

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

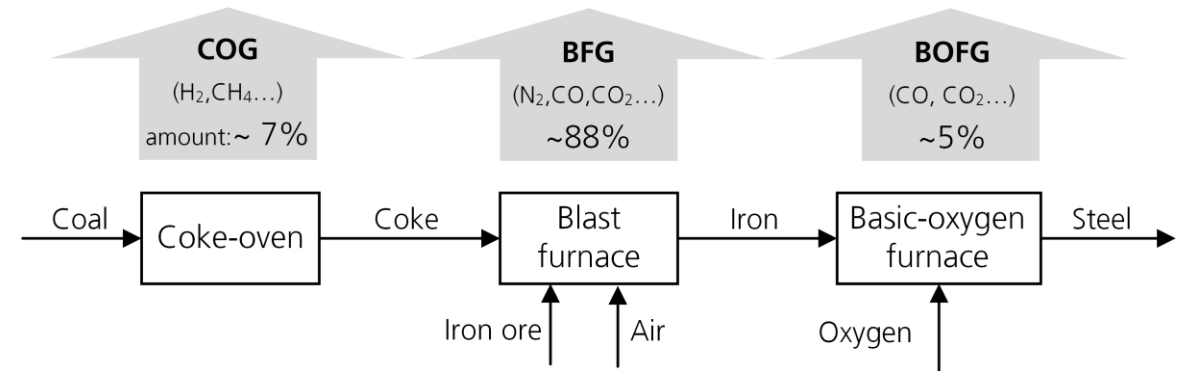
Matthias Sadlowski and Daniel Georg Stupien 07/03/2024

Introduction & Motivation

Conventional steel production

Conventional production with blast furnace route

- 2/3 of German steel production¹⁾
 - Coal as energy carrier
 - Gases with different amounts and concentrations
 - Off-Gases: COG, BFG and BOFG
 - Containing: CO, CO₂, H₂, N₂, CH₄...
 - Today (reference state):
 - Power plants and/or internal utilization (steam, heat...)
 - Subsequently all CO₂ is emitted in the environment
- Leads to 7% of CO₂-emissions in Germany (~50 Mt_{CO2}/a)²⁾



1) Wirtschaftsvereinigung Stahl: Daten und Fakten zur Stahlindustrie in Deutschland. Germany, 2023

2) Somers, Julian: Technologies to decarbonise the EU steel industry. Luxembourg, 2022

Introduction & Motivation

Carbon Capture and Utilization (CCU) in the project Carbon2Chem^{®3)}

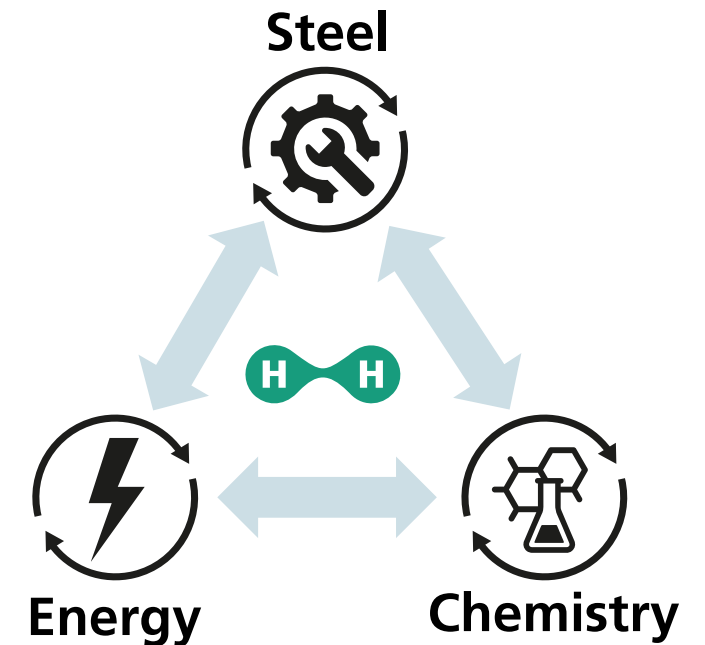
Mitigation strategy of the project C2C[®]

- Steel mill located in Germany (Duisburg) ~ **17 Mt_{CO2}/a**
 - Using off-gases (BFG, BOFG and COG) as a chemical feedstock
 - Production of energy carriers, polymers, fertilizers etc.
 - High demands for energy/raw materials (green hydrogen)
- Sector coupling between different industries

