Closing carbon cycles: Evaluating the performance of multi-product CO$_2$ utilisation and storage configurations in a refinery

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ABSTRACT

Carbon capture and utilisation (CCU) has the potential to provide business cases as CO$_2$ waste streams are turned into feedstock for the synthesis of marketable products. Although CCU could reduce fossil resource demand, its capability as a climate change mitigation option is under debate. In contrast to single-product CCU, this prospective study explores the techno-economic and environmental feasibility of novel systems that include more than one CO$_2$ utilisation product. The combination of multi-product CCU with CO$_2$ storage is also investigated. Two configurations have been designed, in which CO$_2$ is captured in a refinery and converted into dimethyl ether (DME) and polyols, simultaneously (*parallel* configuration) or in two consecutive cycles (*cascade* configuration).

Compared to a reference system without capture, results show that the largest direct CO$_2$ emission reductions are achieved with CCS without utilisation (−70%) but at the expenses of higher total costs (+7%). Multi-product CCU systems show lower fossil depletion and costs than the reference without capture (−10% and −9%, respectively) because of feedstock replacement by the CO$_2$ utilised. Combination of multi-product CCU with storage turns to be the best alternative for reduced climate change potential (−18% relative to the reference) while still been economically feasible. In addition to lower upstream emissions due to fossil feedstock replacement by utilising CO$_2$, process direct emissions diminish owing to storage. No significant differences were found between the cascade and the parallel configurations. The extra effort to recycle CO$_2$ in the cascade configurations is neither penalised nor rewarded.

1. Introduction

Carbon capture and utilisation (CCU) concepts are increasingly been researched, since in addition to reduce CO$_2$ emissions they could result in lower fossil resource demand [1,2]. Moreover, the large capital investment associated with carbon capture could (partially) be compensated because CO$_2$ is converted into valuable products that provide revenues [3,4]. However, the potential of CCU as a pathway to obtain large emission reductions has been debated, due to the short CO$_2$ storage time of many applications, and the difficulties to assess potential displacement effects.

Previous literature studies have investigated CCU options mainly focusing in CO$_2$ conversion into fuels including techno-economic aspects and simple carbon metrics. These studies show that the production of liquid hydrocarbon fuels with commercially proven CCU technology is not yet economically viable [5]. Methanol synthesis from CO$_2$ and renewable hydrogen from electrolysis is only economically feasible for large plant capacity, when by-products are sold and methanol has a high selling price [6], or when the feedstock costs are lower and the CO$_2$ value is high [7]. However, methanol production from captured CO$_2$ has the potential of net reduction of CO$_2$ emissions mainly due to the fossil fuel avoided compared to the conventional MeOH synthesis

process. Other CCU options consider formic acid as final product, which can be used as hydrogen carrier or as fuel for fuel cells [8]. When using renewable electricity and steam, this CO_2 utilisation alternative has lower CO_2 emissions than the corresponding conventional process. In spite of its environmental attractiveness and technically feasibility, CO_2-based formic acid is not yet financially attractive.

CCU has been typically regarded as a technology towards a single end product. The earlier studies indicated that the major drawback is a no yet economically practicability. However, integrated CO_2 conversion into multiple fuels and chemicals in the same facility could benefit from synergies, such as process and equipment integration and more efficient energy and resource use, analogous to the refinery concept. System-wide and detailed assessments of CCU configurations for co-production of fuels and chemicals are not available in literature.

This paper aims to assess whether configurations that combine multi-product carbon capture and utilisation (CCU) and multi-product carbon capture, utilisation and storage (CCUS), are feasible concepts to close carbon cycles in the petrochemical industry. In this study, we investigate the potential benefits and trade-offs of such multi-output configurations.

To answer the research goal, a case study in a refinery was used, where CO_2 is captured at a steam methane reforming (SMR) facility and is utilised into dimethyl ether (DME) and polyols, different target products than those that received more attention in preceding research (*i.e.*, methanol). This case was selected as:

- SMR processes contribute to 20% of the CO_2 emissions at refineries, and refineries account for 10% of the global industrial CO_2 emissions [9].
- CO_2 conversion into fuels is considered as an attractive option to achieve large CO_2 emissions reduction due to its high fuel global market demand (100-times higher than that of chemicals; [10]. Whereas liquid hydrocarbon fuels, methanol or formic acid are still not economically attractive [5,7,8,6], DME has been reported as a cost-effective option to replace conventional transportation fuels [11,12]. Moreover, DME is a sulfur-free fuel with higher cetane number than diesel and leads to very low emissions of particulate matter, NOx, and CO during its combustion [13]. CO_2-based DME appears as a more efficient alternative compared to conventional DME synthesis [14]. CO_2 is used in a methane dry reforming process to produce syngas, which is then directly transformed into DME [15]. This option has large market potential but the CO_2 is stored for a short period of time.
- The second product in the configuration considers CO_2 conversion into chemicals. Urea and salicilic acid synthesis using CO_2 are well-established industrial processes [3]. CO_2-based polyols are a CCU alternative with high potential for market growth, so they can contribute to meet emissions reduction targets. These polyols are already at commercial stage [16,17] and used as precursors of polyurethane flexible foams. The CO_2 incorporated into the polyol is limited to 20 wt% in order to meet the right flexibility of the final product [18]. This option has a lower market potential than fuels but the CO_2 is stored for a longer period of time (decades vs. days).

