

# Process Design for the Directly Coupled Production of Methanol and Formaldehyde Based on CO<sub>2</sub>

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Supporting Information  
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Sustainable hydrogen generation is preferred over production from fossil sources in the context of a carbon-neutral economy. As a result, production costs for CO<sub>2</sub>-based products are estimated to be much higher than those of their fossil equivalents. Hence, it is essential to optimize process chains regarding their hydrogen efficiency. In this study, a concept for the directly coupled production of CO<sub>2</sub>-based methanol and formaldehyde in a modified silver catalyst process is evaluated regarding the utilization of H<sub>2</sub>. Detailed simulations in Aspen Plus allow the comparison to the separately operated synthesis of green methanol and formaldehyde. By directly connecting both production steps, utilization ratios of introduced H<sub>2</sub> and CO<sub>2</sub> could be improved, reaching values of 98 % and 99 %, respectively.

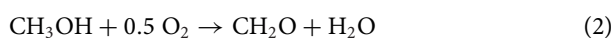
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## 1 Introduction

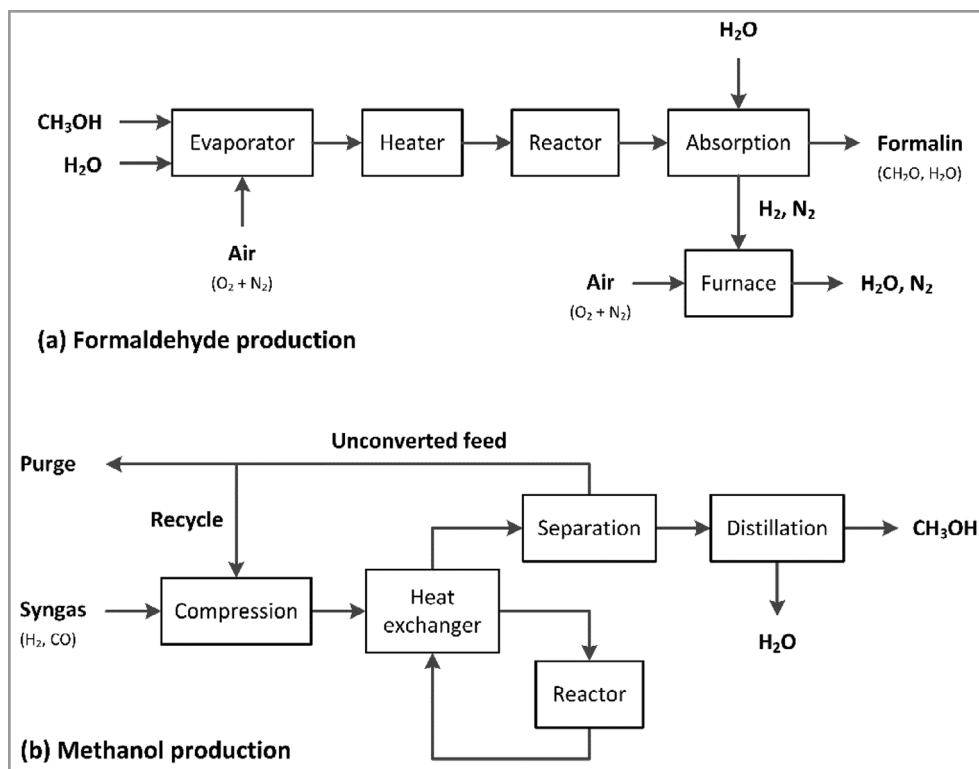
In today's chemical industry formaldehyde takes up a vital role as intermediate C<sub>1</sub> building block. It is the basis of many processes for the synthesis of resins [1], plastics [2], and other valuable products [3–5]. Conventional formaldehyde production is often based on the oxidative dehydrogenation of methanol in so called silver catalyst processes (SCP) [6, 7]. The synthesis can be implemented as water ballast process to ensure longevity of the utilized polycrystalline silver catalyst [7, 8]. In this configuration of the process, schematically shown in Fig. 1a, methanol and water are evaporated under addition of air and then overheated to prevent condensation of the feed stream. Typically, the mixture has a molar methanol-to-oxygen ratio of 2.5 to 4 and a mass-related methanol-to-water ratio of 1.5 [6, 7, 9]. The feed is passed over a thin layer of silver particles at atmospheric pressure and temperatures ranging from 600 to 720 °C [7, 8]. Although it has been implemented industrially since the early twentieth century [6, 8, 10], the reaction system of formaldehyde synthesis is still not sufficiently studied [9, 11–14]. In general, five main reactions (Eq. (1)–(5)) are considered [6, 8, 9, 11–13]. Formaldehyde can be produced from the direct (Eq. (1)) or oxidative dehydrogenation (Eq. (2)) of methanol. There are also combustion reactions of formaldehyde (Eq. (3)) and hydrogen (Eq. (4)) as well as