Research questions of this work

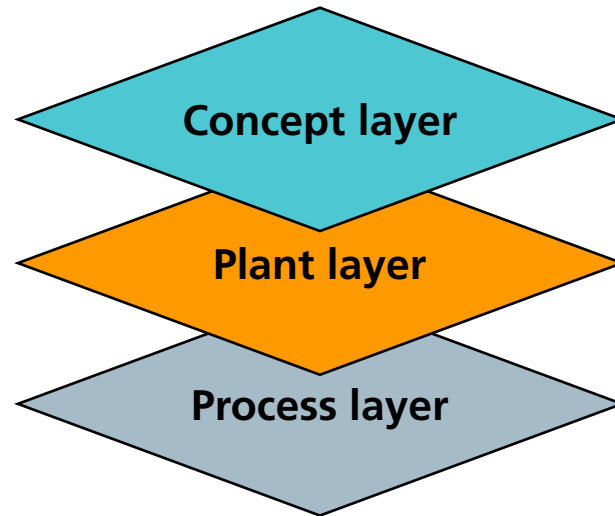
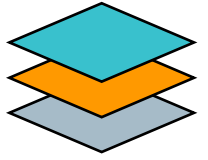
CCU concepts for methanol (MeOH) and acetic acid (AA)

- How are these concepts designed? (plant layout, parameters etc.)
- What are potential key-factors and their future developments?
- How environmentally friendly is this CCU approach?



3) Kolbe, Nina; Tenhumberg, Nils; Bükler, Karsten; Kleinschmidt, Ralph; Oles, Markus: Strategies for Carbon Dioxide Utilization in Highly Volatile Industrial Transformation Pathways. In: Chemie Ingenieur Technik 94 (2022), Nr. 10, S. 1542–1547

Method of this work



- Definition of the desired product with the overall synthesis route
- E.g. MeOH-1, MeOH-2, AA-1, AA-2 etc.

- Selection of plants with interconnections for mass and energy flows
- E.g. PEM for hydrogen, adsorption for hydrogen and CO separation etc.

- Subsystems of the plants modelled in *AspenPlus* (pumps, columns, reactors etc.)
- **Process simulation**
- Results are the technical parameters and amounts of energy/produced chemicals

Key Performance Indicators

- Calculation of techno-ecological KPI's for the CCU concepts

Scenario analysis

- Base-case scenario for a target year
- Variation of key-factors to evaluate the concepts

