TECHNO-ECOLOGICAL EVALUATION OF METHANOL AND ACETIC ACID PRODUCTION FROM STEEL MILL OFF-GASES: A PATHWAY TOWARDS CARBON CAPTURE AND UTILIZATION IN THE STEEL INDUSTRY

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ABSTRACT

This paper presents a techno-ecological comparison of two prospective synthesis routes to produce methanol and, subsequently, acetic acid from steel mill off-gases. Different scenarios for future developments in the energy sector are considered. The main objective is to provide a forward-looking perspective on the techno-ecological possibilities of carbon capture and utilization systems for the steel industry. The proposed scenarios compare the direct conversion of carbon oxides in the blast furnace gas with a process plant system consisting of a pre-conversion, purification, separation, and a reaction unit. The resulting methanol product can be used in a downstream unit together with the carbon monoxide separated from the basic oxygen furnace gas to produce acetic acid. The investigated processes and sub-processes are parameterized using process simulation, where heuristic rules are applied, and fundamental sensitivity analyses are performed to determine optimal operating points. To satisfy the hydrogen demand for the methanol reaction, an additional hydrogen production unit with water electrolysis using grid electricity is required. This creates a sector coupling system between the steel plant, the chemical industry and the energy sector. The methanol production scenarios are evaluated using several key performance indicators specifically designed to target the technological, energy and environmental aspects of the entire synthesis routes. The performance indicators are developed and calculated based on the energy demand and integration potential of the process, the energy demand for hydrogen production, the conversion and recirculation potential of hydrogen, and the projected emission factors for heat and power from the German grid mix.
The results indicate that emissions from the future German grid mix for hydrogen production and the conversion potential of carbon oxides in the methanol reactor are critical factors in determining the technological and environmental viability of the overall carbon capture and utilization system. The evaluated synthesis routes show great potential for carbon capture and utilization to reduce the carbon dioxide emissions from the steel industry, especially when coupled with hydrogen produced from renewable and low-carbon energy sources.

1 INTRODUCTION

Human activities have undoubtedly caused a global temperature increase of 1.1°C since the pre-industrial times, with rapid changes in climate systems and severe impacts on weather extremes and vulnerable populations. Despite increased mitigation efforts, current policies are insufficient, and are likely to lead to a warming of more than 1.5°C this century. (H. Lee *et al.*, 2023)
Global steel production plays a critical role in this area, accounting for approximately 7 % of annual global greenhouse gas emissions (Somers, 2022). Scenarios show that global steel demand will increase to more than 2 Gt a^{-1} by 2050, of which more than 50 % will still be produced by the conventional, high carbon dioxide (CO_2) emitting, coal-based route consisting of a blast furnace and a basic oxygen furnace

https://doi.org/10.52202/077185-0091

(Bellevrat and Menanteau, 2009). More than 90 % of the CO_2 emissions from a conventional steel plant come from the blast furnace process, so the highest potential for reducing the overall emissions lies in reducing CO_2 emissions from the blast furnace gas (BFG) (Collis *et al.*, 2021).
One possible way to reduce these CO_2 emissions is through Carbon Capture and Utilization (CCU). The carbon oxides from the BFG can be used as a carbon source for a variety of chemical products such as methanol, gasoline, plastics and fertilizers (Kolbe *et al.*, 2022). In this paper, we consider the production of two different chemicals, methanol (with additional hydrogen) and acetic acid. To achieve a significant reduction in emissions, it is necessary to select a sustainable and technologically feasible process to produce methanol from BFG. Methanol can be further used to produce acetic acid using captured carbon monoxide (CO) from the basic oxygen furnace gas (BOFG) (Lim *et al.*, 2016).

There are currently several concepts in the literature for producing methanol from steel mill off-gases (SMOG). Bampaou *et al.* (2022) investigate the production costs of methane and methanol from different flue gas mixtures using process simulation. The results show that the main cost driver is the production of hydrogen. Gentile *et al.* (2022) use a different synthesis pathway by converting the BOFG and BFG with a sorption enhanced water gas shift (WGS) and separating the hydrogen with a membrane before the main synthesis unit. Another synthesis pathway consisting of a WGS unit, a CO_2 separation by pressure swing adsorption (PSA) unit and H_2 purification steps before entering the methanol synthesis unit is presented by Porter *et al.* (2022). Girod *et al.* (2020) investigated the use of BFG as a feed gas for methanol synthesis without prior shifting or separation of CO_2. The results show that the carbon and hydrogen utilization is inferior to using pure CO_2 as feed gas, but no economic, energetic, or ecological evaluation was performed.
There is currently no scientific literature on the production of acetic acid from SMOG. There are only a few studies that evaluate the acetic acid production itself, such as Dimian and Kiss (2020), who compared a heterogeneous and homogeneous catalyzed production process.

2 METHODS

2.1 PROCESS SIMULATION

The process simulation models are developed using Aspen Plus V10 and are based on models from the literature. They are used to calculate the electrical, thermal, and cooling energy requirements as well as the waste and product streams for each sub-process. Pressure losses are not considered. Full chemical equilibrium is assumed for each reaction to make the models independent of residence time. For process steps in the methanol synthesis at pressures above 10 bar, we use the Redlich-Kwong-Soave equation of state with modified Huron-Vidal second order mixing rules. Process steps below 10 bars are calculated using the Non-Random-Two-Liquids (NRTL) model for the liquid phase and Redlich-Kwong for the gas phase. The acetic acid process is modelled using NRTL, with the Hayden-O'Connell equation of state for the gas phase for pressure steps below 10 bars and the SR-Polar model for pressures above 10 bar. The operating parameters of the sub-processes are selected based on technical feasibility, heuristic rules and the ecological performance indicators. If the impact of a sub-process can't be quantified directly, we use the minimization of CO_2-emissions for the energy supply as the main criterion. The flow rate and composition of the off-gases BFG and BOFG are taken from a real steel plant in Duisburg (Germany), as reported by Yildirim *et al.* (2018). Prior gas cleaning steps, such as flue gas desulfurization are neglected because they do not have a significant impact on the overall system. The evaluated concepts provide more cooling energy than heating energy. To reduce the complexity of the re-integration of the cooling energy, we assume that 80 % can be re-integrated either on-site for the steelmaking process or for district heating. A detailed Pinch-analysis for the heat integration of the evaluated concepts is not necessary, because the main cooling streams are from exothermic reactors with significantly higher temperatures than the highest temperature of the heating streams for the adsorption or distillation processes ($\Delta T > 100$ K). Therefore, the thermal energy can be integrated within the evaluated subprocesses and concepts. The technical assumptions are estimated based on a five-year construction period and an operating period from 2030 to 2050. Therefore, we set the reference year to the middle of the operating period in 2040.

