream (S23), before the mixture (S24) is fed into the furnace (FURNACE). In the furnace, the mixture is burnt completely, producing hot (>1500 °C) exhaust gasses (S25) which are used for pre-heating the CO₂-

methane mix (H1) and providing the heat required for the dry reforming reaction. In this configuration, recycling the syngas, methane and the produced methanol provide sufficient heat for the dry reforming reaction and burning of additional natural gas was not required. Flue gasses from the furnace (S27) are emitted into the atmosphere.

Fig. 5 presents the Aspen+ process line-up for conventional DME production via methanol dehydration. Complete details of all flows can be found in Appendix I in Supplementary material. Liquid methanol (S1) is pumped (P1) into and mixed (B1) with a methanol recycle stream (S14) before it (S3) is preheated (H1) and fed into (S4) the DME synthesis reactor (DMESYN). In this reactor, the methanol is converted into DME and a mix of DME, methanol and water leaves the reactor (S5). This mixture is then slightly depressurized (B2) and cooled down (H2) before entering the first distillation column (DIS1). In this column, DME is separated from methanol and water and leaves the top of the column at high purity (>99.5%). The remaining water and methanol (S9) exits the column at the bottom and is slightly depressurized (B3) and fed into the second distillation column (DIS2). In the second column, the remaining methanol and water are separated. The water (S11) exits the column at the bottom and the methanol (S12) leaves at the top and is liquefied (H3) and pumped (P2) and mixed (B1) with the input methanol stream (S1).

2.4. Environmental assessment

A hybrid life cycle assessment (LCA) was performed for the three cases: REF, CCU and CCS (description of the cases is presented in Section 2.1). Hybrid life cycle approach combines economic and process data to develop inventories with good detail and completeness and can improve LCA modelling as conventional LCA comprises a high resolution in foreground processes but suffer from incomplete system boundaries. For a more detailed description of hybrid LCA see Hendrickson et al. [20]. Outputs of the technical simulation and data from the Ecoinvent v 2.2 database [13] were used for completing the life cycle inventory (LCI) for the

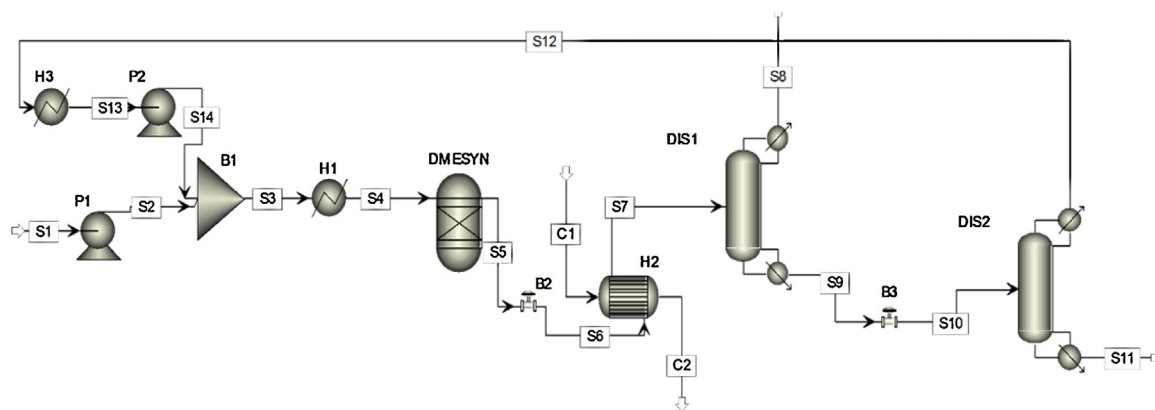


Fig. 5. Process flowsheet conventional DME production via methanol dehydration. Characteristics of each flow can be found in Appendix I in Supplementary material.

operation, background and transport phases of the different processes in all three cases. Impacts from infrastructure of the H₂ and carbon capture unit and novel (utilization) and conventional DME route were quantified by carrying out a hybrid LCI using cost data estimation which was performed using the results of the technical modelling (key assumptions and methodology are explained in Appendix III in Supplementary material). The functional unit in this study is 1 MJ LHV of net energy (energy content of H₂ and DME) produced.

Technical performance values used for the LCI of the CCU case comprised the amount of natural gas consumption, direct CO₂ emissions from combustion of syngas, direct CO₂ emissions from DME conversion, catalyst use, refrigerant consumption (for low temperature cooling during distillation) electricity consumption and water consumption. Technical performance values used for the LCI of the REF case and CCS case comprised methanol consumption, catalyst use, electricity consumption and water consumption. The LCI for methanol production was obtained from the inventory for chemical industries [4] within the Ecoinvent database v2.2 [13] for natural gas based methanol plants.

