Dynamic methanation of by-product gases from the steel industry in the scope of the project i³upgrade

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Outline

- Motivation
- The project i³upgrade
  - Aim of the project
  - Consortium
- Fundamentals
  - Methanation
  - By-product gases from the steel industry
- Experimental setup and results
  - Reactor concept and methanation test rig
  - Experimental results from the methanation of steel work‘s by-product gases
- Conclusion
**CO₂ emissions from integrated steelworks**

- Energy and carbon rich by-product gases emerge process-related
  - Thermodynamic optimum for the consumption of reducing agent is already reached (~498 kg_C/t_hot-metal; theoretical minimum: 414 kg_C/t_hot-metal)\(^{(1)}\)
  - Nowadays used thermally internally
  - Do not cover the entire energy demand → additional fossil fuels necessary

- 27 – 30 % of the total industrial CO₂ emissions originate from steel works\(^{(2,3)}\)
- This equals 5 – 6 % of the total anthropogenic CO₂ emissions\(^{(2,3)}\)
- **Focus of i³upgrade:** Reduction of the CO₂ impact of the integrated steelworks through hydrogen-intensified syntheses

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1) www.eurofer.org
2) A review of thermochemical processes and technologies to use steelworks off-gases, W. Uribe-Soto et al., Renewable and Sustainable Energy Reviews 74 (2017), pp. 809-823
Project objective $i^3$upgrade (1)

- **Aim**: Integration of renewable energies into the steelmaking process and thereby reduction of the CO$_2$ impact of integrated steel works
- **No major changes to the steelmaking process itself**
- Integration of dynamic syntheses (methane, methanol) into an integrated steel works in combination with (renewable) hydrogen
Project objective i³upgrade

- Intelligent process control strategy for dynamic operation with integrated dispatcher tool
- Approach with three control levels, from technical to economic level

Dispatch controller

- prediction of energy costs via neuronal networks
- solving optimization problem (MILP) (e.g. revenue, emissions, capacity ...)

Operating maps (from work packages 1 to 3):
- critical operational parameter
- Process parameter

Site level model
- +, -, p, T, m

Component level
- Model based control approach
- Implementation to industrial SPC system of synthesis reactors

Business case

delivery controller

Plant operation

Reaction control

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www.evt.tf.fau.de  www.i3upgrade.eu
Consortium of i³upgrade

- Term: 1st June 2018 to 30th November 2021; 42 months
- Total budget: 3.3 MM €
- Project administration: European Commission
- Funding: Research Fund for Coal and Steel (RFCS) (Grant Agreement Nr. 800659)
- Consortium: eight European partners
- Coordinator: FAU Erlangen-Nürnberg
By-product gases from the steel industry

- 3 process steps with energy and carbon rich by-product gases
  - Production of coke in coking plant → coke oven gas (COG); max. 65 000 m₃/h
  - Production of pig iron in blast furnace → blast furnace gas (BFG); max. 800 000 m₃/h
  - Production of steel in converter → converter gas (BOFG / CG); max. 75 000 m₃/h
- BFG and BOFG contain high shares of carbonaceous species
- can serve as carbon sources for hydrogen-intensified syntheses

\[
\begin{array}{|c|c|c|c|c|c|c|}
\hline
\text{gas} & \text{N}_2 & \text{CO}_2 & \text{CO} & \text{CH}_4 & \text{H}_2 & \text{C}_n\text{H}_m \\
\hline
\text{COG} & 3.8 & 3.2 & 4.6 & 21.4 & 48.9 & 1.9 \\
\hline
\text{BFG} & 51.0 & 21.0 & 23.0 & - & 4.5 & - \\
\hline
\text{BOFG / CG} & 15.5 & 17.2 & 60.9 & 0.1 & 4.3 & - \\
\hline
\end{array}
\]

**Methanation – Reaction system and main challenge**

- Reaction system containing CO and CO\(_2\) methanation and water-gas-shift reaction
- Formation of solid carbon possible (Boudouard equation)

\[
\begin{align*}
CO + 3 H_2 & \leftrightarrow CH_4 + H_2O & \Delta H_R^0 = -206 \text{ kJ/mol} \\
CO_2 + 4 H_2 & \leftrightarrow CH_4 + 2 H_2O & \Delta H_R^0 = -164 \text{ kJ/mol} \\
CO + H_2O & \leftrightarrow CO_2 + H_2 & \Delta H_R^0 = -41 \text{ kJ/mol} \\
CO_2 + C & \leftrightarrow 2 CO & \Delta H_R^0 = +173 \text{ kJ/mol}
\end{align*}
\]

**to date:** polytropic temperature profile with adiabatic synthesis temperature

1) Maximum temperature must be lower than the maximum temperature of the catalyst, **limited by heat flow density**

2) Low temperature at the reactor outlet for high methane content, **limited by heat exchanger surface**

- Temperature profile with maximum temperature \(T_{max}\) and adiabatic temperature \(T_{ad}\).
- Axial coordinate of reactor \(z_{max}\).
Experimental setup – Structured fixed-bed reactor

- Minimizing the radial heat conductance length in fixed-bed (limiting factor causing hot-spots)
- Alternating reaction zones and heat sinks
- Heat pipes for reactor cooling

