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Assessing the techno-environmental performance of CO_2 utilization via dry reforming of methane for the production of dimethyl ether

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ABSTRACT

CO_2 utilization is gaining attention as a greenhouse gas abatement strategy complementary to CO_2 storage. This study explores the techno-environmental performance of CO_2 utilization trough dry reforming of methane into syngas for the production of dimethyl ether (DME). The CO_2 source is a hydrogen production unit at a refinery, where solvent based CO_2 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 CO_2 capture and a case with CO_2 capture and storage. Results of the technical assessment show that although 94% of the captured CO_2 can be utilised for DME production, only 9% of CO_2 is avoided in the entire process as a result of direct CO_2 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 CO_2 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 CO_2 utilization options, the complex environmental trade-offs make it difficult to draw robust conclusions on the performance.

1. Introduction

CO_2 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, CO_2 capture research has mostly focused on long term CO_2 storage, but CO_2 utilization options are gaining attention as alternative for CO_2 storage especially in scenarios where CO_2 storage is not feasible or economic incentives for CO_2 utilization are available. Potential CO_2 utilization options include enhanced oil recovery (EOR), biological conversion, mineralisation and chemical conversion into chemicals, fuels or materials such as plastics [30,36].

Converting CO_2 into fuels or fuel additives is an interesting CO_2 utilization option as the transport sector has become a large contributor to GHG emissions. However, reforming CO_2 requires a large amount of additional energy due to the chemically non-reactive nature of CO_2. The potential of reforming CO_2 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]. CO_2 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 CO_2 into fuels and fuel additives. Hydrogenation of CO_2 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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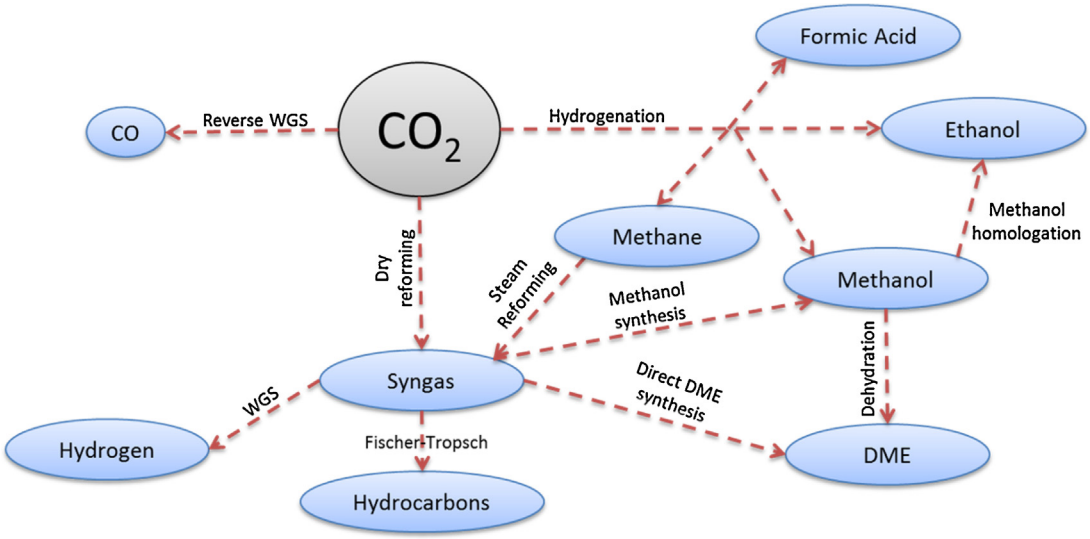

Fig. 1. Schematic representation of main production routes of CO_2 utilization into fuel.

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 CO_2 and methane producing syngas:

$$CO_2 + CH_4 \rightarrow 2\ CO + 2H_2\ \Delta H_{298K} = +247\ \text{kJ/mol} \quad (1)$$

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 CO_2 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 H_2/CO present in the syngas. Syngas from dry reforming has a H_2/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 2[2] unless extra hydrogen is added [25,28,34]. However, syngas with a H_2/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 DME comprehends the simultaneous conversion 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]:

$$CO + 2H_2 \leftrightarrow CH_3OH\ \Delta H_{298K} = -90.9\ \text{kJ/mole} \quad (2)$$

$$CO2 + 3H_2 \leftrightarrow CH_3OH + H_2O\ \Delta H_{298K} = -41.1\ \text{kJ/mole} \quad (3)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2\ \Delta H_{298K} = -50.1\ \text{kJ/mole} \quad (4)$$

$$CH_3OH \leftrightarrow CH_3OCH_3 + H_2O\ \Delta H_{298K} = -23.4\ \text{kJ/mole} \quad (5)$$

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 H_2 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 CO_2 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 CO_2 to produce DME trough 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 CO_2 emissions are actually reduced as well as the change in impact of other environmental indicators.

2. Methodology

2.1. System boundaries

CO_2 utilization via dry reforming and direct DME synthesis can be considered an add-on utilization process, and therefore it could be applied to any CO_2 source. In this study a refinery was selected as the CO_2 source, because CO_2 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 H_2 production was specifically chosen as CO_2 source because H_2 units significantly contribute to the refineries' GHG emissions and efficient CO_2 capture from this process is possible [26]. In this study, a H_2 production unit of 59 kt/year with capture of 330 kt CO_2 per year

[1] Occurrence of reverse water gasc shift (RWGS) reaction tends to decrease the H_2/CO ratio [34].
[2] $CO + 2H_2 \rightarrow CH_3OH$.