Workflow

CCU concepts and the selected plants

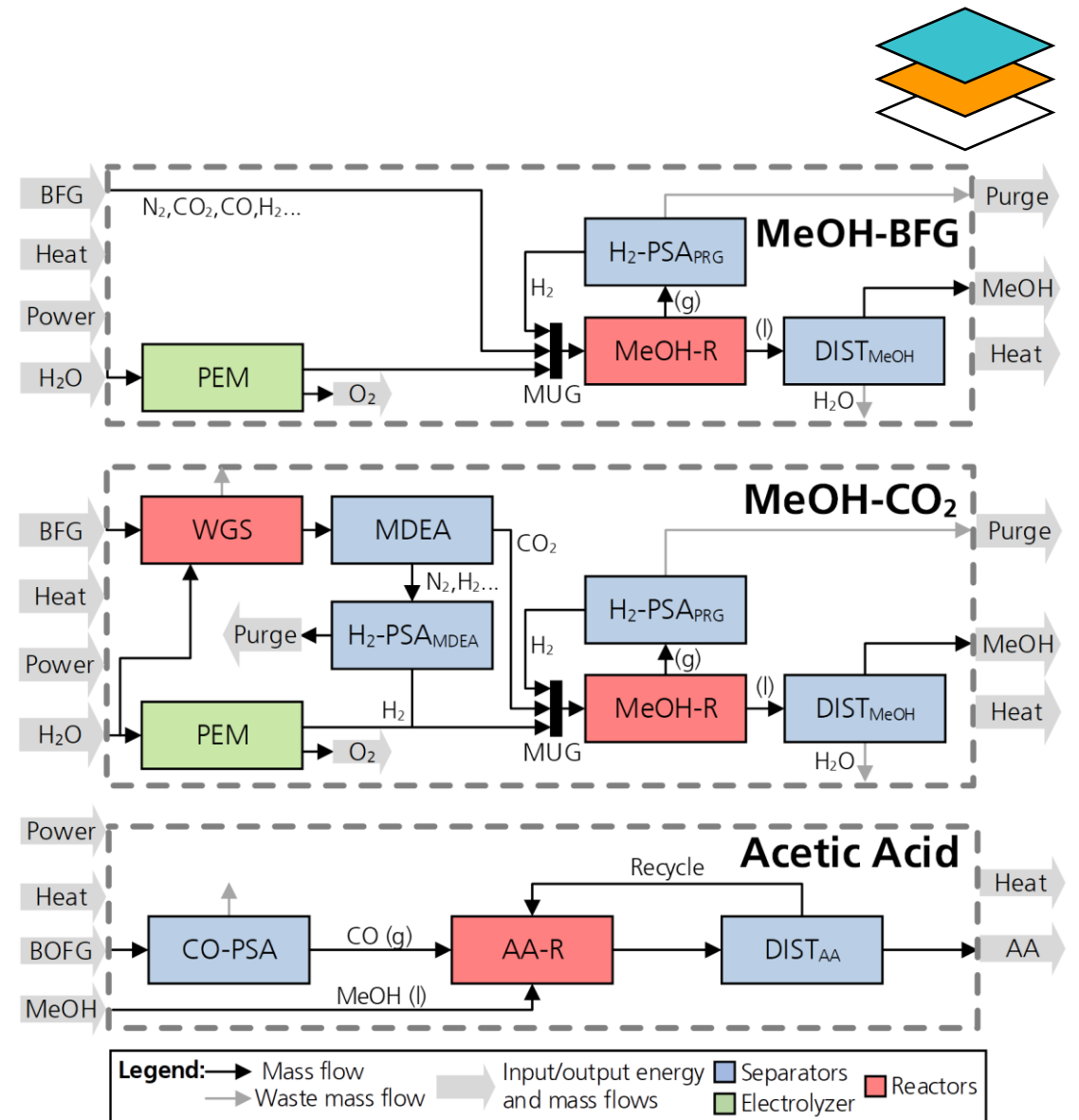
Including concept and plant layer

Concepts

- **MeOH-BFG:** Direct from blast furnace gas (with N₂)
- **MeOH-CO₂:** From conditioned blast furnace gas (no N₂)
- **Acetic Acid:** Downstream production from methanol and CO (separated from the BOFG)
- Off-gas COG is neglected

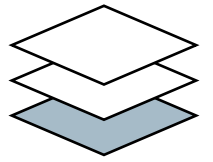
Plants

- Additional hydrogen from PEM (German grid mix)
- Different plants for separation of CO₂, H₂ and CO
- WGS = water gas shift reactor (converts CO to CO₂)
 - Subsequently the CO₂ is separated with MDEA plant
- DIST = distillation columns



Technical parameters from the process layer

E.g. for acetic acid concept for the plants AA-R and DIST_{AA}



AA-R (acetic acid reactor)