the thermal decomposition of the aldehyde (Eq. (5)) to be factored in.



To ensure minimal thermal decomposition of the aldehyde, gas-hourly space velocities of up to 250 000 h<sup>-1</sup> [7] are realized and the hot product is quenched right underneath the catalyst bed within 0.2 s [15]. Methanol conversion can be as high as 97 % [6, 15, 16] with formaldehyde selectivities up to 90 % [6, 8, 15–18]. In a final step, the gained aldehyde is chemically absorbed in water leading to an aqueous solution

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**Figure 1.** Block flow diagram of conventional production of formaldehyde (a) and methanol (b).

with 37 to 55 wt % of formaldehyde as final product [1, 6, 8, 19]. Additionally, a hydrogen-rich gas stream is obtained that is typically used for heat generation [6–8]. Due to its high concentration of  $\text{N}_2$  introduced to the process with the air used as oxygen source, a chemical use of the released  $\text{H}_2$  is not practical [20–22].

Methanol is traditionally produced from fossil syngas ( $\text{H}_2 + \text{CO}$ ) in a preceding process [23–25]. Ideally, the ratio of hydrogen to carbon monoxide is slightly larger than 2 in the inlet gas stream [23, 25]. In a first step, the feed stream is compressed to pressures between 50 and 100 bar [23–25] before it is preheated with the help of hot product gases. At temperatures between 250 and 300 °C [23–25], the feed stream is converted to methanol over  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  (CZA) catalysts [24–26]. Methanol is formed in hydrogenation reactions of  $\text{CO}$  (Eq. (6)) and  $\text{CO}_2$  (Eq. (7)). Simultaneously, the reverse water-gas shift reaction (Eq. (8)) occurs.



The reactions can take place in a multi-tubular reactor for which temperature regulation is implemented either as boiling water cooling or cold syngas quenching [23, 24]. After the conversion, the unreacted feed is separated from the product and recycled to the inlet compression.

The liquid product stream, consisting of methanol and water, is distilled to reach the desired purity for following applications. A block flow diagram of methanol synthesis is provided in Fig. 1b.

In the light of sustainable production chains, a purely  $\text{CO}_2$ -based methanol synthesis is subject of recent and ongoing research [25, 27–31]. Pioneering companies such as Carbon Recycling International and HIF Global have taken up operation of plants with production capacities of up to  $1 \text{ Mt a}^{-1}$  of green methanol, bringing  $\text{CO}_2$ -based methanol synthesis on the verge of commercialization [32, 33]. Preferred  $\text{CO}_2$  sources are cleaned flue gases e.g. from cement or steel industries and atmospheric  $\text{CO}_2$  that has been collected via direct air capture. Techno-economic evaluations of the process from different authors [34–37] suggest that the key factor for feasibility is lowering costs of the needed sustainable hydrogen. The same can be said for most  $\text{CO}_2$ -based syntheses, which is why in a future carbon-neutral economy hydrogen will become a crucial resource. Unfortunately, any sustainable alternative for hydrogen generation is significantly more expensive than technologies based on fossil resources [38]. For this reason, processes and process chains depending on green hydrogen must be optimized regarding their hydrogen efficiency. Especially promising in this endeavor seems to be the investigation of production chains that include both process steps that require hydrogen as well as those that release it.