Results from process simulations [27] were used to quantify material (natural gas, ZnO adsorbent for desulphurization, water) and energy (electricity) inputs for H₂ production. Catalyst consumption (for SMR and water gas shift reactor) was obtained from [42] and the amount of adsorbent for the PSA unit was calculated using the adsorbent bed productivity reported by [10]. Life cycle inventory for catalyst and separation agents were modelled using the information for manufacturing of chemicals [4] in Ecoinvent v 2.2 database [13]. The lifetime of all catalysts was assumed to be 5 years as catalysts can be operated up to 5 years in a

conventional H₂ production unit [48]. 95% CO₂ capture from the CO₂ produced in the SMR was assumed [26]. Emissions associated with solvent degradation in the carbon capture unit were accounted based on MDEA degradation for post-combustion application [8].

The LCI for natural gas production and transport processes was based on the Dutch natural gas basket with 75.5% of the natural gas produced domestically and the rest being imported mainly from Norway, Russia and UK [14,15]. Inventories for country specific natural gas production processes [11] were obtained from Ecoinvent v2.2 [13] with estimated transport distances to the case refinery location (assumed to be Rotterdam).

Inventories for the required on-site infrastructure (SMR unit, CO₂ capture, CO₂ compression train, chemical reactors etc.) were modelled using the hybrid approach. Capital cost for the plant islands were allocated to different economy sectors of the multiregional sectorial cash flow EXIOBASE 2 database [46]; the methodology for the applied capital cost assessment is described in Appendix III in Supplementary material. CO₂ transport and injection infrastructure was modelled by adapting the inventory reported for natural gas pipeline and well infrastructure [11] in the Ecoinvent v2.2 database [13] based on volume of CO₂ being transported. Complete details on the LCI modelling are provided in Appendix II in Supplementary material.

Environmental impacts over 18 different impact categories were evaluated per functional unit using the ReCiPe impact characterization method [38]. Human toxicity potential for MDEA was estimated using the characterisation factors employed for MEA reported by Veltman et al. [47] as characterisation factor for MEA emissions are not included in the ReCiPe database.

Table 4
Performance indicators technical assessment.

Performance indicators (per kg DME produced)	Conventional DME production (REF and CCS case)	Dry reforming+ direct DME synthesis (CCU case)
CO ₂ emitted (kg)	–	1.60
CO ₂ utilised (kg)	–	1.76
CO ₂ avoided (kg)	–	0.15
Methanol consumption (kg)	1.40	–
Methane consumption (kg)	–	0.64
Total methane consumption (kg) ¹⁾	0.86 ²⁾	0.64
Electricity consumption (kWh)	1.3E-03	0.81
Cooling water requirement (kg)	23.9	77.2
Catalyst consumption, γ /Al ₂ O ₃ (mg)	0.79	–
Catalyst consumption, Ni/Rh/Al ₂ O ₃ (mg)	–	4.29
Catalyst consumption, Pd/ZnO/Al ₂ O ₃ (mg)	–	3.70
Refrigerant (Freon-22) consumption (mg)	–	0.08

1) The total methane consumption is not a direct performance indicator, but is included in this table to compare the overall feedstock consumption of both production routes.

2) Methanol consumption is translated into methane consumption assuming 0.61 kg methane is used for the production of 1 kg methanol [13].

3. Results

Table 4 shows the main performance indicators (mass and energy balances) of the technical assessment of conventional DME production and CO₂ utilization by dry reforming and DME synthesis. The dry reforming route requires 0.64 kg methane/kg DME, whereas 1.40 kg methanol/kg DME is used for conventional DME production. As 0.86 kg methane is required for the conventional production of 1.40 kg methanol [13], total chemical feedstock consumption is slightly reduced in the dry reforming route compared to the conventional production. Besides, there is a potential energy efficiency benefit as the production of methanol, which is more energy intensive than the production of methane, is also avoided in the dry reforming route.

The CO₂ balance of the dry reforming route shows that the CO₂ emitted in the process approaches the CO₂ initially utilised. CO₂ emitted in the process includes CO₂ emissions from heat production for dry reforming (33%), CO₂ directly formed during DME synthesis (61%) and unconverted CO₂ (6%). In addition to the direct CO₂ emissions from the process, also a large amount of electricity is required, predominately by the compression of the syngas.