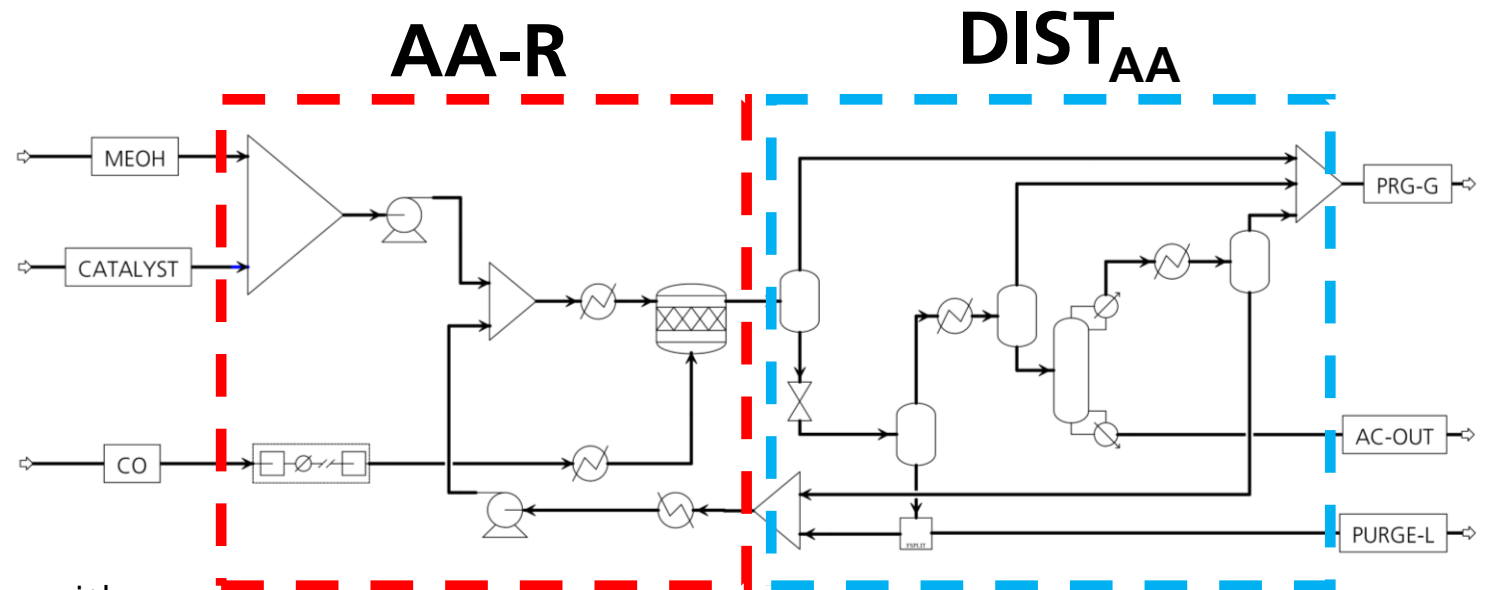
- Modelled as Monsanto/Cativa process^{4,5)}
 - MeOH + CO (+ catalyst) → AA
 - isothermal at 190 °C and 35 bar

DIST_{AA} (purification of acetic acid)

- Tray column with catalyst recycle
- Byproducts are purged

→ Integrated process simulation of all plants with the off-gas conditions and purity or energy specs

→ **Results: Energy demands and produced amounts of acetic acid**



4) Dimian, Alexandre C.; Kiss, Anton A.: Novel energy efficient process for acetic acid production by methanol carbonylation. In: Chemical Engineering Research and Design 159 (2020), S. 1–12

5) Sunley, Glenn J.; Watson, Derrick J.: High productivity methanol carbonylation catalysis using iridium. In: Catalysis Today 58 (2000), Nr. 4, S. 293–307

Key Performance Indicators (KPI's)

Three KPI's are used

Emission Reduction Efficiency → CO₂ avoidance through CCU (in %, can be negative)

$$ERE = \frac{\text{Avoided Emissions}}{\text{Emissions from off-gases (reference)}}$$

- Scope 1 (direct from off-gases) and Scope 2 (indirect from heat and electricity) CO₂-emissions
- Cross sectoral waste heat integration for Scope 2 emissions (on-site, steel plant or district heat)

Carbon Binding Ratio → Bounded with the CCU approach (0 – 100 %)

$$CBR = \frac{\text{Carbon bounded in chemical product}}{\text{Carbon in off-gases (reference)}}$$

Internal Loop Hydrogen Efficiency → Hydrogen utilization factor (0 – 100 %)

$$LHE_{INT} = \frac{\text{Hydrogen input} - \text{Hydrogen purged}}{\text{Hydrogen input}}$$

High values
are beneficial

Scenario analysis and assumptions

Base-case scenario and key-factors

Technical and ecological parameters for the base-case are from simulation and/or assumptions

- The base-case year is set to 2040, covering plant operations from 2030 to 2050
- Contains over 20 parameters, including emission factors, efficiencies, purities, and integration potentials
- Selection of three key-factors with high impact on Scope 2 emissions

Tab. 01: Energy related key-factors of the CCU concept in 2040.