https://doi.org/10.52202/077185-0091

2.2 BOUNDRIES AND DEVELOPED KEY PERFORMANCE INDICATORS (KPI)

The KPI's used to evaluate the ecological and technical viability of the process are based on the *loop carbon efficiency* (LCE) and *loop hydrogen efficiency* (LHE) as proposed by Nestler *et al.* (2018). We modify the LCE to include the emissions for the energy demand and the avoided emissions by replacing conventional heating with natural gas. Substitution of emissions from conventionally produced methanol is not considered, as it is highly dependent on uncertain future technology developments and energy sources. We consider CO_2 as defined by the Greenhouse Gas Protocol in Ranganathan *et al.* (2004) to calculate Scope 1 (direct emissions) and Scope 2 (indirect emissions from energy demand). The resulting KPI, defined as *emission reduction efficiency* (ERE), is given in equations (1) to (4).

$$ERE = \frac{\text{Avoided Emissions}}{\text{Avoidable Emissions BFG+BOFG}} \cdot 100\% \tag{1}$$

$$ERE = \frac{\dot{n}_{\text{CO+CO2,BFG}} + \dot{n}_{\text{CO,BOFG}} - (\dot{n}_{\text{CO+CO2,Scope 1}} + \dot{n}_{\text{CO2,Scope 2}})}{\dot{n}_{\text{CO+CO2,BFG,t.a.}} + \dot{n}_{\text{CO,BOFG,t.a.}}} \cdot 100\% \tag{2}$$

$$\dot{n}_{\text{CO2,Scope 2}} = (\dot{Q}_{\text{heat}} - f_{\text{int}} \cdot (\dot{Q}_{\text{cool}} + \dot{Q}_{\text{cool,PEM}}) + \dot{n}_{\text{CO,BOFG}} \cdot LHV_{\text{CO}}) \cdot ef_{\text{ng}} + (P_{\text{el}} + P_{\text{el,PEM}}) \cdot ef_{\text{el}} \tag{3}$$

$$\dot{n}_{\text{CO2,Scope 1}} = \sum \dot{n}_{\text{CO+CO2+MeOH+AA,PRG}} \tag{4}$$

The calculation of the LHE as proposed by Nestler *et al.* (2018) is modified to account for the production of acetic acid. The modified KPI of the LHE (LHE_{int}) is used to account for the different carbon oxide ratios in the feed gas of the methanol synthesis unit. The unused and purged hydrogen (H_2) from the process includes both pure H_2 and H_2 bound in reaction products other than water.

$$LHE_{\text{int}} = \frac{\dot{n}_{\text{H2,MUG}} - \dot{n}_{\text{H2,PRG}}}{\dot{n}_{\text{H2,MUG}}} \cdot 100\% \tag{5}$$

The *carbon binding ratio* (CBR) was chosen as the technical KPI to evaluate the performance of the synthesis loops as characterized by the methanol yield.

$$CBR = \frac{\dot{n}_{\text{MeOH,Prod}}}{\dot{n}_{\text{CO+CO2,BFG}}} \cdot 100\% \tag{6}$$

In comparing the two proposed methanol concepts, we also consider the lower heating value (LHV) of the SMOG and potential uses as a feedstock for other chemical processes for each purge stream.

3 SYNTHESIS ROUTES, SCENARIOS AND ASSUMPTIONS

3.1 METHANOL CONCEPTS

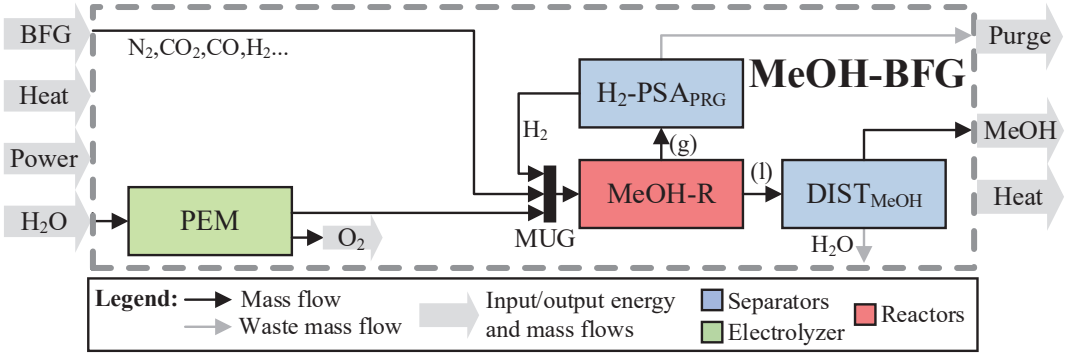

Figure 1: Methanol synthesis concept "BFG"