The results also indicate that a larger amount of cooling water is required in the dry reforming case, mainly due to the cooling steps required between the compression stages of the syngas. Catalyst consumption is also larger, mainly due to a larger volume of the reactors compared to conventional production of DME. Refrigerant is consumed in the novel process for low temperature cooling during the distillation step for separating remaining syngas and CO₂ from methanol and DME.

The technical performance indicators are used as key process data for the life cycle inventory to assess the environmental performance of the different cases over the entire life cycle. Fig. 6 presents the life cycle environmental impacts for the storage (CCS) and utilization (CCU) cases relative to the reference case (REF) and the process contribution analysis for the three value chains (absolute values are provided in Appendix IV in Supplementary material).

3.1. Climate change potential (CCP)

Climate change potential (CCP) is slightly decreased by approximately 8% for the CCU case compared to the reference case. CCP of the CCU case is 37% higher than the CCP of the CCS case. The relatively low net CCP avoidance in the CCU case is the consequence of the direct CO₂ emissions from syngas combustion for the dry reforming process (9.7 E–3 kg CO_{2eq}/MJ), indirect emissions from electricity consumption required for syngas compression for DME conversion and direct emissions from DME conversion (2.4E–2 kg CO_{2eq}/MJ) and indirect emissions from the supply of additional natural gas (2.1E–3 kg CO_{2eq}/MJ). These emissions almost completely compensate the CCP reduction related to the captured CO₂ emissions in the SMR (2.5E–2 kg CO_{2eq}/MJ) and to the substitution of methanol (1.5E–2 kg CO_{2eq}/MJ).

The CCP in the CCU case mostly originates from CO₂ formation during DME conversion (39%), emissions from the furnace for H₂ production (33%) and emissions from the furnace for dry reforming (16%). The CCP of the DME conversion process is driven by direct CO₂ formation (64%) and background impacts from electricity generation required for syngas compression. The CCP associated