Description	Symbol	Values
Surplus heat integration factor	f_{int}	80 %
Grid mix CO ₂ emission factor (2040)	ef_{el}	110 g _{CO₂} /kWh _{el}
Efficiency of water electrolysis (PEM)	η_{PEM}	70 %

Today ~ 370⁶⁾

- The scenario analysis involves varying key factors by $\pm 10\%$

6) Umweltbundesamt: CO₂-Emissionen pro Kilowattstunde Strom stiegen in 2022. URL <https://www.umweltbundesamt.de/themen/co2-emissionen-pro-kilowattstunde-strom-stiegen-in>. addressed on: 04/01/2024

Comparison of the methanol concepts

MeOH-BFG (BFG direct to reactor) and MeOH-CO₂ (converted CO₂ separated from BFG to reactor)

All KPI's are superior for the MeOH-CO₂ concept

Higher ERE (year 2040): Lower Scope 1 but higher Scope 2 emissions in MeOH-CO₂. Overall specific emissions:

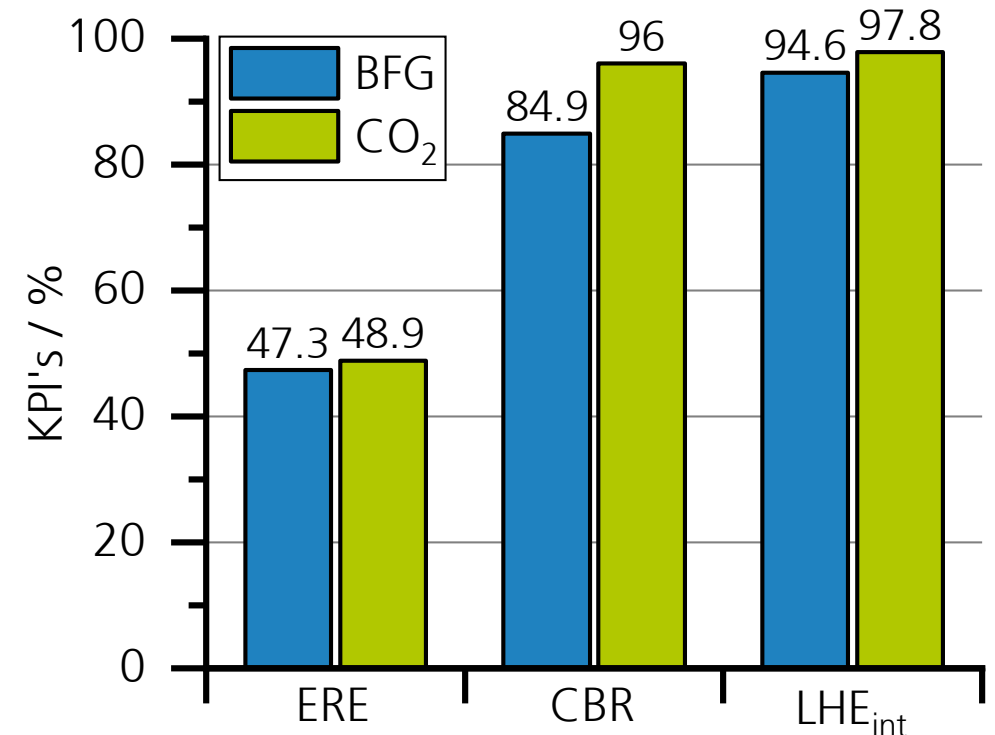
→ CO₂: 0.72 t_{CO2}/t_{MeOH} // BFG: 0.85 t_{CO2}/t_{MeOH}

CBR: Higher values in MeOH-CO₂ concept

→ more methanol production due to higher partial pressure of CO₂ (nearly 40% inert N₂ in the BFG concept)

LHE_{INT}: High utilization of hydrogen for both concepts

BUT: ERE with grid mix in year 2022 leads to negative values for both concepts. → More CO₂ emissions are generated than avoided due to the high electricity CO₂ emission factors ef_{el}