Within this work, a concept for the directly coupled  $\text{CO}_2$ -based production of methanol and formaldehyde is

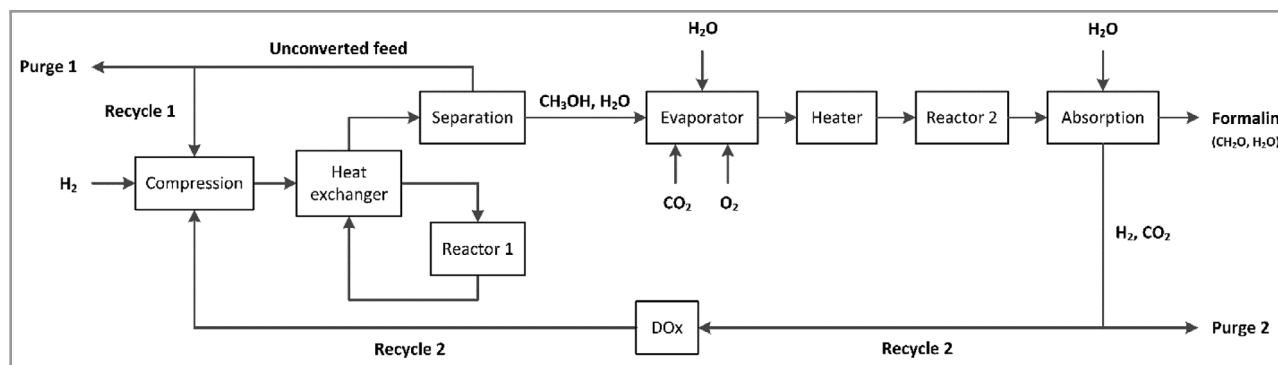


Figure 2. Block flow diagram of directly coupled production of methanol and formaldehyde based on  $\text{CO}_2$ .

introduced and the effects of process coupling on hydrogen efficiency as well as overall process performance are discussed. Results include a comparison to different versions of separately operated green methanol synthesis and formaldehyde production. All regarded processes are assessed based on flowsheet simulations in Aspen Plus.

## 2 Process Design

### 2.1 Overview

In the present work, three different process chains for the production of  $90 \text{ kt a}^{-1}$  of formaldehyde are considered. Starting point for all cases is the  $\text{CO}_2$ -based synthesis of the required  $110 \text{ kt a}^{-1}$  of methanol. Sustainable methanol production is then combined with either the conventional or a modified silver catalyst process. For the latter, a mixture of  $\text{CO}_2$  and  $\text{O}_2$  is used as oxygen supply instead of air (for further explanation see Sect. 2.2).

Feed  $\text{CO}_2$  is assumed to be obtained from cleaned waste gas streams of industrial processes at  $25 \text{ }^\circ\text{C}$  and atmospheric pressure. Needed hydrogen is considered at  $25 \text{ }^\circ\text{C}$  and  $30 \text{ bar}$  as these are common conditions for electrolytically generated  $\text{H}_2$ . For simplification, both raw materials are considered with a purity of  $100 \%$ . Reaction conditions for methanol synthesis are set to  $70 \text{ bar}$  and  $259 \text{ }^\circ\text{C}$ . As proposed by Campos et al. [34], the reactor section is split into three consecutive isothermal units with intermediate product condensation to positively influence the thermodynamic equilibrium. Each converter has a length of  $11 \text{ m}$  and contains  $1085$  tubes with an inner diameter of  $3.75 \text{ cm}$ . For the CZA catalyst, a density of  $1775 \text{ kg m}^{-3}$  is assumed leading to a mass of  $14.0 \text{ t}$  for each reactor module.

Aside from methanol, all feed streams of formaldehyde production are considered at  $25 \text{ }^\circ\text{C}$  and  $1.013 \text{ bar}$ . As oxygen source, either air from the environment or oxygen produced as side product in the installed electrolysis are regarded. The feed mixture is heated to  $120 \text{ }^\circ\text{C}$  before it is fed to the reactor which is operated at  $680 \text{ }^\circ\text{C}$  and atmospheric pressure.

The absorption column exhibits four steps with intermediate cooling as it is installed for instance at BASF facilities [15]. The single fixed bed consists of polycrystalline silver for which the density is assumed to be  $10\,050 \text{ kg m}^{-3}$ . At a diameter of approximately  $2.9 \text{ m}$  and a height of  $2.5 \text{ cm}$  about  $1.0 \text{ t}$  of catalyst is needed. All plants are considered to be operated for  $8000 \text{ h a}^{-1}$ .