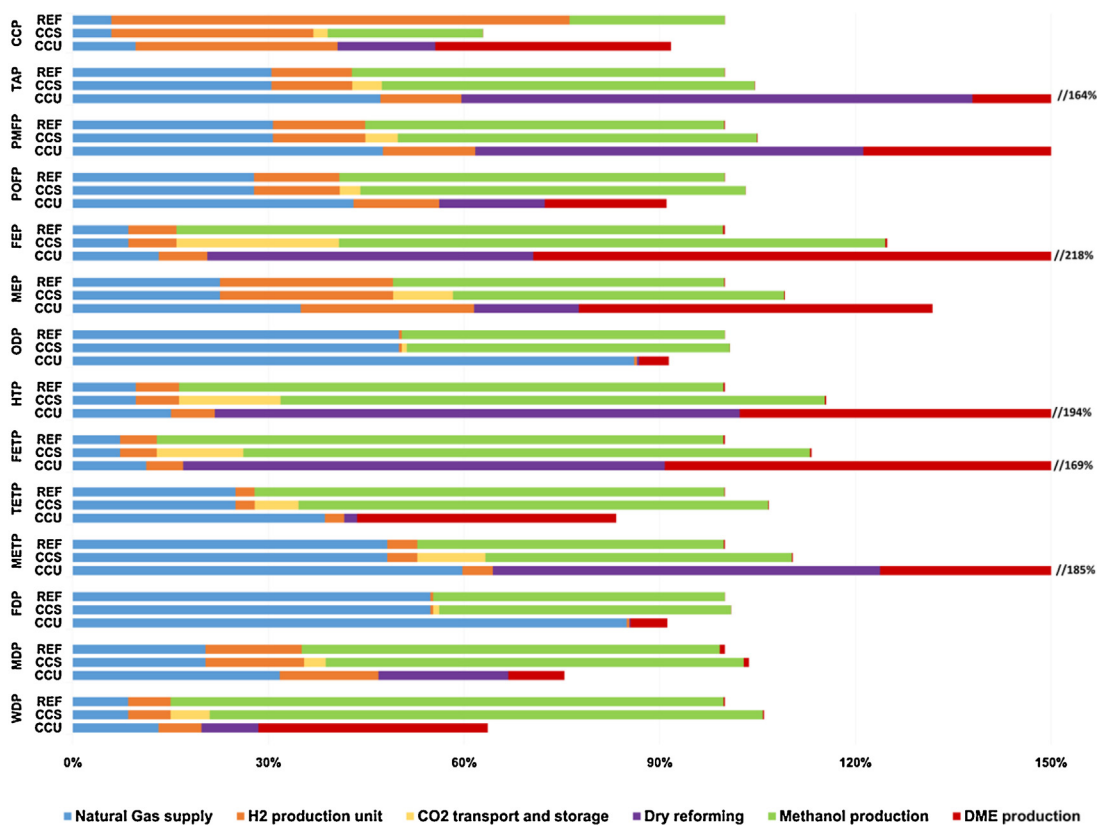


Fig. 6. Environmental impacts for the different environmental categories relative to the reference case. Process are divided into contributions from natural gas supply (including production and transport), H₂ production, CO₂ compression and storage (CCS case), dry reforming and DME production (CCU case), and methanol production (REF and CCS case). Effects of production of chemicals and utilities are included in the according processes, except for natural gas due to the large contribution of natural gas production processes.

with the dry reforming process comprises CO₂ emissions from syngas combustion in the furnace and unconverted CO₂. The CCP of H₂ production is caused by CO₂ emissions from the furnace (92%) and uncaptured CO₂ from the SMR (7%). Natural gas transport processes account for 57% of the CCP of the natural gas supply chain (mainly due to CO₂ and CH₄ combustion emissions in gas turbines to provide electricity in compression station).

The CCP in the REF case is dominated by H₂ production (70%) which is mainly attributed to CO₂ emissions from the SMR (60%) and furnace (40%). The CCP of H₂ production is halved in the CCS and CCU case as 90% of the CO₂ is captured from the SMR in these cases. The CCP associated to methanol production contributes significantly (24% in REF and 34% in CCS), while the CCP related to CO₂ transport and storage only contributes marginally (<4%) to the total CCP in the REF case.

3.2. Other environmental impacts

The CCS case increases the impact of all other environmental indicators except climate change potential (CCP), because CO₂ is captured, transported and stored at the cost of additional utilities (mostly electricity for compression) and chemicals (mostly solvent for capture), while the reduction of CO₂ emissions only improves the CCP performance. The CCU case provides a more diverse picture, as the impact of some indicators is actually reduced compared to the CCS case while some other indicators show an increase in the impact.

The environmental impact is reduced in the CCU case compared to the REF and CCS cases for indicators where impacts of conventional methanol production in the REF and CCS cases are larger than the impacts associated with additional supply of natural gas, the dry reforming process and the DME production process in the CCU case. The CCU case shows lower impacts in the categories:

- *Photochemical oxidant formation potential (POFP)*. POFP is reduced by 9% and 11% compared to the Ref and CCS cases, respectively. Almost half (47%) of the total POFP originates from natural gas production and transport, mainly caused by the combustion related emissions (NO_x, CO and CH₄) in the production plant and compression stations. The large impact of methanol production in the REF case (55%) and CCS case (53%) associated with combustion emissions from methanol production and the natural gas value chain more than compensate POFP impacts related to fossil based electricity generation in the CCU case.
- *Ozone depletion potential (ODP)*. ODP is 9% lower than both the REF case and CCS case. 94% of the ODP occurs in the natural gas value chain as a result of emissions of compounds such as chlorodifluoromethane and halon related to natural gas transport. Similar impacts of background natural gas transport processes in the methanol value chain in the REF and CCS case offset the additional natural gas required in the CCU case.
- *Terrestrial eco-toxicity potential (TETP)*. TETP is reduced by 16% and 22% compared to the Ref case and CCS case, respectively. The TETP is driven by the DME production process (48%), mainly caused by disposal of wood ash for bio-fuelled power plants, and the disposal of waste in natural gas value chain (46%). In the REF and CCS case, methanol production is the largest contributor (72% in REF and 67% in CCS) attributed to the liquid effluents from the methanol plant and to waste disposal during the natural gas consumption along the methanol value chain.
- *Fossil depletion potential (FDP), metal depletion potential (MDP) and water depletion potential (WDP)*. FDP, MDP and WDP are reduced by 10%, 32% and 37%, respectively, compared to the REF case and by 9%, 27% and 40%, respectively, compared to the

CCS case. FDP is dominated by the natural gas value chain (93%) and the decrease is the result of reduced natural gas consumption in the CCU case. The main contributor to MDP is the infrastructure development of the natural gas value chain (42%) followed by the impacts associated with Rh mining for the synthesis of the dry reforming process (26%). Reduced natural gas consumption and avoided methanol production infrastructure leads to lower MDP in the CCU case. WDP is mainly attributed to the novel DME production process (55%) caused by cooling water demand of the process and the indirect cooling water use of electricity production. WDP associated with methanol production is considerably higher (85% of REF, 80% of CCS) resulting in reduced WDP in CCU.