Process modelling of the commercial-scale CO_2 source (SMR unit in the refinery), the CO_2 capture unit and CO_2 conversion processes (DME and polyols) serves as basis for an integrated techno-economic and environmental assessment. The environmental evaluation follows a life cycle-assessment approach incorporating climate change and fossil depletion indicators since fuel savings could be a relevant benefit of CCU options (Pérez-Fortes et al., [6]. A comparison among the different CCU and CCUS configurations is carried out to identify the economic and environmental hotspots of each system.

2. Methodology

2.1. Scoping

For the purpose of assessing multi-product CCU and multi-product CCUS systems, two configurations were defined. The CO_2 source in all cases is a hydrogen manufacturing unit of a refinery equipped with carbon capture. In the first configuration (*parallel*) the synthesis of DME and polyol happens in parallel, using the CO_2 stream captured at the hydrogen unit. In the second configuration (*cascade*) the CO_2 captured in the hydrogen unit is first used in the synthesis of DME. The CO_2 released during DME processing is then re-captured and used as feedstock for polyols synthesis. In addition, two reference configurations were considered. One reference case consisting of H_2 production at the refinery without carbon capture, and a storage case that only incorporates CO_2 capture, transport and storage. In total, six different systems were defined (see below). Note that it is assumed that the CCU products would displace fossil based counterparts, and therefore in the systems where there is no utilisation (*REF* and *CCS* cases), DME and polyol are still produced but in the conventional manner.

- **Case 1. Reference (REF)**: H_2 unit of a refinery without CO_2 capture + conventional DME + conventional polyol production (no CO_2 utilisation).
- **Case 2. Storage-only (CCS)**: H_2 unit of a refinery with CO_2 capture and storage + conventional DME + conventional polyol production (no CO_2 utilisation).
- **Case 3. Multi-product CCU, Parallel**: H_2 unit of a refinery with CO_2 capture + CO_2-based DME + CO_2-based polyol production. After capture, the CO_2 stream is split into two parts. One part of the CO_2 is used for CO_2-based polyol synthesis and the rest is used for CO_2-based DME production. There is no CO_2 storage.
- **Case 4. Multi-product CCU, Cascade**: H_2 unit of a refinery with CO_2 capture + CO_2-based DME + CO_2-based polyol production. The CO_2 captured from the H_2 unit is first used for DME production. During DME production 90% of the used CO_2 is re-emitted [19]. Part of the CO_2 released in the DME process is then re-captured, and utilised in CO_2-based polyol synthesis. The rest of the CO_2 is released to the atmosphere. There is no CO_2 storage.
- **Case 5. Multi-product CCUS, Parallel**: H_2 unit of a refinery with CO_2 capture + CO_2-based DME + CO_2-based polyol production. After capture, the CO_2 stream is split into two parts. One part of the CO_2 is used for CO_2-based polyol synthesis and the rest is used for CO_2-based DME production. The CO_2 released during DME synthesis is re-captured and sent to storage.
- **Case 6. Multi-product CCUS, Cascade**: H_2 unit of a refinery with CO_2 capture + CO_2-based DME + CO_2-based polyol production. The CO_2 captured from the H_2 unit is first used for DME production. The CO_2 released in the DME process is then re-captured, a part of it is utilised for CO_2-based polyol synthesis and the rest is stored.

The total systems were divided into system areas (SA) as shown in Fig. 1 and Table 1. Each SA corresponds to a part of the value chain or process type (e.g., natural gas production and transport, hydrogen manufacturing unit, polyol synthesis, etc.). The division on SAs allows transparently communicate differences in the type and level of modelling complexity among SAs and clearly identify the sub-processes with the largest contributions to the costs and environmental impacts.

In all cases, three final products (H_2, DME and polyol) are produced. To size the configuration we chose a SMR unit with a typical commercial-scale production capacity (59 kt/a of hydrogen; [20,21]. From this unit, 95% of the direct CO_2 emissions (337 CO_2 kt/a) are captured via chemical absorption [21]. CO_2-DME synthesis requires 1.76 kg CO_2/kg of DME [19], thus 192 kt/a CO_2-DME could be produced from the CO_2 captured at the SMR unit. Because it is not realistic to have a plant that uses all the CO_2 for polyol, we assumed the capacity of the