https://doi.org/10.52202/077185-0091

The reference case for methanol synthesis is the BFG concept as shown in Figure 1. The BFG, together with hydrogen produced by a proton exchange membrane (PEM) electrolyzer unit connected to the German grid, is fed directly to the MeOH synthesis unit (MeOH-R). The synthesis unit is based on the process proposed by Girod *et al.* (2020). For the PEM, we assume a 70 % efficiency in terms of net calorific value and a waste heat production of 10 % of the electrical energy consumption (Shiva Kumar and Himabindu, 2019). The hydrogen in the exhaust gas of the MeOH-R is recycled using a hydrogen PSA (H_2-PSA_{PRG}) with an electricity demand of 0.5 MWh t_{H2}^{-1}, a hydrogen capture efficiency of 90 %, and an assumed hydrogen purity of 100 % (Ren *et al.*, 2020). The methanol reactor is modeled as an isothermal equilibrium reactor (RGibbs) at 80 bars and 250°C with variable recycle rate RR and stochiometric number SN. No side reactions other than the water gas shift reaction are considered. The crude methanol product, consisting mainly of water and methanol, leaves the recycling loop via condensation of the high boiling components and is purified using a RadFrac distillation column ($DIST_{MeOH}$) at atmospheric pressure. The top condenser temperature is set to 40 °C and the optimum reflux and distillate-to-feed ratios are determined using design specifications for product purity of methanol. The target molar purity for the methanol is 99.5 % because the downstream acetic acid synthesis can handle a small amount of water in the feed. The number of stages and the position of the feed have been chosen so that an additional stage with an optimum feed position reduces the heat requirement of the distillation column by less than 5 %. As a result, the $DIST_{MeOH}$ has 17 stages with the feed above the 13th stage for the BFG concept.

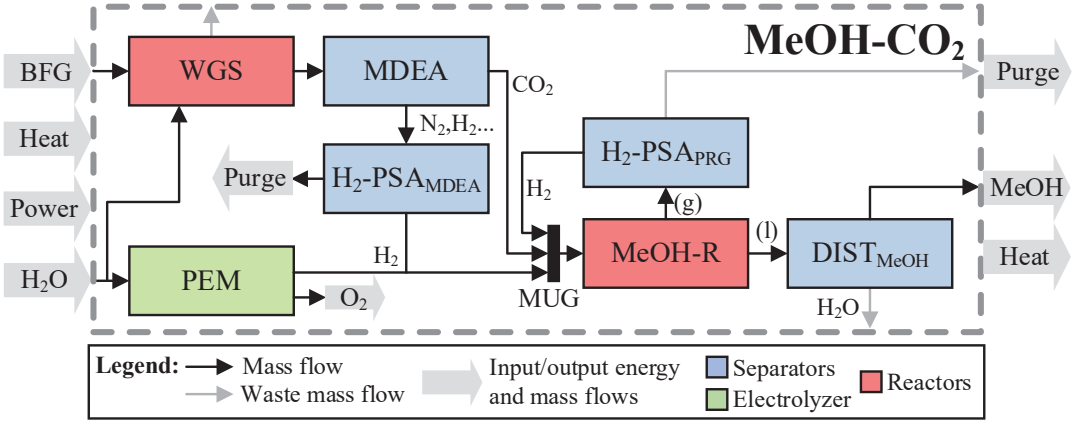

Figure 2: Methanol synthesis concept "CO_2"

The concept of methanol synthesis from CO_2 as shown in Figure 2 is based on the BFG concept with two additional conversion and separation steps for the BFG. The first step is the WGS unit with water recycling, which converts CO with water to CO_2 and additional H_2. The stochiometric molar ratio of water/CO in the WGS feed is set to 2. The product gas from the WGS is fed to a CO_2 absorption unit using a mixture of 30 wt.% MDEA and 70 wt.% water as a solvent for CO_2. The absorption is modelled according to Adams *et al.* (2014) with a total CO_2 capture efficiency of 99.5 %. In addition, the operating point considers that the excess heat from the stripper can be recovered internally in the absorption and desorption unit of the MDEA plant. The off-gas is fed to a H_2-PSA_{MDEA} with the same performance characteristics as the H_2-PSA_{PRG} for cleaning the methanol synthesis off-gas. The two hydrogen streams from the H_2-PSA_{MDEA} and PEM and the separated CO_2 stream from the MDEA are used as a feed to the MeOH-R. The $DIST_{MeOH}$ has 17 stages with the feed above the 14th stage.

3.2 ACETIC ACID CONCEPT

Figure 3 shows the acetic acid concept using methanol produced by the previously described methanol synthesis concepts as a feedstock. The acetic acid reactor (AA-R) concept is derived from a study by Sunley and Watson (2000). For the feed composition and reaction yield, we chose the one with the lowest rate of side reactions as reported by Sunley and Watson (2000).

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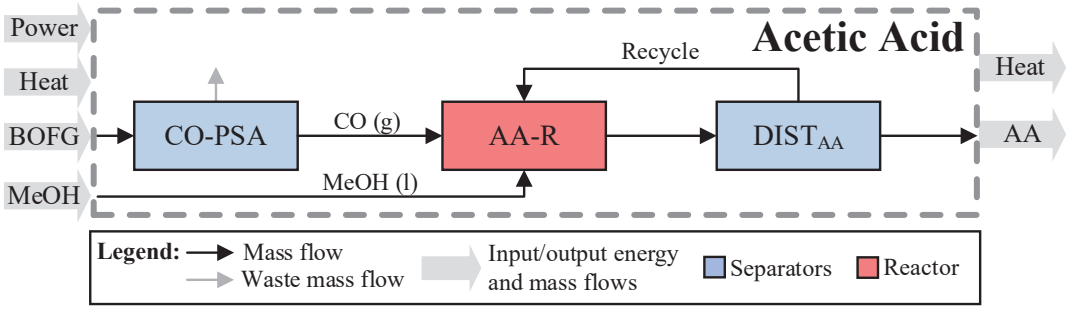