The impact of catalyst use (mainly Rhodium) in the dry reforming process and electricity demand of the syngas conversion for the DME production leads to an increase in environmental impact for the indicators:

- *Terrestrial acidification potential (TAP)*. TAP is increased by 65% and 52% compared to the REF case and CCS case, respectively. This increase is mainly driven by the impacts from the dry reforming process accounting for 47% of the life cycle value for this indicator, consequence of NO_x and SO_x emissions during Rhodium refining. The large contribution of methanol production in the REF case and CCS case (67% and 64% respectively) is the result of emissions from the combustion of natural gas in the furnace of the methanol plant and from the distillation towers.
- *Particulate matter formation potential (PMFP)*. PMFP is increased by 50% and 43% compared to the REF case and CCS case, respectively. This increase is mainly caused by the impacts from the dry reforming process, the supply of extra natural gas and the DME novel process that are responsible of 40%, 30% and 20% of the life cycle value for this indicator in the CCU case. PMFP from the dry reforming value chain is mainly caused by the emission of NO_x, SO_x and particulates in the Rhodium mining process. Combustion emissions at the natural gas plant facilities are the main contributor to PMFP for the natural gas supply and fossil based power generation required for compressing the syngas is the main contributing process associated with DME production.
- *Freshwater eutrophication (FEP) and marine eutrophication (MEP) potential*. FEP increases by 118% and 73% compared to the CCU case and CCS case, respectively, and MEP by 31% and 20%, respectively. FEP and MEP are mainly driven by the impacts from the DME novel process (67% and 41%) due to the impacts of fossil fuelled electricity production (mainly related to the disposal of coal mining waste). Disposal of sulfidic tailings associated to rhodium mining is the second largest contributor (23%) for FEP. In the REF and CCS case, methanol production contributes mostly to FEP (84% and 67%, respectively) primarily caused by coal mining disposals in the underlying electricity production processes, and to MEP (51% and 46%, respectively) due to combustion emission at methanol production site.
- *Human toxicity potential (HTP)*. HTP increases by 94% and 68% compared to the REF case and CCS case, respectively. The largest contributors are the DME process (47%), mainly due to coal mining disposal from electricity production (47%), and dry reforming process (41%), caused by sulfidic tailings and liquid effluents from the rhodium mining. In the REF case and CCS case, the methanol value chain is the main contributor (83% and 72%, respectively) as a result of disposal of the liquid effluents from the methanol plant (containing formaldehyde and phenols).
- *Freshwater eco-toxicity potential (FETP) and marine eco-toxicity potential (METP)*. FETP and METP are increased by 69% and 78%, respectively, compared to the REF case and by 62% and 43%,

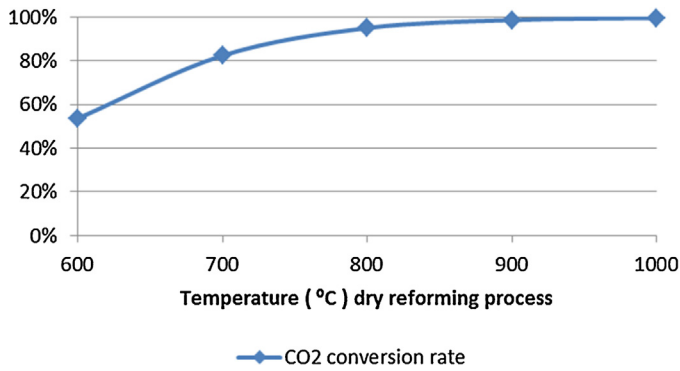


Fig. 7. Sensitivity of the temperature of the dry reforming process on the CO₂ conversion rate.

respectively, to the CCS case. The DME production process is the major contributor (46% for FETP, 34% for METP), largely attributed to the disposal of coal mining tailings in coal production for electricity generation, followed by the dry reforming process (43% for FETP, 32% for METP) as a consequence of rhodium mining disposals. FETP from methanol production is mainly attributed to the liquid effluents from the plant and METP originates from background electricity generation for the power consumed in the methanol production plant.

The indicators *Ionising radiation potential (IRP)*, *Agricultural land occupation potential (ALOP)* and *Urban land occupation (ULOP)* are increased in the CCU case compared to the REF and CCS case, predominately due to the electricity consumption required for syngas compression for the DME production process. The used Dutch electricity mix includes a small share of nuclear power and relatively large biogenic share which are responsible for the increases for IRP and ALOP in the CCU case, respectively.

