

# VTiU

**Verfahren**TECHNIK  
*des industriellen Umweltschutzes*

## Dynamic Methanation of By-product Gases from Integrated Steelworks

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ICPS 2019, Vienna, 19-Nov-2019

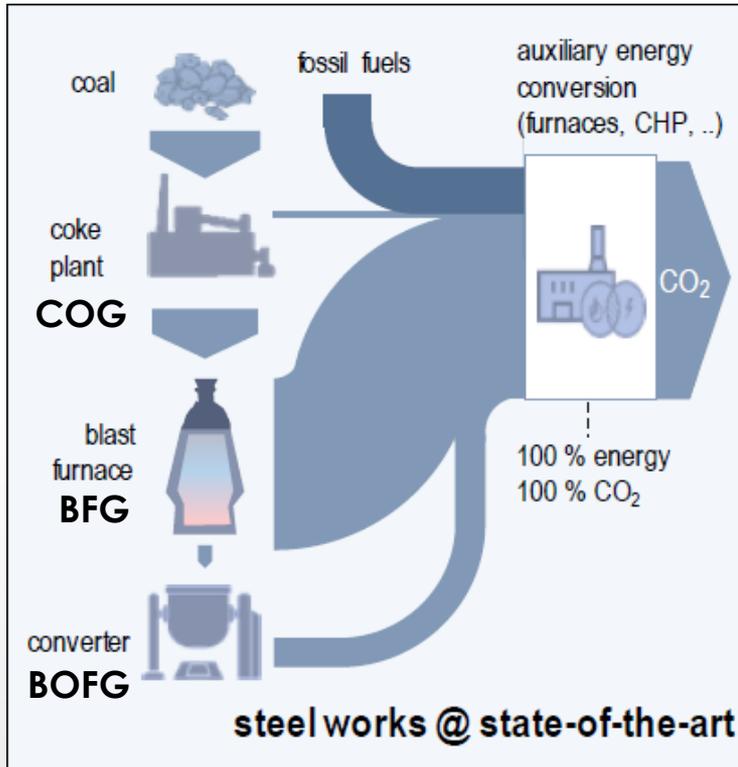
DEPARTMENT FÜR

**Umwelt- & EnergieverfahrenSTECHNIK**



G I G

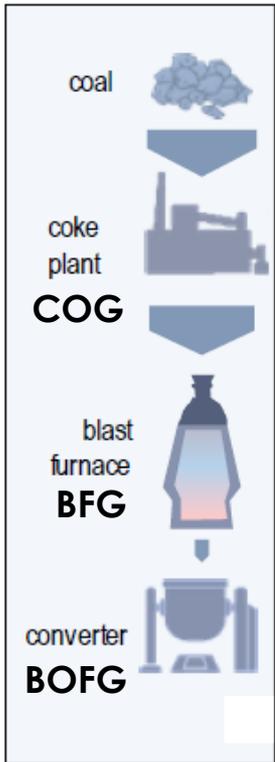
- Motivation
- The project ***i<sup>3</sup>upgrade***
- Methanation of steelworks gases
  - Test rig at Montanuniversität Leoben
  - Steady-state experiments
  - Dynamic conditions
  - Catalyst comparison (bulk vs. honeycombs)
- Conclusion & outlook



- Energy & C-rich by-product gases
- Used internally - not sufficient to meet total energy demand
- Thermodynamic optimum of process control reached
  - Additional fossil fuels needed
- Exemplary plant: 9.2 Mio. t/a CO<sub>2</sub><sup>(1)</sup>

27-30% of industrial CO<sub>2</sub>-emissions are from integrated steelworks<sup>(2,3)</sup>    ≅ 5-6% of all human-caused CO<sub>2</sub>-emissions<sup>(2,3)</sup>

1) UMWELTERKLÄRUNG 2018, Aktualisierte Umwelterklärung für die Standorte Linz und Steyrling, [https://www.voestalpine.com/stella/files/de/Umwelterklaerung\\_2018\\_DE.pdf](https://www.voestalpine.com/stella/files/de/Umwelterklaerung_2018_DE.pdf)  
 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  
 3) A. Hasanbeigi, 2017, <https://www.globalefficiencyintel.com/new-blog/2017/nfographic-steel-industry-energy-emissions>



