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# Assessing the environmental potential of carbon dioxide utilization: A graphical targeting approach

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## Abstract

Carbon Capture and Utilization (CCU) has the potential to reduce both greenhouse gas emissions and fossil fuel use. However, the conversion of $CO_2$ is intrinsically difficult due to its low energetic state. Thus, a positive environmental effect of a $CO_2$-consuming reaction cannot be taken for granted. In this work, we therefore present a graphical method to identify promising reaction schemes using $CO_2$ as a feedstock. Reactant mixtures leading to minimal life-cycle greenhouse gas (GHG) emissions are determined. The optimal reaction schemes strongly depend on the reactants' global warming potential (GWP); in the case of CCU, the future GWP values of $CO_2$ and $H_2$ are particularly critical and subject to major uncertainty today. The graphical method therefore provides GWP targets for $CO_2$ capture and $H_2$ production technologies. The method is demonstrated for the production of methanol. Five optimal reaction schemes are identified depending on the GWP values of $CO_2$ and $H_2$. Thus, four threshold relations for the GWP of $CO_2$ and $H_2$ are derived showing directly under which conditions the utilization of $CO_2$ as a feedstock is environmentally preferential.

**Keywords**: Carbon Capture and Utilization, LCA, Methanol, $CO_2$ Conversion

## 1. Introduction

The utilization of captured $CO_2$ is drawing increasing attention [1]. With progress in capture technologies, high purity $CO_2$ can become abundantly available, e.g. from fossil fueled power plants. Using $CO_2$ as a feedstock for the production of chemicals and fuels might allow for a reduction of both greenhouse gas emissions and fossil fuel depletion. However, major challenges have to be overcome to implement CCU on a large scale: new products and pathways have to be identified and the reaction must be exergonic [2]. Systematic methods to identify promising candidate reactions are therefore desirable. Patel et al. [3] recently introduced a thermodynamic process design framework. The framework can directly be employed to identify promising $CO_2$-based reactions from a thermodynamic perspective. But the utilization of CCU is most often motivated environmentally. Therefore, we extend the framework from Patel et al. [3] by an optimization step based on ecological criteria such as the GWP. This extension enables the identification of the ecologically optimal composition of reactants and products. In a further step, the method can be used to determine GWP targets for $CO_2$ capture and $H_2$ production technologies.
In Section 2, the graphical method is introduced for the example of methanol production. In Section 3, results are presented before conclusions are given in Section 4.

## 2. Graphical Targeting Approach

After a short description of methanol production, the graphical design framework by Patel et al. [3] is briefly summarized and then extended for environmental analysis.

*2.1. Methanol production from $CO_2$*

Methanol production from $CO_2$ has been evaluated both from a thermodynamic [4] and a simplified environmental [2] perspective. Most studies focus on the evaluation of one particular reaction, namely:

$$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O \tag{1}$$

Although reaction (1) is thermodynamically feasible, it might not be environmentally optimal. The following section will provide a graphical method to obtain an ecologically optimal scheme for the production of methanol. The approach is directly applicable to any other compound of the form $C_xH_yO_z$.

*2.2. Obtaining an ecologically optimal reaction scheme*

From a thermodynamic perspective, a reaction must fulfill the mass, energy and entropy (in terms of Gibbs energy) balances. Patel et al. [3] use these balance equations as constraints for a linear program (LP). We adopt the approach for the production of any compound of the form $C_xH_yO_z$ at standard conditions (298K, 1 bar). The considered components (reactants or by-products) are limited to methane ($CH_4$), water ($H_2O$), oxygen ($O_2$), carbon dioxide ($CO_2$) and hydrogen ($H_2$):

$$\nu_1\ CH_4 + \nu_2\ H_2O + \nu_3\ O_2 + \nu_4\ CO_2 + \nu_5\ H_2 \rightarrow C_xH_yO_z \tag{2}$$