### 2.2 Directly Coupled Process

In order to increase overall hydrogen efficiency of a combined production of methanol and formaldehyde, it is crucial to avoid thermal exploitation of the  $\text{H}_2$ -rich off-gas of the SCP. A beneficial alternative would be the recirculation of hydrogen to methanol synthesis and thus the enhancement of the utilization ratio. As the separation of hydrogen and nitrogen is difficult [20–22], it is necessary to modify the SCP so that no nitrogen is included in the flue gas. Instead of air, a mixture of  $\text{CO}_2$  and  $\text{O}_2$  is added to the liquid feed stream ( $\text{CH}_3\text{OH} + \text{H}_2\text{O}$ ) in the evaporator.  $\text{CO}_2$  then takes up the role as inert component during formaldehyde synthesis, serving for explosion prevention and heat regulation. After this simple modification, the gas stream leaving the absorption column consists mainly of  $\text{CO}_2$  and  $\text{H}_2$ , with traces of  $\text{CO}$  and  $\text{H}_2\text{O}$ . This stream can then easily be fed to the initial compression stage of methanol production. Fig. 2 shows the block flow diagram of a directly coupled production of  $\text{CO}_2$ -based methanol and formaldehyde in a modified SCP.

As can be seen in Fig. 2 at the considered scale of the plant, a thermal purification of the raw methanol is no longer needed and the distillation step can be omitted. At the same time an additional process step for oxygen removal, e.g. in the form of catalytic deoxygenation (DOx) [39], is required in the recycling loop between the two synthesis steps to prevent reoxidation of the CZA catalyst [37]. To avoid accumulation of impurities, small amounts of internal and connecting recycling streams are purged. The released gas streams are collected and used as fuel for overheating the steam exiting the cooling system of the methanol reactors.

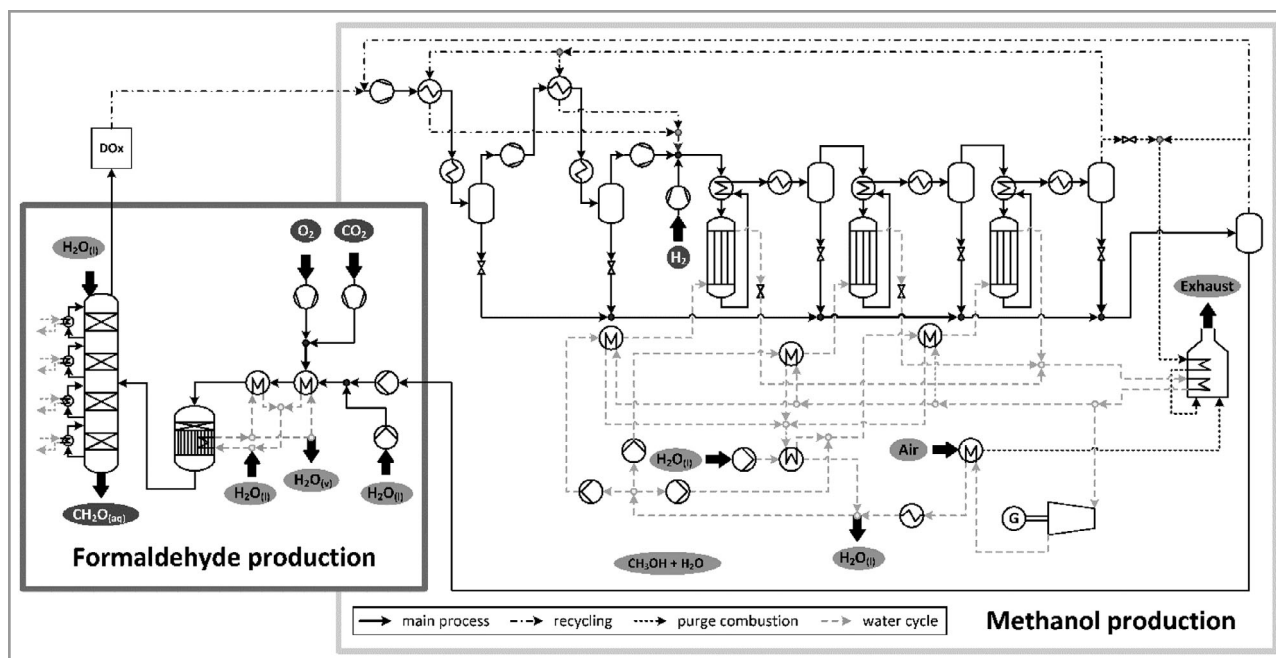


Figure 3. Process flow chart of directly coupled CO<sub>2</sub>-based production of methanol and formaldehyde.