	COG		BFG		BOFG
[Vol.-%]	Min	Max	Min	Max	Mean
<b>CO<sub>2</sub></b>	1	5.4	<b>16</b>	<b>26</b>	<b>17.2</b>
<b>CO</b>	3.4	5.8	<b>19</b>	<b>27</b>	<b>60.9</b>
<b>H<sub>2</sub></b>	36.1	61.7	1	8	4.3
<b>N<sub>2</sub></b>	1.5	6	44	58	15.5
<b>CH<sub>4</sub></b>	15.7	27	-	-	0.1
<b>C<sub>n</sub>H<sub>m</sub></b>	1.4	2.4	-	-	-

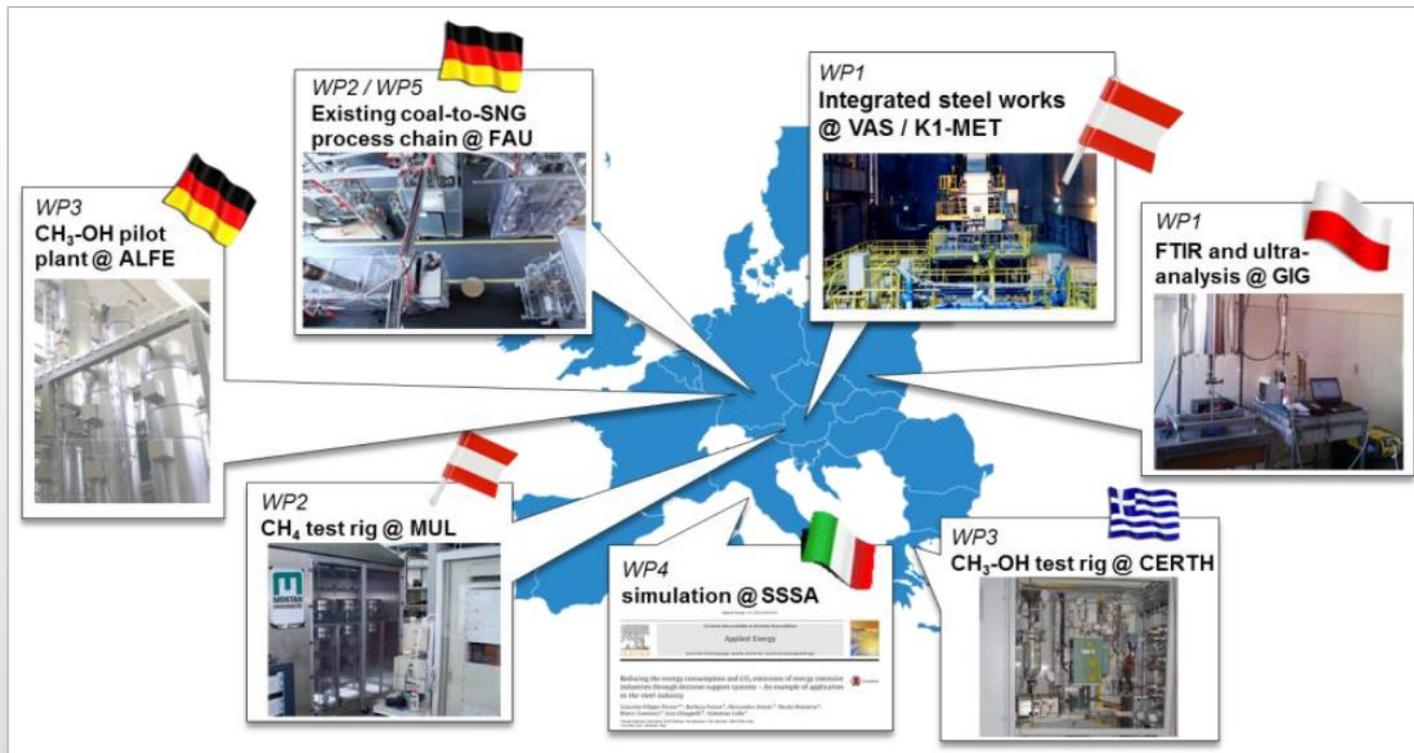
\* Best Available Techniques (BAT) Reference Document for Iron and Steel Production, Industrial Emissions Directive 2010/75/EU Integrated Pollution Prevention and Control, 2013