Figure 3: Acetic acid synthesis concept

The synthesis pressure for the acetic acid reaction is set to 35 bar, and the isothermal reactor is operated at 190 °C. To obtain the required partial pressure of CO, it is fed in stochiometric excess with a factor of 1.05 (moles of CO per mole of MeOH). The modelled reactions are taken from Dimian and Kiss (2020). The liquid promoters are recycled via condensation of the high-boiling components at ambient pressure together with a portion of the AA product while the non-condensable off-gases are purged. The solid catalyst is negligible in the total mass and energy balance of the reaction process and is therefore not modelled. The required CO is provided by a pressure swing adsorption (CO-PSA) from the BOFG of the steel plant. The CO-PSA is modelled as a black box with energy consumption and separation parameters provided by Lim *et al.* (2016) with a CO capture efficiency of 90 %. The distillation column for the acetic acid purification ($DIST_{AA}$) is a RadFrac distillation model operating at atmospheric pressure. The operating point was chosen using the same methodology as for the $DIST_{MeOH}$, resulting in 25 stages and the feed above stage 13. The distillation recycle stream contains a mixture of the solvent and the homogeneous catalyst.

3.3 Scenarios

We compare the BFG and the CO_2 synthesis concepts using the previously described KPIs, adjusting stoichiometric numbers (SN) and recycle ratios (RR) to determine the optimal operating conditions for each process. The optimal operating points serve as the reference (Ref) for the scenario evaluation.
The impact of three key factors, electricity CO_2-emission factor (ef_{el}), PEM electrolysis efficiency (η_{Pem}) and heat integration factor (f_{int}) on the ERE is evaluated by changing them by ± 10 %.
Four scenarios for acetic acid production are evaluated: One scenario for the maximum yield of captured CO in BOFG (max) and one scenario for half of this yield (half). A scenario using waste heat (noCO) to consider replacing the combustion heat of the captured CO with natural gas. The last scenario considers only enough BFG to produce methanol to convert the entire amount of CO from the BOFG to acetic acid (min). The BFG emissions used to calculate the ERE are adjusted accordingly.

3.4 Additional assumptions

Table 1 shows the energy sources, and their emissions and Table 2 lists and summarizes the technical assumptions used for the further techno-ecological evaluation of the synthesis concepts. The energy sources in Table 1 are for the target year 2040 and are therefore subject to uncertainties. Our assumptions for the electricity grid mix are in line with the current German energy policy of 85% renewables by 2040. Other assumptions are derived from mass and energy balances (e.g., natural gas emissions and energy demand of PSA) or literature.

Table 1: Considered energy sources and their CO_2-emissions

Energy	CO_2 emissions (g_{CO2} kWh^{-1})	Reference Year	Source
Electricity	109 (ef_{el})	2040	Assumption: 85 % renewables in the German grid mix according to German energy policy (2024)
Natural Gas	201 (ef_{ng})	-	(Juhrich, 2022)

https://doi.org/10.52202/077185-0091

Table 2: Technical assumptions for the sub-processes

Unit	Operating Parameter	Value	Source
Compressors (non H_2)	Max temperature	150 °C	(Stewart, 2018)
	η_{is}	82 %	(Hirschberg, 1999)
Compressors (H_2)	Max temperature	150 °C	(Stewart, 2018)
	η_{is}	80 %	(Aasadnia and Mehrpooya, 2018)
H_2-PSA	Capture efficiency (H_2)	90 %	(D.-Y. Lee and Elgowainy, 2018)
	Energy demand	0.5 MWh t_{H2}^{-1}	
	Product purity	100 %	
CO_2-Absorption (MDEA)	Solvent mixture	30 wt.% MDEA 70 wt.% water	(Adams *et al.*, 2014)
	Capture efficiency (CO_2)	99.5 %	o.A.
	Absorber & desorber stages	20	o.O.
CO-PSA	Capture efficiency (CO)	90 %	(Lim *et al.*, 2016)
	Energy demand	0.206 kWh kg_{CO}^{-1}	
	Product purity	100 %	

4 RESULTS

4.1 METHANOL CONCEPTS (CO_2 AND BFG) FOR THE REFERENCE SCENARIO

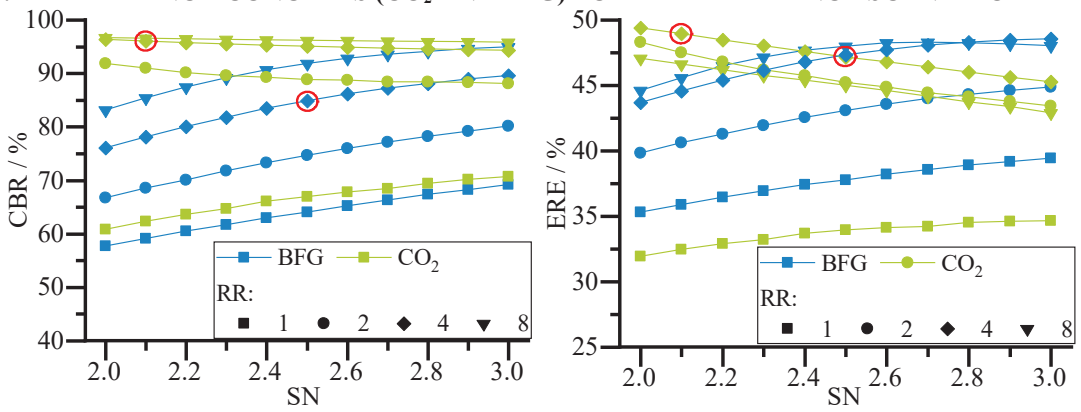

Figure 4: Comparison of CBR and ERE for both methanol concepts

Figure 4 shows the KPIs of CBR and ERE for various RRs ranging from 1 to 8 and SN ranging from 2 to 3. The CBR and ERE values for the BFG concept (blue) increase with increasing SN and RR. However, for the CO_2 concept (green), the KPIs with RR > 1 decrease with increasing the SN and increase with increasing the RR. However, a high RR leads to an energy inefficient process with larger plant sizes and additional equipment, and a high SN leads to more hydrogen demand, which is mostly not converted in the reactor. For the optimal operating point, RR and SN should be low and therefore, a trade-off between the efficiency (high ERE and high CBR) and the process parameters (RR and SN) should be chosen. We define the optimal operating point for the CO_2 concept at SN = 2.1 and RR = 4 (red circles in Figure 4), because the reaction always operates with a small excess of hydrogen at SN > 2.0 (Bampaou *et al.*, 2023). For the BFG concept, we chose SN = 2.5 and RR = 4. Higher SN or RR values don't lead to significantly higher KPIs but have a negative impact on the plant size and the hydrogen utilization. The operating points are fixed for the following evaluation of the concepts.