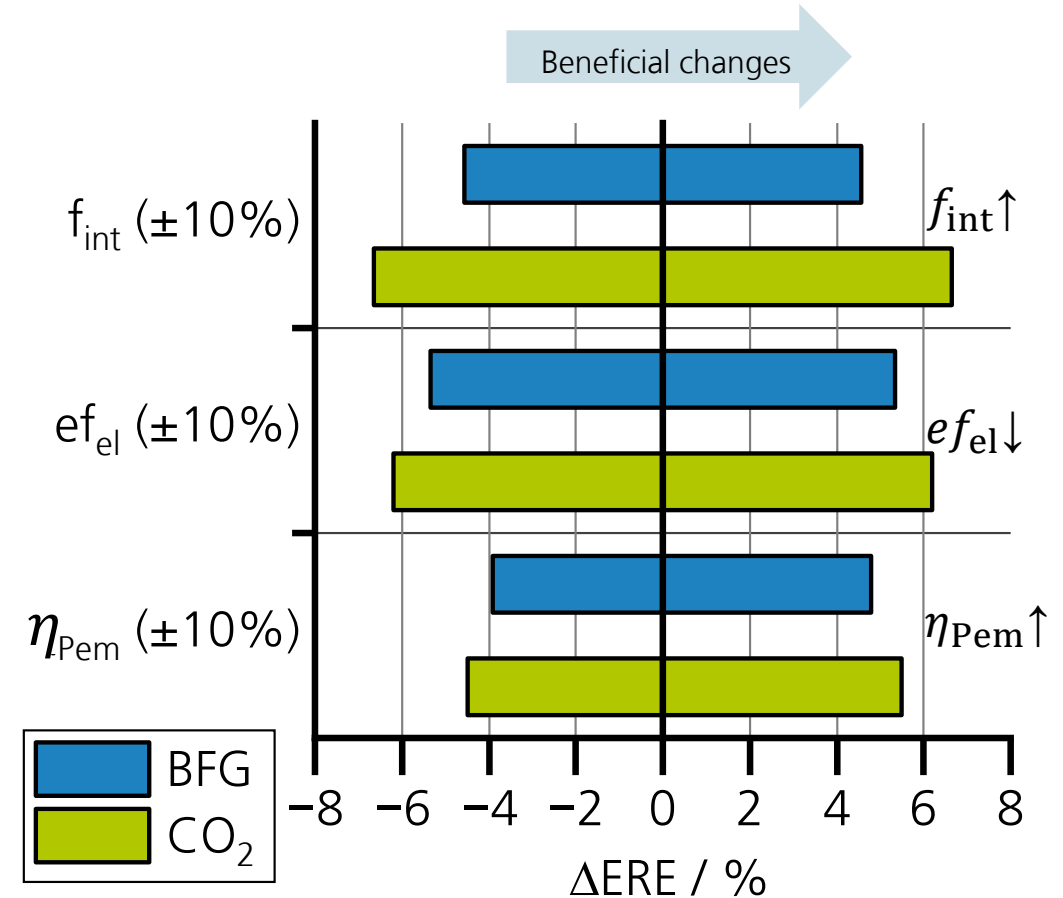
Key-factor variation for methanol concepts

Impact on the Emission Reduction Efficiency (ERE)

The influence on the ERE is of the same order of magnitude for all key-factors (± 4 to 6.5%)

- Impact on CO₂ concept is higher due to:
 - more electricity demand
 - higher surplus heat amounts (WGS and PEM)
- Beneficial changes for higher heat integration + PEM efficiency and lower CO₂ emission factors (ef_{el})
 - CO₂: $f_{int} > ef_{el} > \eta_{Pem}$
 - BFG: $ef_{el} > f_{int} > \eta_{Pem}$
- CBR and LHE_{INT} remain constant as key-factors only affect the indirect emissions (Scope 2). The amounts of hydrogen, chemical products, etc. are therefore constant

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Downstream acetic acid (AA) production