The stochiometric coefficient of the product $C_xH_yO_z$ is always fixed to 1. The other components are reactants for negative and by-products for positive stochiometric coefficients $\nu_i$. The mass, energy and entropy balances can be written as follows [3]:

$$0 = \nu_1 + \nu_4 + x \tag{3}$$

$$0 = 4\,\nu_1 + 2\,\nu_2 + 2\,\nu_5 + y \tag{4}$$

$$0 = \nu_2 + 2\,\nu_3 + 2\,\nu_4 + z \tag{5}$$

$$\Delta h^{R,0} = \Delta h^{f,0}{}_{CxHyOz} + \textstyle\sum_i \nu_i\, \Delta h^{f,0}{}_i \leq 0 \tag{6}$$

$$\Delta g^{R,0} = \Delta g^{f,0}{}_{CxHyOz} + \textstyle\sum_i \nu_i\, \Delta g^{f,0}{}_i \leq 0 \tag{7}$$

In this work, a reaction with a minimal environmental impact is sought after. Since the focus of CCU is on greenhouse gas emissions, the method is exemplified using the GWP as an environmental impact category. Only the supply of the reactants is considered to contribute to the GWP of the reaction whereas no benefit, i.e. no avoided burden, is given to any of the by-products.

For the methanol example, the GWP values for $CH_4$, $H_2O$ and $O_2$ are taken from the ecoinvent database [5] whereas these of $CO_2$ and $H_2$ are treated as variable. The resulting optimization problem can be formulated as follows:

$$\min \quad OF = -\textstyle\sum_i \nu^R_i\, GWP_i \tag{8}$$

$$\text{s.t.} \quad (3)-(7) \ \text{where}\ \nu_i^R = \begin{cases} \nu_i, \text{if}\ \nu_i < 0 \\ 0, \text{if}\ \nu_i \geq 0 \end{cases} \tag{9}$$

Due to the discontinuity (9) of the objective function (OF), the problem is not an LP. A formulation as a mixed-integer linear program (MILP) is possible. However, it is

insightful to decompose the solution space into regions with different, but continuous OFs leading to several LPs. These regions are particularly conveniently determined by the graphical approach by Patel et al. [3] using so-called zero lines.

The procedure is demonstrated for the example of methanol synthesis where $CO_2$ and/or $CH_4$ act as potential carbon sources ($v_1 \leq 0$, $v_4 \leq 0$ ). Figure 1 shows the amount of $H_2$ produced or required as a function of the $CO_2$ amount used as feedstock. The zero lines represent stochiometries with zero amounts of a certain compound ($v_i = 0$, $i=1,\ldots,5$), zero reaction enthalpy ($\Delta h^{R,0}=0$) or zero Gibbs energy ($\Delta g^{R,0}=0$). Here, the $\Delta h^{R,0}=0$ constraint (6) is dominated by the $\Delta g^{R,0} \leq 0$ constraint (7) due to a negative reaction entropy and is neglected for clarity in Figure 1.

The objective function $OF_k$ is continuous within each region $k$ bounded by the zero mass balance lines. In Figure 1, four regions ($k=1,\ldots 4$) exists, hence four LPs are solved. For example in region $k=3$, the following objective function is used:

$$OF_3 = - (\nu_1 GWP_1 + \nu_3 GWP_3 + \nu_4 GWP_4 + \nu_5 GWP_5) \tag{11}$$

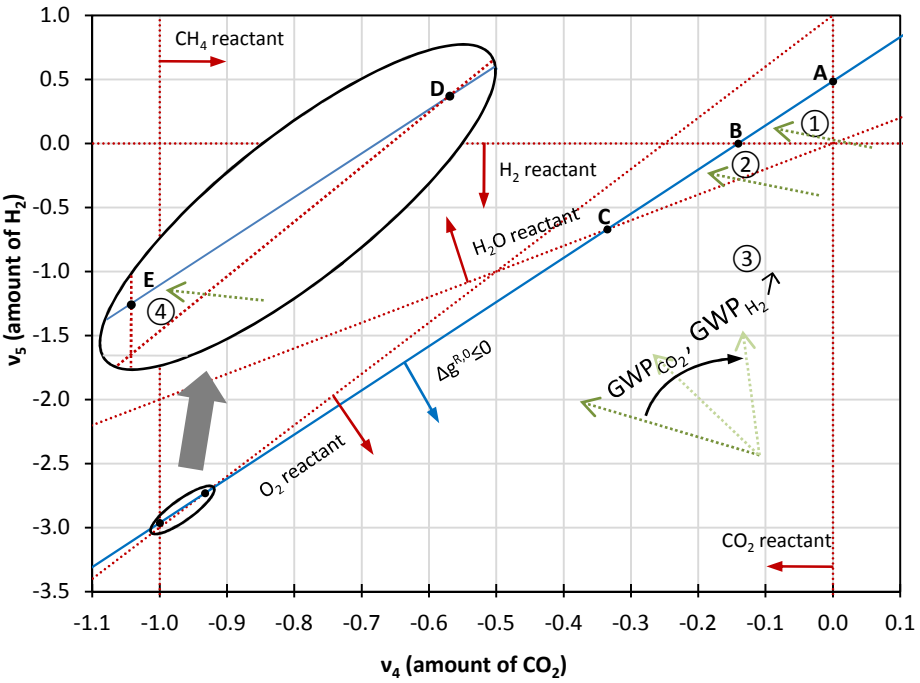


**Figure 1:** Solution space of (MI)LP for methanol synthesis with $CO_2$ as a potential feedstock. The (qualitative) dotted vectors pointing towards the regional optimal solution turn clockwise with increasing GWP values of $CO_2$ and $H_2$.

As for any LP, the optimal solution of every region is at a corner. A vector $\vec{n}_{OS,k}$ pointing towards the local (minimal) optimal solution (OS) can be defined as:

$$\vec{n}_{OS,k} = \begin{pmatrix} -\partial OF/\partial \nu_4 \\ -\partial OF/\partial \nu_5 \end{pmatrix} \tag{12}$$

For region 3, the vector $\vec{n}_{OS,3}$ is given by

$$\vec{n}_{OS,3} = \begin{pmatrix} \frac{\partial v_1}{\partial v_4} GWP_1 + \frac{\partial v_3}{\partial v_4} GWP_3 + GWP_4 \\ \frac{\partial v_1}{\partial v_5} GWP_1 + \frac{\partial v_3}{\partial v_5} GWP_3 + GWP_5 \end{pmatrix} = \begin{pmatrix} -GWP_1 - 2GWP_3 + GWP_4 \\ ½ GWP_3 + GWP_5 \end{pmatrix} \quad (13)$$

The global optimal solutions for given GWP values are obtained as follows: the vectors $\vec{n}_{OS,k}$ are plotted and the local optimal corners are identified. With the corners' reactant mixtures computed from (3) – (5), the objective function values $OF_k$ (8) are compared to determine the global optimal solution.

*2.3. Threshold values for the GWP of $CO_2$ and $H_2$*

The GWP of $CO_2$ and $H_2$ are the critical factors in determining the environmental potential of a CCU scheme: How much additional $CO_2$ was produced in preparing the $CO_2$ feedstock? How was the – usually required – hydrogen produced? Most CCU proposals rely on projections about the future supply of the required feedstock. The presented graphical method allows for a convenient determination of GWP target values for future $CO_2$ capture and $H_2$ production technologies.

Eq. (13) shows that the vectors $\vec{n}_{OS,k}$ depend on the values $GWP_4$ ($CO_2$) and $GWP_5$ ($H_2$). All vectors turn clockwise if the GWP of $CO_2$ or $H_2$ increases. Only vector $n_{OS,1}$ does not depend on hydrogen. This general behavior can be used to identify possible optimal corners. For example, the vector $\vec{n}_{OS,3}$ always points upwards in positive direction of $v_5$ since $(½\ GWP_3+GWP_5) \geq 0$.

The optimal solution moves from its current to a neighboring corner if the vector $\vec{n}_{OS,k}$ is orthogonal to the zero-line connecting these corners. This condition is fulfilled if:

$$m_{zero-line} = -\frac{n_{OS,k,1}}{n_{OS,k,2}} = -\frac{\partial OF_k / \partial v_4}{\partial OF_k / \partial v_5}, \quad (14)$$

where $m_{zero-line}$ denotes the slope of the zero line. The derivatives of the OF depend on the $GWP_i$ values. The $GWP_i$ values fulfilling Eq. (14) are called *local GWP threshold values* since values just below or above the threshold values result in different optimal solutions in a region *k*. For the two degrees of freedom ($GWP_4$ and $GWP_5$), it is convenient to compute threshold lines.