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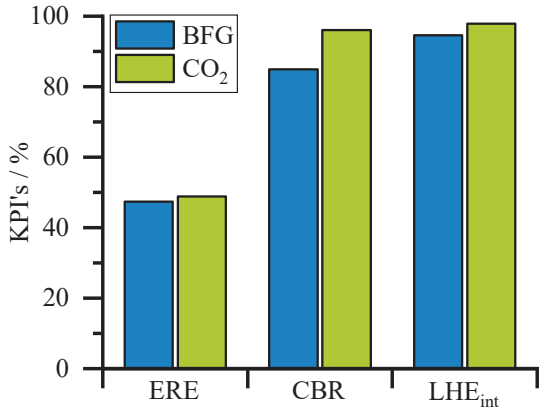

Figure 5: Comparison of KPI's for both methanol concepts

As shown in Figure 5, the resulting CBR is 84.9 % for BFG and 96.0 % for CO_2. The resulting ERE is 47.3 % for BFG and 48.9 % for CO_2. The operating point of the CO_2 concept has a higher ERE value than any operating point of the BFG concept. The hydrogen utilization, calculated as the LHE_{int} of the H_2 in the make-up gas (MUG), is 97.8 % for the CO_2 concept and 94.6 % for the BFG concept.
It should be noted, that when using the ef_{el} of the year 2020 (~373 g/kWh_{el}), the BFG concept has a negative ERE of –77.5 % and the CO_2 concept has a negative ERE of –95.6 %. This result indicates the importance of the future energy source to produce methanol from SMOG. The ERE is zero for the BFG concept with an ef_{el} of 208.58 g/kWh_{el} and for the CO_2 concept with an ef_{el} of 198.18 g/kWh_{el}.
Two other important factors when comparing the scenarios are the purge gas compositions and the inert gas fraction of the reactor feed. While the purge gases with impurities from the methanol synthesis (MeOH-R) can only be used for heat generation (combustion), the purge gas leaving the H_2-PSA_{MDEA} in the CO_2 concept can be reintegrated. This purge gas has a molar composition of 36 % H_2 and 62 % nitrogen. Therefore, it can be used for other reactions, e.g., as feed for an ammonia synthesis plant. The reactor feed of the BFG concept has an inert gas fraction of more than 40 % (mostly nitrogen), which also has a negative impact on the size, energy demand and real performance of the reactor.

4.2 METHANOL CONCEPTS SCENARIO VARIATION (CO_2 AND BFG)

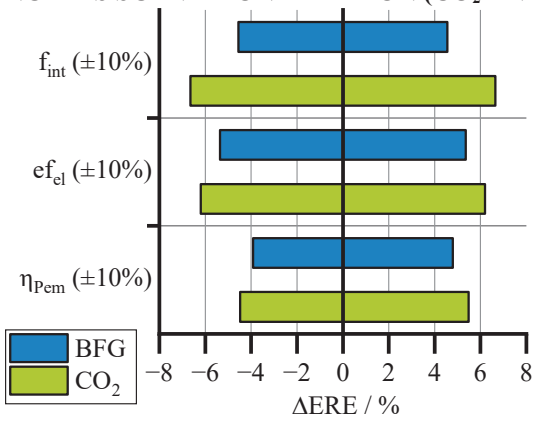

Figure 6: Sensitivity analysis and relative change of ERE

Figure 6 shows the results of the sensitivity analysis of the three key factors from Section 3.3 and the impact of the ERE. In the reference case, the electricity emission factor (ef_{el}) is for the year 2040, the heat energy integration factor (f_{int}) is 80 %, and the PEM efficiency (η_{Pem}) is 70 %. When all factors are varied by ±10 %, the largest impact on the BFG concept is observed in the ef_{el} factor, leading to a ΔERE

https://doi.org/10.52202/077185-0091

change of 4.6 % in both directions. For the CO_2 concept, f_{int} has the largest impact on the ERE with a ΔERE of ±6.7 %. Despite the recovery of a large amount of the H_2 needed for the reaction via the H_2-PSA_{MDEA} from the MDEA off-gas, the higher carbon conversion and the higher H_2 demand of the CO_2 hydrogenation to methanol result in a stronger influence of ef_{el} and η_{Pem} on the ERE in the CO_2 concept than in the BFG concept. The higher impact of the heat integration factor on the CO_2 scenarios can be explained by the overall higher thermal energy demand and waste heat production of the MDEA and WGS unit.

The results in Table 3 show, that the BFG concept has a lower specific energy demand for all considered energies from heating, cooling, and electrical energy for methanol production in the reference scenario. Nevertheless, the CO_2 concept has a higher ERE due to a higher conversion of the carbon oxides from CO_2 and CO compared to the BFG concept. Therefore, more methanol can be produced from the BFG in the CO_2 concept. In addition, the higher conversion results in lower Scope 1 emissions in the CO_2 concept at 0.05 t_{CO2}/t_{MeOH} compared to 0.25 t_{CO2}/t_{MeOH} in the BFG concept. Most of the CO_2 emissions in both concepts are Scope 2 emissions. The high electrical energy consumption for the hydrogen production via PEM electrolysers has the largest impact. For both concepts, more than 90 % of the Scope 2 emissions can be attributed to the hydrogen production. The CO_2 concept requires more hydrogen and therefore has slightly higher Scope 2 emissions of 0.67 t_{CO2}/t_{MeOH} compared to the BFG concept with 0.60 t_{CO2}/t_{MeOH}. As a result, the CO_2 concept has a total specific CO_2 emission of 0.72 t_{CO2}/t_{MeOH}, which is 15 % lower than the total specific emissions of the BFG concept.