The overheated steam is used to generate electrical power in a Rankine cycle. Another, smaller water cycle is considered between the quench, evaporator and heater in the SCP. A detailed process flowsheet of the coupled production is presented in Fig. 3.

### 2.3 Process Performance Indicators

In order to evaluate process performance, mass and energy balances are taken into account. Above all, overall hydrogen efficiency  $\eta_{\text{H}_2, \text{PC}}$  of the process chains is calculated as follows:

$$\eta_{\text{H}_2, \text{PC}} = \frac{\dot{m}_{\text{H}_2, \text{f}} - \dot{m}_{\text{H}_2, \text{p}}}{\dot{m}_{\text{H}_2, \text{f}}} \quad (9)$$

where  $\dot{m}_{\text{H}_2, \text{f}}$  is the mass stream of fresh hydrogen fed to the process chain at the inlet of methanol production and  $\dot{m}_{\text{H}_2, \text{p}}$  is the hydrogen mass that is contained in all purged streams. The utilization ratio of CO<sub>2</sub>  $\eta_{\text{CO}_2, \text{PC}}$  is also considered:

$$\eta_{\text{CO}_2, \text{PC}} = \frac{\dot{m}_{\text{CO}_2, \text{f}} - \dot{m}_{\text{CO}_2, \text{e}}}{\dot{m}_{\text{CO}_2, \text{f}}} \quad (10)$$

where  $\dot{m}_{\text{CO}_2, \text{f}}$  is the mass stream of CO<sub>2</sub> added to the feed of both methanol and formaldehyde production and  $\dot{m}_{\text{CO}_2, \text{e}}$  is the directly emitted CO<sub>2</sub>. The latter contains unconverted CO<sub>2</sub> from methanol synthesis as well as the amount formed during formaldehyde production (see Eq. (3)).

### 3 Process Simulation

For all considered process chains flowsheet simulations were implemented in Aspen Plus V11. All equipment was modeled with the Non-Random Two-Liquid property method with a second set of binary parameters (NRTL2), with the exception of the methanol reactor modules and the absorption column in the SCP.

The methanol reactor system was simulated using the Redlich-Kwong-Soave equation with modified Huron-Vidal mixing rules (RKSMHV2) as is common practice in literature [40–42]. A rigorous plug flow reactor (RPlug) was chosen and the kinetic model developed by Campos et al. [43] was implemented as Langmuir-Hinshelwood-Hougen-Watson (LHHW) reaction model. The necessary parameters can be found in the Supporting Information. A co-current flow of cooling water was chosen.

The chemical absorption of formaldehyde in water was simulated with the help of the model proposed by Bongartz et al. [44], using ideal gas properties (IDEAL) and describing nonideality of the liquid phase through the UNIFAC model. The solubility of the included permanent gases in the liquid phase was also taken into account, leading to traces of CO<sub>2</sub>, CO, H<sub>2</sub> and O<sub>2</sub> in the final product. The column was simulated as rigorous RadFrac model with 4 stages and heat being removed on the top and bottom stages. The product gas was fed to the column on the lowest stage, while water was added at the head of the column.

Heat exchangers were implemented as HeatX for all major units. If cooling water was used as second fluid, but was not

**Table 1.** Simulation results and performance indicators for the considered process chains for formaldehyde production.

Item	Case 1	Case 2	Case 3
$\dot{m}_{\text{H}_2,\text{f}}$ [t h <sup>-1</sup> ]	2.62	2.62	2.33
$\dot{m}_{\text{H}_2,\text{p}}$ [t h <sup>-1</sup> ]	0.35	0.35	0.06
$\dot{m}_{\text{CO}_2,\text{f}}$ [t h <sup>-1</sup> ]	19.04	52.49	17.42
$\dot{m}_{\text{CO}_2,\text{e}}$ [t h <sup>-1</sup> ]	1.98	35.42	0.24
$P$ [MW]	2.78	2.78	3.08
$\dot{Q}$ [MW]	-9.67	-9.67	-15.86
$\eta_{\text{H}_2,\text{PC}}$ [%]	86.70	86.70	97.51
$\eta_{\text{CO}_2,\text{PC}}$ [%]	89.61	32.52	98.61

utilized in the steam cycle, simple heater models were used. A minimal temperature difference of 10 °C was set for all heat exchangers. Compressors and turbines were assumed as Compr with polytropic ASME method and an efficiency of 72 %.