3.3. Sensitivity analyses

For the technical modelling of dry reforming and direct DME synthesis processes, a sensitivity analysis has been conducted on key process parameters in order to explore the operation ranges of the system and to assess the impact of varying process conditions on the technical performance of the system.

In this study, the dry reforming process is selected to operate at 800 °C, while ranges from 600 to 1040 °C have been reported in literature [17,33,34,37]. In this study, a temperature of 800 °C was selected as this temperature is high enough to enable a high CO₂ conversion rate [17] but low enough to limit carbon deposition [34]. Fig. 7 presents the CO₂ conversion rate as a function of the operation temperature of the dry reforming process in our process model. At 800 °C, 95% of the CO₂ is converted to syngas. Lowering the temperature decreases the CO₂ conversion rate rapidly (82% at 700 °C), which is not compensated by the lower heat demand of the process. However, rising the temperature only slightly

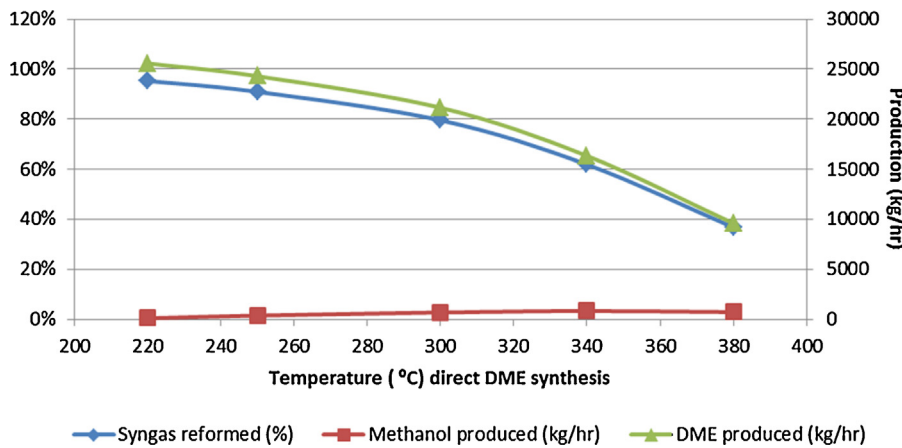


Fig. 8. Sensitivity of the temperature of direct DME synthesis on the syngas reforming ratio, methanol production and DME production.

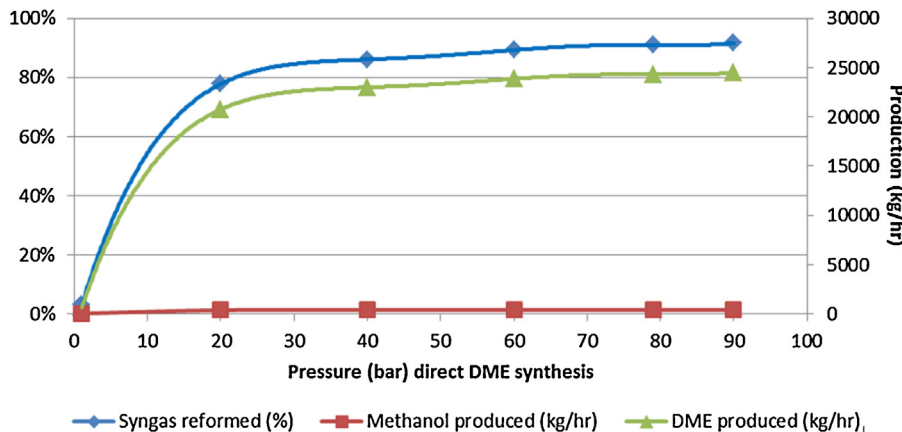


Fig. 9. Sensitivity of the pressure of direct DME synthesis on the syngas reforming ratio, methanol production and DME production.

increases the CO₂ conversion rate as it is already relatively close 100%. Operating the dry reforming reaction at higher temperature does not improve the efficiency of the process as gains from increased CO₂ conversion are offset by the need to combust additional methane to achieve the larger heat demand of the process.

Direct DME synthesis with a Pd/ZnO/Al₂O₃ catalyst is reported to operate well within a temperature range of 250–380 °C and a pressure of 79 bar [24]. Fig. 8 shows the impact of the temperature of the direct DME synthesis process on the syngas reforming ratio and amount of methanol and DME produced for the process model used in this study. At lower temperatures, direct DME synthesis is more efficient and is also accompanied by less co-production of methanol (from <400 kg/h at 250 °C to >800 kg/h at 340 °C). These findings are in agreement with the results produced by Lebarbier et al. [24].