Table 3: Techno-ecological performance indicators for MeOH concepts

Symbols	Unit	BFG concept	CO_2 concept
MeOH Prod	t_{MeOH}/h	1004.9	1141.8
P_{el} /MeOH Prod	MWh/t_{MeOH}	0.45	0.83
Q_{heat}* / MeOH Prod	MWh/t_{MeOH}	2.37	5.25
Q_{cool}* / MeOH Prod	MWh/t_{MeOH}	3.82	7.02
$P_{el, PEM}$ / MeOH Prod	MWh/t_{MeOH}	7.33	7.40
$Q_{cool, PEM}$* / MeOH Prod	MWh/t_{MeOH}	0.73	0.74
CO_2-emissions (Scope 1)	t_{CO2}/t_{MeOh}	0.25	0.05
CO_2-emissions (Scope 2)	t_{CO2}/t_{MeOh}	0.60	0.67
CO_2-emissions (total)	t_{CO2}/t_{MeOh}	0.85	0.72

*All values without heat integration factor, crude energy demands

4.3 ACETIC ACID CONCEPTS (FROM METHANOL CO_2 AND BFG)

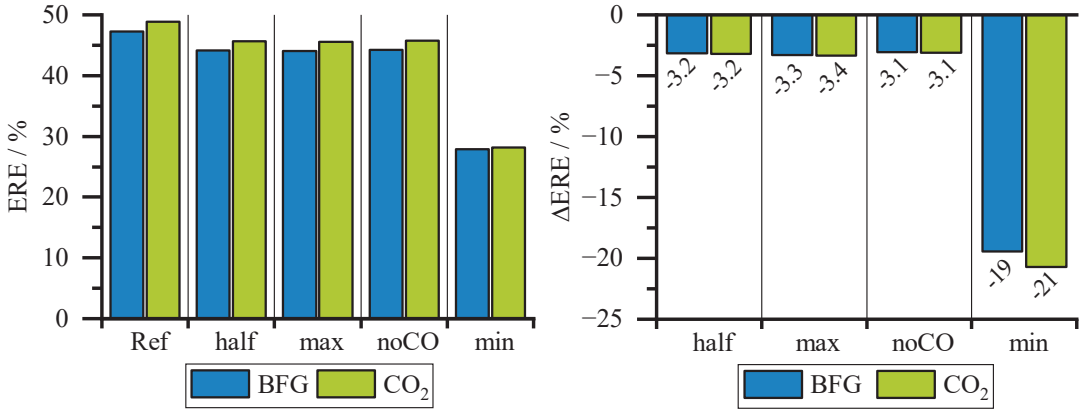

Figure 7: Impact of acetic acid production on ERE

https://doi.org/10.52202/077185-0091

The impact of the acetic acid production from methanol on the ERE is shown in Figure 7. The reference scenario (Ref) and the four scenarios from Section 3.3 (max, half, noCO and min) are considered.
The half, max and noCO scenarios show only slightly reduced ERE for both concepts. The impact is relatively small, because the BOFG quantities are lower than the BFG quantities, so only 134.7 t_{AA}/h of acetic acid can be produced (see Table 4). This amount is almost 10 times smaller than the amount of methanol from 1004.9 t_{MeOH}/h (BFG concept) or 1141.8 t_{MeOH}/h (CO_2 concept). Therefore, only a small amount of methanol can be used in the acetic acid production concept, which leads to an order of magnitude higher impact of the upstream methanol concept than the acetic acid production concept on the ERE. However, the small reduction in the ERE is due to the Scope 1 emissions from unused or unreacted CO and the increase in the denominator of the ERE by including the maximum technically avoidable CO emissions in the BOFG. The electricity demand of the CO-PSA and the compression, the heat integration as well as the substitution of CO for the steel plant do not significantly reduce the ERE. This result leads to an overall reduction of the ERE by a ΔERE of about 3 % in the max, half and noCO scenarios for both concepts.
However, if only as much methanol is produced as can be converted to acetic acid, the ERE is almost halved, resulting in a ΔERE of –19 % and –21 % for the BFG and CO_2 concepts, respectively. Therefore, the acetic acid production has a negative impact on the ERE in all the investigated scenarios. The KPIs of CBR and LHE_{int} do not change significantly because no additional hydrogen is required (only CO and MeOH) and the conversion rates of methanol to acetic acid are high (see X_{MeOH} Table 4). Table 4 shows all energy requirements, conversion rates and amounts of acetic acid produced and CO used from BOFG.

Table 4: Techno-ecological performance indicators for AA-R concept

Symbols	Unit	Value
CO captured	t/h	70.5
Acetic acid product	t/h	134.7
X_{CO}	%	93.5
X_{MeOH}	%	98.2
P_{el}	MWh/t_{MeOH}	0.12
Q_{heat}*	MWh/t_{MeOH}	1.11
Q_{cool}*	MWh/t_{MeOH}	2.28