A relative tolerance of 10<sup>-6</sup> was allowed for all process units. Convergence was reached using the Broyden method with a maximum error of 10<sup>-4</sup>. More detailed explanations of relevant parameters and assumptions can be found in the [Supporting Information](#).

## 4 Results and Discussion

In the presented conceptual study, three process chains, which all start with the CO<sub>2</sub>-based production of methanol, were evaluated. This first sub-process was either followed by the conventional SCP (case 1) or a separately operated CO<sub>2</sub>-modified SCP (case 2), or was directly coupled to the CO<sub>2</sub>-modified SCP (case 3) to gain formaldehyde as a final product. It was assumed that large amounts of CO<sub>2</sub> added act as inert component and do not influence the reaction system of formaldehyde formation (Eqs. (1)–(5)). Neglecting the effect of any impurities contained in captured CO<sub>2</sub>, is justifiable as common impurities like H<sub>2</sub>S, SO<sub>2</sub>, CO, H<sub>2</sub>O, H<sub>2</sub>, NO<sub>x</sub>, N<sub>2</sub> and O<sub>2</sub> would also be present in the conventional process using air [45, 46]. The most important values for mass and energy balances as well as the introduced performance indicators of cases 1–3 are summarized in Tab. 1. Results were obtained from the implemented flow-sheet simulations in Aspen Plus and will be discussed in the following.

### 4.1 Mass Balance

With an operating time of 8000 h a<sup>-1</sup>, the aim of all considered cases was to produce 13.8 t h<sup>-1</sup> of methanol as intermediate and 11.3 t h<sup>-1</sup> of formaldehyde as final product. With 19.0 t of CO<sub>2</sub> fed to the process chain, this leads to a methanol yield of 0.72 t of methanol per ton of CO<sub>2</sub>

supplied, if the CO<sub>2</sub>-based methanol synthesis is operated independently from a conventional SCP (case 1). This result is in good agreement with studies on CO<sub>2</sub>-based methanol production that have been published prior to this work [34, 40, 42]. In case 2, where sustainable methanol production is followed by a separately run CO<sub>2</sub>-modified SCP, the same mass related yield equals 0.26. The mass related over all methanol yield is significantly lower for this scenario, because CO<sub>2</sub> has to be introduced as reactant to methanol production and also independently as inert component for the adapted SCP. This leads to an increased demand of 52.5 t h<sup>-1</sup> for CO<sub>2</sub>. For a directly coupled production of green methanol and formaldehyde according to case 3, 0.79 t of methanol can be produced per ton of CO<sub>2</sub> supplied. The reduced need for fresh CO<sub>2</sub> for the directly coupled process chain, can be traced back to the formation of CO<sub>2</sub> in the SPC (see Eq. (3)). Because the two synthesis steps are directly linked by the outer recycle stream, only 17.4 t of CO<sub>2</sub> have to be supplied to the process chain. The resulting amount of CO<sub>2</sub> is then used as inert component in the SCP and subsequently as reactant for methanol production.

Since there is no possibility to chemically utilize the hydrogen released during the dehydrogenation of methanol, if the process steps are not connected, 2.6 t h<sup>-1</sup> of fresh hydrogen have to be added to the feed stream in cases 1 and 2. This demand can be reduced to 2.3 t h<sup>-1</sup>, when a recycling loop is established between the SCP and methanol production, as considered in case 3.

### 4.2 Energy Balance

For all three cases, heat integration resulted in self-sufficiency of the process chain. Excess heat released in the exothermic reactions of methanol formation was used in a Rankine cycle to generate electricity. This way, the power consumption  $P$  could be reduced from 4.5 MW, 4.6 MW, and 4.8 MW to 2.8 MW, 2.8 MW, and 3.1 MW for cases 1–3, respectively. The slight increase in power demand for the directly coupled process option can be attributed to the larger feed stream that needs to be compressed in the CO<sub>2</sub>-compression section. In addition to the needed CO<sub>2</sub>, the recycled gas stream is entered there in this scenario. The reduction of the required compression capacity for the hydrogen feed cannot make up for this increase.