Fig. 9 presents the impact of the pressure of the DME synthesis on the on the syngas reforming ratio and amount of methanol and DME produced for the process model used in this study. The decrease in syngas reforming ratio and DME production is only limited when lowering the pressure in the range of 40–90 bar but becomes more substantial once pressures below 20 bar are considered. No significant impact is observed on the amount of methanol co-produced at different pressure rates. As the difference between the syngas reforming ratio at the selected pressure of 79 bar (91%) and at 40 bar (86%), is relatively small, and the electricity requirement of compression the syngas significantly contributes to the environmental performance of the technology, it is interesting to investigate to what extent the environmental performance would improve if direct synthesis could be operated at 40 bar instead of 79 bar.

Fig. 10 presents the life cycle GHG emissions for the CCU case with DME synthesis pressures of 40 bar, 60 bar and 79 bar (original CCU case). Although lower pressures decrease the electricity consumption, this decrease is not sufficient to compensate the lower syngas conversion to DME rates. As such, even if the DME synthesis process could operate at lower pressures, no significant CCP reduction is expected to be obtained when modifying the operating pressures.

4. Discussion and conclusion

4.1. Technical assessment

The technical modelling conducted in this study served as the basis for exploring the techno-environmental performance of CO₂ utilization by dry reforming of natural gas for the production of dimethyl ether (DME). As the goal of the study was to explore the performance of this utilization route, a relative low modelling resolution was selected for the process. Process optimization and heat integration with other refinery processes have not been considered. In the process model, the heat required for the dry reforming process is generated by combustion of excess syngas, and waste heat streams, such as the flue gas from the furnace, are not utilised. If excess heat would be available at the refinery, this could be used to (pre)heat the CO₂ and methane. Less syngas would then be required for heat generation and the amount of methane used for the dry reforming process could be reduced, potentially improving the technical and environmental performance of the technology. However, this improvement would be limited to the portion of syngas that can be converted to DME. If there is a large amount of waste heat available, one might consider recycling the syngas into the DME reactor to increase the syngas conversion rate and DME production and therefore improve the performance of the production process.

The catalysts for the dry reforming process and DME synthesis were selected based on their promising performance reported in literature. The process conditions applied in the process model are considered the optimum conditions for the selected catalysts [17,24]. Nevertheless, there is a wider range of conditions in which the dry reforming process and DME synthesis can be operated. The sensitivity analysis performed on the process conditions (Section 3.3) showed that altering these conditions only has a limited effect on the performance of the technology. Further improving the catalysts, enabling higher CO₂ conversion rates at lower temperatures during the dry reforming reaction and higher syngas conversion rates at lower pressure during the DME synthesis, could potentially reduce the amount of heat and electricity required during the process. However, potential gains are expected to be limited as this study already assessed novel catalysts and selected

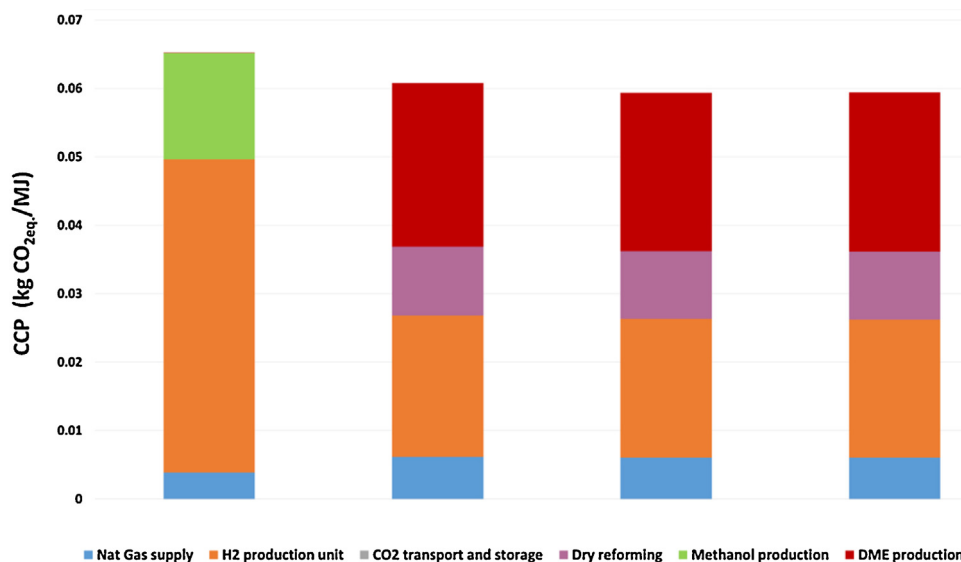


Fig. 10. Life cycle CO₂ equivalent emissions in g per MJ H₂ and DME produced for the reference case (REF) and the CO₂ utilization case (CCU) for different applied DME synthesis process pressures divided in contributions from natural gas production, H₂ production, dry reforming process, DME synthesis, methanol production and CO₂ transport and storage.

process conditions, especially for the dry reforming reaction, are already close to the thermodynamic minimum.