*All values without heat integration

5 CONCLUSION

The optimal operating point of the BFG concept for methanol production leads to an ERE of 47.3 % and a daily production of about 24.1 $kt_{MeOH}\ d^{-1}$. The optimal operating point of the CO_2 concept for methanol production can produce 27.4 $kt_{MeOH}\ d^{-1}$ with an ERE of 48.9 %. Both concepts consider the technological and ecological conditions of the reference year 2040 and account for the Scope 1 and Scope 2 CO_2 emissions. As for the other KPIs, the CO_2 synthesis has a significantly higher CBR of 96.0 % and LHE_{int} of 98.9 %. Therefore, the methanol production with the CO_2 concept shows a higher techno-ecological potential than the BFG concept. Previous studies have mentioned the importance of good hydrogen utilization, so the loss of hydrogen in the BFG synthesis, as well as the multiple uses of hydrogen in the MDEA off-gas of the CO_2 concept, make it difficult to justify the use of the BFG concept. Another challenge for the BFG concept is the high inert gas volume in the reactor feed of 40 % (mostly nitrogen), which is likely to result in higher technical challenges and lower performance.
Two of the main impacts on the ERE are the emission factor of electricity (ef_{el}) due to the high energy demand for hydrogen production and feed gas compression and the heat integration (f_{int}) of the waste heat from the reaction units. Due to the highly exothermic nature of the water gas shift reaction, the methanol reaction and the acetic acid reaction, a large amount of heat could be used to displace fossil fuels used for the steel plant and district heating. Another important key factor is the energy efficiency

https://doi.org/10.52202/077185-0091

of the PEM electrolyser (η_{Pem}). The PEM is the main contributor to Scope 2 emissions, so higher efficiency can lead to a higher ERE and therefore better ecological production.
The downstream production of acetic acid has a small impact on the overall system, because the lower amounts of BOFG cannot satisfy the high amounts of methanol produced. Therefore, in the scenarios with high methanol production (max, half and noCO), the production of acetic acid slightly reduces the ERE by a ΔERE of about 3 %. The impact can be reduced by maximizing the use of CO through process optimization or reintegration. In the scenario where only as much methanol is produced as can be used in the production of acetic acid (min), the ERE decreased about –19 to –21 %. In all scenarios, the CBR and LHE_{INT} key performance indicators for the additional acetic acid production don't change significantly. In conclusion, the additional acetic acid production after the methanol production only affects the KPI of the ERE in all investigated scenarios. The impact is always negative, so the additional production of acetic acid doesn't give any ecological benefit according to the ERE.

6 OUTLOOK

The models developed and the results obtained are a first reference for the further development of a combined methanol and acetic acid process based on SMOG. Therefore, further investigation of the energy integration of the process into the steel plant as well as district heating should be the next development step. This should be evaluated using different displacement factors based on the temperature level as well as the usable amount. The technical feasibility as well as the performance of the CO-PSA should be validated using BOFG from the steel plant. The supply of hydrogen and electricity was confirmed as a key factor. The dynamic nature of the prices and emissions of both resources results in the need for a dynamic model. This can then be used to model fluctuations in the availability of SMOGs and associated emissions to determine realistic operating scenarios. However, the choice of when and how much of each chemical to produce is not only a techno-ecological challenge. Further studies will consider the economic aspects of investment costs, operating costs and the market value and volume of the products.

NOMENCLATURE

AA	acetic acid
AA-R	acetic acid reactor
BFG	blast furnace gas
BOFG	basic oxygen furnace gas
CBR	carbon binding ratio (%)
CCU	Carbon Capture and Utilization
DIST	distillation
ef	CO_2-emission factor (kg_{CO2} kWh^{-1})
ERE	emission reduction efficiency (%)
f	heat integration factor (%)
KPI	key performance indicator
LCE	loop carbon efficiency (%)
LHE	loop hydrogen efficiency (%)
LHV	lower heating value (kWh $kmol^{-1}$)
$\dot{n}$	molar flow rate (kmol h^{-1})
MeOH	methanol
MUG	make-up gas
o.A.	own assumption
o.O.	own optimization result
P_{el}	power flow (MW)
PEM	proton exchange membrane electrolyzer
PSA	pressure swing adsorption
$\dot{Q}$	heat flow (MW)
RR	recycling ratio (mole/mole)

https://doi.org/10.52202/077185-0091

SN	stochiometric number	(mole/mole)
SMOG	steel mill off-gases	
WGS	water gas shift	
X	conversion rate	(%)
ΔT	temperature difference	(K)
η	efficiency	(%)

Subscript

cool	cooling energy
el	electricity
heat	heating energy
int	internal
is	isentropic
ng	natural gas
PEM	proton exchange membrane electrolyser
PRG	purge
Prod	produced
stage	stage number in column
t.a.	technologically avoidable

REFERENCES

Aasadnia, M., & Mehrpooya, M. (2018). Large-scale liquid hydrogen production methods and approaches: A review. *Applied Energy*, *212*, 57–83. https://doi.org/10.1016/j.apenergy.2017.12.033

Adams, T. A., Salkuyeh, Y. K., & Nease, J. (2014). Processes and simulations for solvent-based CO_2 capture and syngas cleanup. In Fan Shi (Ed.), *Reactor and Process Design in Sustainable Energy Technology* (pp. 163–231). Elsevier. https://doi.org/10.1016/B978-0-444-59566-9.00006-5

Bampaou, M., Haag, S., Kyriakides, A.-S., Panopoulos, K. D., & Seferlis, P. (2023). Optimizing methanol synthesis combining steelworks off-gases and renewable hydrogen. *Renewable and Sustainable Energy Reviews*, *171*, 113035. https://doi.org/10.1016/j.rser.2022.113035

Bampaou, M., Panopoulos, K., Seferlis, P., Sasiain, A., Haag, S., Wolf-Zoellner, P., Lehner, M., Rog, L., Rompalski, P., Kolb, S., Kieberger, N., Dettori, S., Matino, I., & Colla, V. (2022). Economic Evaluation of Renewable Hydrogen Integration into Steelworks for the Production of Methanol and Methane. *Energies*, *15*(13), 4650. https://doi.org/10.3390/en15134650

Bellevrat, E., & Menanteau, P. (2009). Introducing carbon constraint in the steel sector: ULCOS scenarios and economic modeling. *Revue De Métallurgie*, *106*(9), 318–324. https://doi.org/10.1051/metal/2009059