The procedure for obtaining global GWP threshold values is as follows: the potential local optimal corners are identified using (12) with variable GWP values for $CO_2$ and $H_2$. By applying (14) to the zero-lines that connect these corners, relations for the local GWP threshold values are derived. Whether these local values are also global threshold values can be checked in analogy to the procedure in 2.2.

## 3. Results

The proposed method is used to determine the global GWP threshold values for $CH_3OH$ production. In this case, five global environmentally optimal solutions can be found in dependence of the GWP of $CO_2$ and $H_2$ (corners A to E in Figure 1). Hence, four threshold lines can be computed, see Figure 2. If the GWP of $CO_2$ is above 0.276 kg $CO_2$eq./kg $CO_2$, the use of $CO_2$ as a feedstock for methanol synthesis is environmentally not advisable and methane should be employed as carbon source. If the GWP of $CO_2$ is below that value, it is always preferential to (partially) use $CO_2$ as a feedstock. How much $CO_2$ should be used, depends also on the GWP of $H_2$, see Figure 2.

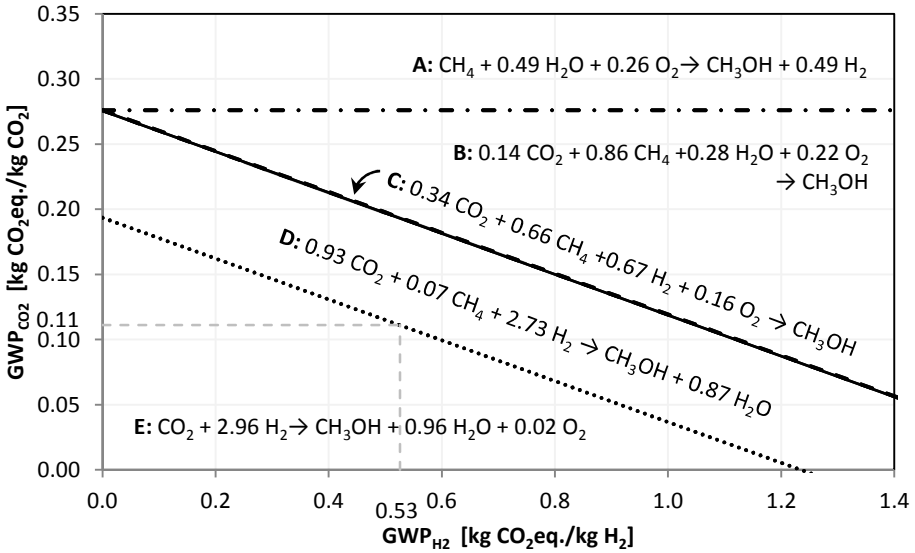


**Figure 2:** Environmentally optimal reactions as a function of the GWP of $CO_2$ and $H_2$.

Figure 2 can be used to define GWP targets for technologies. For example, in a power plant with a 90% $CO_2$ capture rate where all of the remaining 10% are allocated to the captured $CO_2$ stream, the GWP of $CO_2$ is 0.11 kg $CO_2$eq./kg $CO_2$ (=0.1/0.9). Please note that this allocation procedure provides a worst case value for the GWP of $CO_2$. Still, with this worst case value, $CO_2$ should always be used as a feedstock. Moreover, $CO_2$ should be the only carbon source if the GWP of $H_2$ is below 0.53 kg $CO_2$eq./kg $H_2$.

## 4. Conclusions

Environmentally optimal reaction schemes for CCU can be obtained by introducing environmental impact coefficients into the process design framework by Patel et al. [3]. The resulting graphically-based targeting method gives further valuable insight into the process: threshold values for the GWP of $CO_2$ and $H_2$ can be derived that are tipping points between different reaction schemes. A worst case analysis shows that methanol production from $CO_2$ captured from power plants is a promising CCU scheme.

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