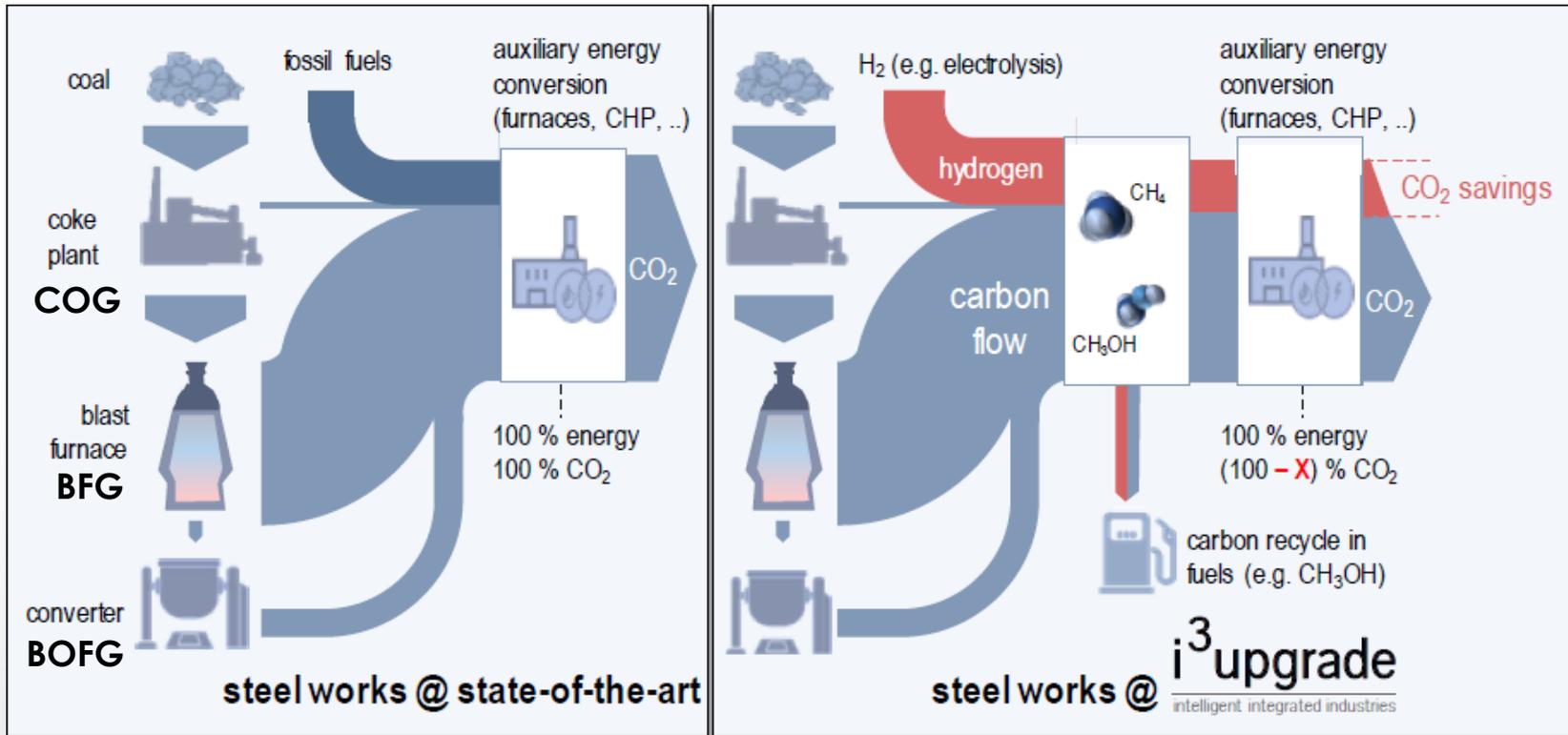
✓ High C-content in BFG & BOFG

✓ Source for hydrogen-intensified methane synthesis

- Coke → Coke Oven Gas (COG) ~ 65,000 Nm<sup>3</sup>/h
- Pig iron → Blast Furnace Gas (BFG) ~ 800,000 Nm<sup>3</sup>/h
- Steel → Converter Gas (BOFG) ~ 75,000 Nm<sup>3</sup>/h

- Duration: June 2018 - November 2021
- Administration: European Commission
- Funding: Research Fund for Coal and Steel (RFCS)
- Budget: 3.3 MM €