Heat losses ( $\dot{Q}$ ) caused by cooling low temperature streams added up to 9.7 MW in cases 1 and 2 and 15.9 MW in case 3. The large difference is caused by the omission of the distillation step in the directly coupled process. If methanol production is operated separately and thus distillation is required, a part of the low-temperature cooling sections can be used to heat the reboiler of the column. To further enhance the efficiency of the coupled process chain, applications for low-temperature heat streams should be found.

### 4.3 Process Performance

Under the assumption, that all required electricity is obtained from sustainable and carbon-free energy sources, CO<sub>2</sub> emissions of the process chains have two origins. CO<sub>2</sub> can either be present in purge streams before combustion or be formed by oxidation reactions of CO, methanol, or formaldehyde contained in the rejected streams. In case of the conventional SCP, overall CO<sub>2</sub> emissions amount to 2.0 t h<sup>-1</sup> leading to a CO<sub>2</sub> utilization ratio of 90 %. The absolute value increases drastically, when considering separately operated green methanol production and the CO<sub>2</sub>-modified SCP, resulting in 35.4 t h<sup>-1</sup> CO<sub>2</sub> being emitted. This is due to the fact, that the CO<sub>2</sub> used as inert gas in the SCP is of no use after it leaves the absorption column. Thus, only 0.33 t CO<sub>2</sub> are abated per ton that is supplied to the process chain. The discharge can be reduced to 0.2 t h<sup>-1</sup> of CO<sub>2</sub>, if sustainable methanol production is directly coupled to the adapted SCP. Since the recycling loop also leads to a decreased demand of fresh CO<sub>2</sub>, the utilization ratio of this process chain is 99 %. This shows that direct coupling of the mentioned processes, has a positive effect on overall CO<sub>2</sub> utilization.

As there is no H<sub>2</sub> recycled, hydrogen efficiency is 87 % for cases 1 and 2. Of the required H<sub>2</sub>, 0.35 t are rejected with the purge and waste streams of methanol and formaldehyde production. However, if released H<sub>2</sub> is fed back to methanol synthesis, only 0.06 t h<sup>-1</sup> are entered into combustion and thus wasted. With the demand being reduced at the same time, hydrogen efficiency is enhanced to 98 % and hence increased by 11 percentage points.

## 5 Conclusion and Outlook

In this paper, a process for the directly coupled CO<sub>2</sub>-based production of methanol and formaldehyde is designed and an initial conceptual study is provided. The main goal of the concept is to increase overall hydrogen efficiency by recycling H<sub>2</sub> from formaldehyde production back to the feed of methanol synthesis. In order to do so, the regarded silver catalyst process for formaldehyde synthesis has to be modified. This is achieved by utilizing CO<sub>2</sub> instead of N<sub>2</sub> as inert component in the SCP. The investigation includes the comparison of the suggested process chain to two other concepts where either the conventional or the adapted SCP was operated independently from CO<sub>2</sub>-based methanol production. The processes were simulated in Aspen Plus and main process parameters were assessed. It was shown, that directly coupling the processes not only increases overall hydrogen efficiency by 11 percentage points but also has a positive effect on CO<sub>2</sub> utilization. The latter was enhanced by 9 percentage points when compared to the separate operation of green methanol production and a classic SCP.

To evaluate the concept more thoroughly, flowsheet simulations will be implemented for different plant sizes and their performance will be compared to the results presented here. Further optimization of the concept could be achieved by finding suitable applications for so far unused low temperature heat streams. Detailed techno-economic assessments will clarify which parameters have the most significant influence on profitability. In order to verify feasibility of the CO<sub>2</sub>-modified SCP, experimental studies will also be carried out in the future.

### Supporting Information

Supporting Information for this article can be found under DOI: <https://doi.org/10.1002/cite.202300183>.

### Acknowledgment

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### Symbols used

$\dot{m}$	[t h <sup>-1</sup> ]	mass flow
$P$	[MW]	electric power
$\dot{Q}$	[MW]	heat flow

### Greek letters

$\eta$	[-]	efficiency, utilization ratio
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### Sub- and Superscripts

e	emission
f	feed
p	purge
PC	process chain

### Abbreviations

CZA	Cu/ZnO/Al <sub>2</sub> O <sub>3</sub>
DOx	deoxygenation
SCP	silver catalyst process

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