Upstream with both methanol concepts

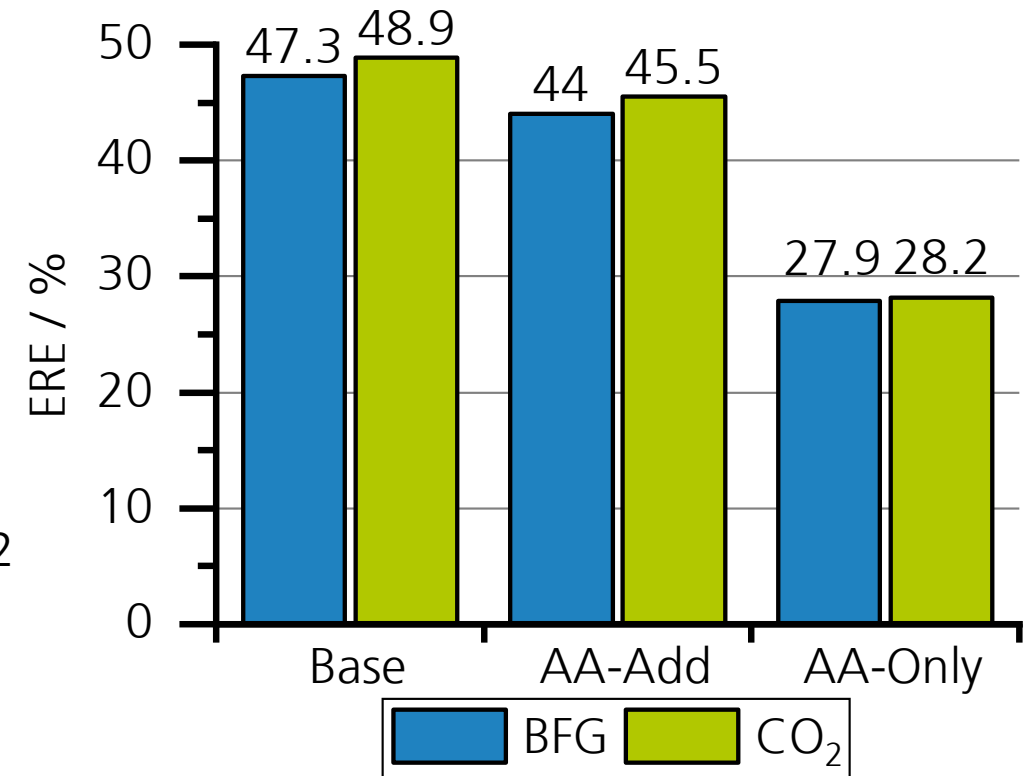
Concept is the Monsanto/Cativa™ process

Scenarios: Base-case methanol, AA-Add and AA-Only

- AA-Add scenario, ERE slightly reduced ($\Delta\text{ERE} \sim -3\%$)
→ Just small amounts of methanol can be utilized
- AA-Only scenario, all MeOH can be converted, negative impact ($\Delta\text{ERE} \sim -20\%$)
 - Lack of BOFG as a heat source for the steel mill
 - Replacement of energy has a big negative impact on Scope 2

→ Acetic acid production negatively impacts the ERE

→ But ERE is still positive



Comparison between methanol and downstream acetic acid production

Discussion

KPI's for downstream acetic acid production

- Methanol production $> 1000 t_{\text{MeOH}}/\text{h}$ in both concepts
 - $1005 t_{\text{MeOH}}/\text{h}$ in BFG and $1141 t_{\text{MeOH}}/\text{h}$ in CO_2 concept
 - AA production is limited to about $135 t_{\text{AA}}/\text{h}$ due to insufficient CO supply from BOFG
 - Just $70 t_{\text{MeOH}}/\text{h}$ (7 %) can be converted to AA (AA-Add scenario)
- **Therefore, the effect of downstream acetic acid production is minor compared to methanol concepts**
- There is no significant impact from other technical parameters either
 - High conversion rates for AA synthesis ($> 95\%$)
 - No further hydrogen is required
 - Neglectable additional energy requirements
- **Therefore, CBR and LHE_{INT} remain nearly constant for acetic acid production**

Conclusion and Outlook

- Environmentally friendly production of methanol and acetic acid from steel mill off-gases is possible
 - > 40% CO₂ avoidance for both methanol concepts in 2040
 - MeOH-CO₂ > MeOH-BFG
 - The CO₂ emission factor from the grid mix should decrease significantly to avoid negative ecological impacts
 - Otherwise, green hydrogen can be used (e.g. produced carbon-neutral from PV etc.)
 - Carbon and hydrogen can be captured/bounded in large amount (CBR and LHE ≥ 80% in all concepts)
 - Acetic acid can only utilize 7% of the potential producible methanol from BFG
 - More methanol production from one steel mill than currently in all of Germany possible
 - Acetic acid has a slightly negative impact on the ERE
 - However, acetic acid has a greater economic value compared to methanol; thus, the simultaneous production of both chemicals can be economically advantageous → this should be investigated in further work
 - **Outlook:** Investigation of other chemicals (DME, Urea, Ammonia, Methane etc.)
- Using a time-dependent optimization model to identify the economic optimal CCU concept and plant sizes

**Thank you for your attention.
If you have any questions, feel free to ask!**

Contact information

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