- Block of stainless steel with drillings for
  - 9 reaction channels filled with commercial catalyst
  - 16 drillings for water heat pipes for heat dissipation
  - 12 pre-heating channels
  - Gas inlet, outlet and redirection

- Electrical heating especially for start-up by heating cartridges
- Cooling of heat pipe condenser zones by compressed air
**Heat dissipation with heat pipes**

- Passive component for heat dissipation
- Transport of high power densities over long distances with low temperature difference
- Principle: Transmission of the enthalpy of vaporization between the heat source and the heat sink in a closed two-phase system
- Liquid backflow usually driven by capillary forces

**Fundamentals**

- **Heat dissipation with heat pipes**
  - Passive component for heat dissipation
  - Transport of high power densities over long distances with low temperature difference
  - Principle: Transmission of the enthalpy of vaporization between the heat source and the heat sink in a closed two-phase system
  - Liquid backflow usually driven by capillary forces

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**Test rig and performed experiments**

**Test rig**
- Two stage methanation concept
- Intermediate water sequestration
- Pressures up to 5 bar
- Commercial Ni/Al\(_2\)O\(_3\) catalyst with high Ni loading (~ 50 wt.-%)
- Gas analyser for permanent gases

**Performed experiments**

Steady-state methanation of BFG and BOFG with different
- Syngas powers / volume flow rates
- Stoichiometric ratios

Dynamic methanation of BFG and BOFG by step attempts
- Up to ± 20 % in syngas power / volume flow rate
- Over- to sub-stoichiometric regime
Temperature control with heat pipes

- Maximum temperature can be limited below the catalyst limit
- $T_{max} \sim 150$ K lower than expectable adiabatic synthesis temperature
- Dynamic adaption of cooling power to the different operating points necessary

**Axial temperature profiles of the structured reactor for different steady-state syngas powers** (synthetic BOFG, $\sigma_{H2} = 1.04$, $p = 4$ bar)

Positioning of measurement:
- Automated TC in thermowell
Product gas composition of BOFG methanation

- Full CO$_x$ conversion after two-stage process with intermediate H2O sequestration
- Constant product gas quality after two-stage process over a wide syngas power range
- Significant amount of N$_2$ (~31 vol.-%) in the product gas

Gas compositions after the 1$^{st}$ and 2$^{nd}$ methanation stage for different steady-state syngas powers (synthetic BOFG, $\sigma_{H2} = 1.04$, $p = 4$ bar)
Yield and conversion of dynamic BFG methanation

- Full methane yield after two-stage methanation, $X_{H_2} \approx 95\%$ (over-stoichiometric methanation)
- Slight shift of conversion from 1$^{st}$ to 2$^{nd}$ stage; kinetic limitation assumed
- Dynamic experiments: no influence of step width and cycle time on $Y_{CH_4,CO_x}$ and $X_{H_2}$

Hydrogen conversion

\[
X_{H_2} = \frac{\dot{n}_{H_2,0} - \dot{n}_{H_2}}{\dot{n}_{H_2,0}}
\]

methane yield

\[
Y_{CH_4,CO_x} = \frac{\dot{n}_{CH_4} - \dot{n}_{CH_4,0}}{\dot{n}_{CO_2,0} + \dot{n}_{CO,0}}
\]

Hydrogen conversion and methane yield after the 1$^{st}$ and 2$^{nd}$ methanation stage for different steady-state syngas powers (ye/rd/bk) and dynamic experiments (bu) (synthetic BFG, $\sigma_{H_2} = 1.04$, $p = 4$ bar)
Temperature response during dynamic BFG methanation

- Prompt and significant jumps of the hot spot temperature (~30 K) for jumps in syngas power by 1.6 kW
- Mean temperature level (represented by heat pipe working temperature) shows sluggish response
  → Short-term fluctuations in syngas power require no adaption of cooling capacity

Timely resolved temperature profiles (structured reactor) for jumps in syngas power by 1.6 kW in 5 min cycles ($\sigma_{H2} = 1.04$, $p = 4$ bar, $V_{cool} = 85$ Nl/min)
Gas quality of product gases from BFG and BOFG methanation

Classification of product gas quality from BFG / BOFG methanation as measured and calculated N\textsubscript{2} free (limits according to DVGW G260)

Measured gas compositions
- Good match of $W_s/H_s$ ratio
- Not injectable to gas grid, high share of N\textsubscript{2}

Calculated N\textsubscript{2} free gas compositions
- Some operating points would reach H gas quality
- Influence of H\textsubscript{2} dilution increases
Conclusion

- **Aim i³upgrade**: Integration of renewable energies into the steelmaking process and thereby reduction of the CO₂ impact of integrated steel works
- Dynamic H₂ intensified methanation with steelworks’ by-product gases as carbon source
- Results from steady-state and dynamic experiments
  - Heat pipe cooled structured reactor is suitable for advanced temperature control
  - Constant product gas quality over a wide syngas power range (after two-stage process with intermediate H₂O sequestration)
  - Dynamic experiments:
    - No influence of step width and cycle time on \( Y_{\text{CH}_4,\text{CO}_x} \) and \( X_{\text{H}_2} \)
    - Prompt temperature response at hot spot
    - Sluggish response of mean temperature, dampening character of the reactor
  - Gas quality not sufficient for grid injection because of high shares of N₂

Thank you for your attention!