The results of the technical assessment show that the CO₂ almost all CO₂ that is utilised in the process is emitted again during the process (1.60 kg CO₂ is emitted per 1.76 kg CO₂ utilised for the production of 1 kg DME). The majority, over 60%, of the CO₂ emitted in the process is formed during the syngas conversion into DME and cannot be avoided or reduced. Even though the remaining CO₂ emissions (from heat production and unreacted CO₂) could be reduced by further process optimization or improvement, the CO₂ avoidance potential of this CO₂ utilization route will always remain confined by the CO₂ formation during the DME synthesis.

4.2. Environmental assessment

A hybrid life cycle assessment (LCA) was conducted to compare the environmental performance of the CO₂ utilization via dry reforming for the production of DME (CCU) with a storage case (CCS) and a reference case (REF). The CCU case slightly reduces climate change potential (CCP) compared to the REF case, despite the large amount of CO₂ emissions from DME synthesis and background processes of production of electricity required for the syngas compression. These CO₂ emissions are compensated by the background life cycle GHG emissions of methanol production and the non-captured CO₂ emissions in the H₂ production unit in the refinery. However, although the reduction on the CCP is lower in the CCU than in the CCS case, the CCU case performs slightly better for some categories while the performance of some other indicators is drastically reduced. As such, the environmental trade-offs of CCU appear more complex than those of CCS, and strongly depend on the value of decreasing CCP at the cost of increasing impacts in other indicators.

In this study, a comparative life cycle assessment is performed by system expansion: the utilization case is compared to a reference case in which an equal amount of products, H₂ and DME, are delivered to the system. When using system expansion, the choice of reference system might be the most important assumption affecting the comparative LCA results for CO₂ utilization [41]. This is underlined in this study, as the conventional DME production, especially the background processes for methanol production, largely contributes to the LCA results of the reference case. In the reference case, DME is considered to be produced by direct synthesis of methanol (methanol dehydration), and the production process for the required methanol for this process is assumed to be equal to the average global methanol production as included in the Ecoinvent database [13]. Direct synthesis of DME from methanol is considered the most common method to produce DME [6]. Methanol is mostly produced from natural gas, but can also be produced from a wide variety of different feedstocks, including biomass and waste [39]. However, applying a different reference system, in which a lower environmental footprint of the production methods of methanol and/or electricity is considered, might strongly affect the reported differences in the LCA results between utilization case and reference case.

4.3. Performance CCU

The performance results of the CO₂ utilization case illustrates that the CO₂ reduction potential is limited compared to that of CCS case. The climate change potential (CCP) over the life cycle is 37% higher in the utilization case compared to CCS case while still 8% lower compared to the REF case. CO₂ utilization options generally have a significant lesser GHG emission reduction potential compared to CCS [9]. Comparing the CCP of CO₂ utilization with CO₂ storage is therefore not sufficient to fully understand the

performance of CO₂ utilization. CCP reduction of CO₂ utilization technologies is reported in the range of 4–48% [9]. The CCP reduction of dry reforming for the production of DME is at the lower end of this range.

CCS increases the impact of all other environmental indicators except CCP while the direction of the impact of CO₂ utilization in these indicators is not consistent. The environmental picture for CO₂ utilization options is still under development contrary to that of CCS [7]. Some studies assessed in Cuéllar-Franca and Azapagic [9] are reported to have lower impacts in other environmental categories than CCS. While this holds in this study for some of the indicators (such as ozone depletion potential and fossil, metal and water depletion), concerns arise due to the substantial increase in some of the environmental indicators, such as freshwater eutrophication potential, human toxicity potential and agricultural land occupation.

Therefore, it remains difficult to draw robust conclusions on the total environmental performance of CO₂. However, if avoiding climate change is considered the key driver for CCU, the potential GHG reduction of the utilization case is low compared to CCS and the potential environmental benefits of this CO₂ utilization option seem limited. This study points out the importance of carrying out integrated technical assessment and LCA to gain better insights in the performance of CCU options.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcou.2016.06.005>.

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