Collis, J., Strunge, T., Steubing, B., Zimmermann, A., & Schomäcker, R. (2021). Deriving Economic Potential and GHG Emissions of Steel Mill Gas for Chemical Industry. *Frontiers in Energy Research*, *9*, Article 642162. https://doi.org/10.3389/fenrg.2021.642162

Dimian, A. C., & Kiss, A. A. (2020). Novel energy efficient process for acetic acid production by methanol carbonylation. *Chemical Engineering Research and Design*, *159*, 1–12. https://doi.org/dimian

Gentile, G., Bonalumi, D., Pieterse, J. A., Sebastiani, F., Lucking, L., & Manzolini, G. (2022). Techno-economic assessment of the FReSMe technology for CO_2 emissions mitigation and methanol production from steel plants. *Journal of CO2 Utilization*, *56*, 101852. https://doi.org/10.1016/j.jcou.2021.101852

Girod, K., Lohmann, H., Schlüter, S., & Kaluza, S. (2020). Methanol Synthesis with Steel-Mill Gases: Simulation and Practical Testing of Selected Gas Utilization Scenarios. *Processes*, *8*(12), 1673. https://doi.org/10.3390/pr8121673

 https://doi.org/10.52202/077185-0091

Hirschberg, H. G. (Ed.). (1999). *Springer eBook Collection*. *Handbuch Verfahrenstechnik und Anlagenbau: Chemie, Technik, Wirtschaftlichkeit*. Springer Berlin Heidelberg. https://doi.org/10.1007/978-3-642-58357-5

Juhrich, K. (2022). *CO_2-Emissionsfaktoren für fossile Brennstoffe.* Umweltbundesamt.

Kolbe, N., Tenhumberg, N., Büker, K., Kleinschmidt, R., & Oles, M. (2022). Strategies for Carbon Dioxide Utilization in Highly Volatile Industrial Transformation Pathways. *Chemie Ingenieur Technik*, *94*(10), 1542–1547. https://doi.org/10.1002/cite.202200041

Lee, D.-Y., & Elgowainy, A. (2018). By-product hydrogen from steam cracking of natural gas liquids (NGLs): Potential for large-scale hydrogen fuel production, life-cycle air emissions reduction, and economic benefit. *International Journal of Hydrogen Energy*, *43*(43), 20143–20160. https://doi.org/10.1016/j.ijhydene.2018.09.039

Lee, H., Calvin, K., Dasgupta, D., Krinner, G., Mukherji, A., Thorne, P. W., Trisos, C., Romero, J., Aldunce, P., Barrett, K., Blanco, G., Cheung, W. W., Connors, S., Denton, F., Diongue-Niang, A., Dodman, D., Garschagen, M., Geden, O., Hayward, B., . . . Connors, S. L. (2023). *IPCC, 2023: Climate Change 2023: Synthesis Report. Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, H. Lee and J. Romero (eds.)]. IPCC, Geneva, Switzerland.* https://doi.org/10.59327/IPCC/AR6-9789291691647.001

Lim, Y.-I., Choi, J., Moon, H.-M., & Kim, G.-H. (2016). Techno-economic Comparison of Absorption and Adsorption Processes for Carbon Monoxide (CO) Separation from Linze-Donawitz Gas (LDG). *Korean Chemical Engineering Research*, *54*(3), 320–331. https://doi.org/10.9713/kcer.2016.54.3.320

Nestler, F., Krüger, M., Full, J., Hadrich, M. J., White, R. J., & Schaadt, A. (2018). Methanol Synthesis - Industrial Challenges within a Changing Raw Material Landscape. *Chemie Ingenieur Technik*, *90*(10), 1409–1418. https://doi.org/10.1002/cite.201800026

Porter, R. T., Cobden, P. D., & Mahgerefteh, H. (2022). Novel process design and techno-economic simulation of methanol synthesis from blast furnace gas in an integrated steelworks CCUS system. *Journal of CO2 Utilization*, *66*, 102278. https://doi.org/10.1016/j.jcou.2022.102278

Ranganathan, J., Corbier, L., Bhatia, P., Schmitz, S., Gage, P., & Oren, K. (2004). *The Greenhouse Gas Protocol: A Corporate Accounting and Reporting Standard REVISED EDITION.*

Ren, L., Zhou, S., & Ou, X. (2020). Life-cycle energy consumption and greenhouse-gas emissions of hydrogen supply chains for fuel-cell vehicles in China. *Energy*, *209*, 118482. https://doi.org/10.1016/j.energy.2020.118482

Shiva Kumar, S., & Himabindu, V. (2019). Hydrogen production by PEM water electrolysis – A review. *Materials Science for Energy Technologies*, *2*(3), 442–454. https://doi.org/10.1016/j.mset.2019.03.002

Somers, J. (2022). *Technologies to decarbonise the EU steel industry* (EUR). Europäische Kommission. https://op.europa.eu/o/opportal-service/download-handler?identifier=fd3b326a-8aed-11ec-8c40-01aa75ed71a1&format=pdf&language=en&productionSystem=cellar&part= https://doi.org/10.2760/069150

Stewart, M. (2018). Reciprocating compressors, 655–778. https://doi.org/10.1016/B978-0-12-809895-0.00009-0

Sunley, G. J., & Watson, D. J. (2000). High productivity methanol carbonylation catalysis using iridium. *Catalysis Today*, *58*(4), 293–307. https://doi.org/10.1016/S0920-5861(00)00263-7

Yildirim, Ö., Nölker, K., Büker, K., & Kleinschmidt, R. (2018). Chemical Conversion of Steel Mill Gases to Urea: An Analysis of Plant Capacity. *Chemie Ingenieur Technik*, *90*(10), 1529–1535. https://doi.org/10.1002/cite.201800019

ACKNOWLEDGEMENT

This research was conducted as part of the Carbon2Chem® project. The authors would like to thank the German Federal Ministry of Education and Research (BMBF) for its financial support of this project.

https://doi.org/10.52202/077185-0091