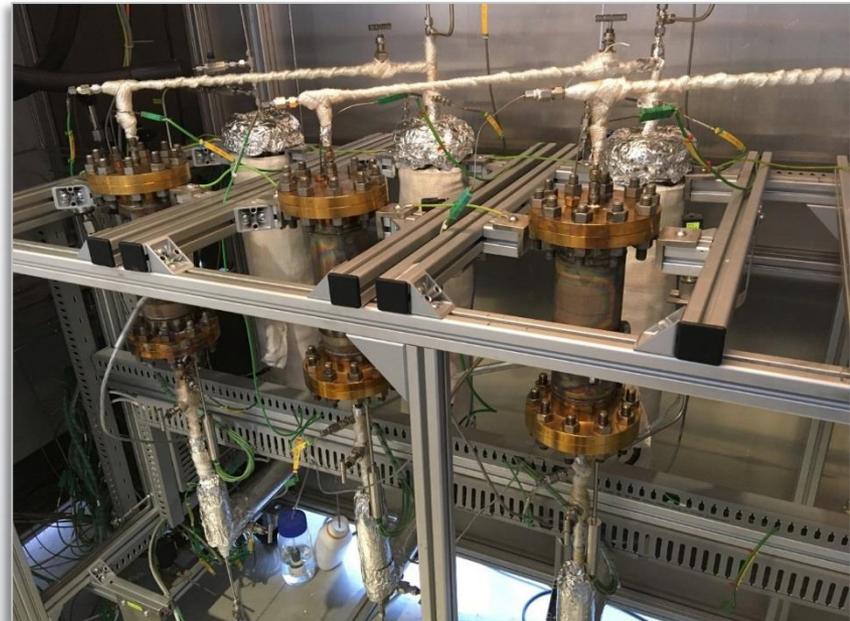




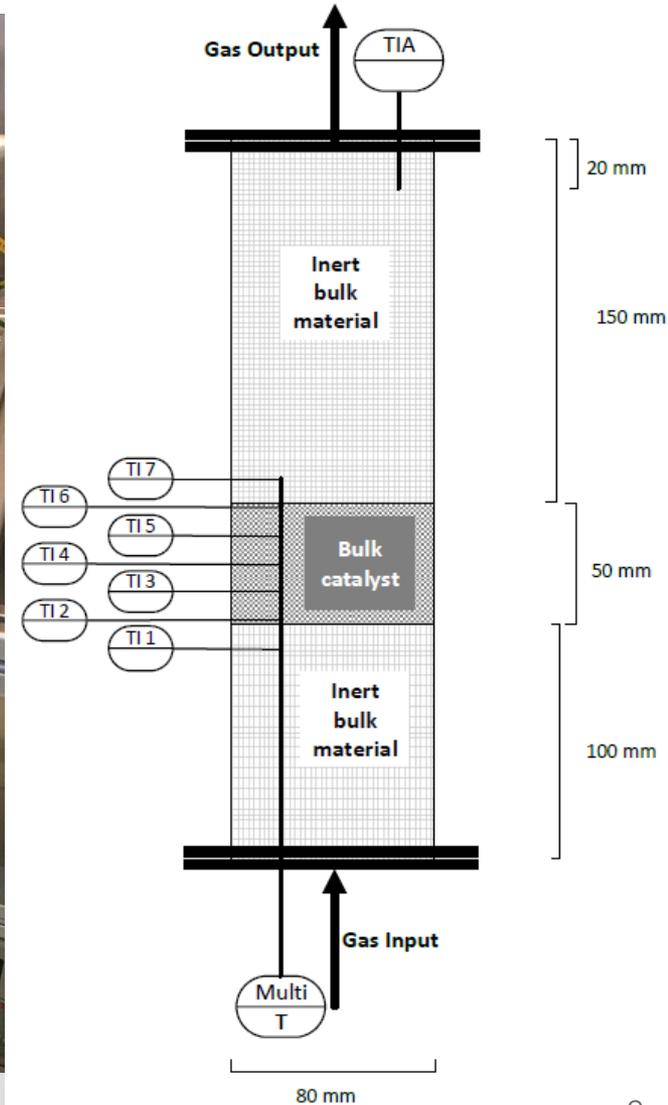
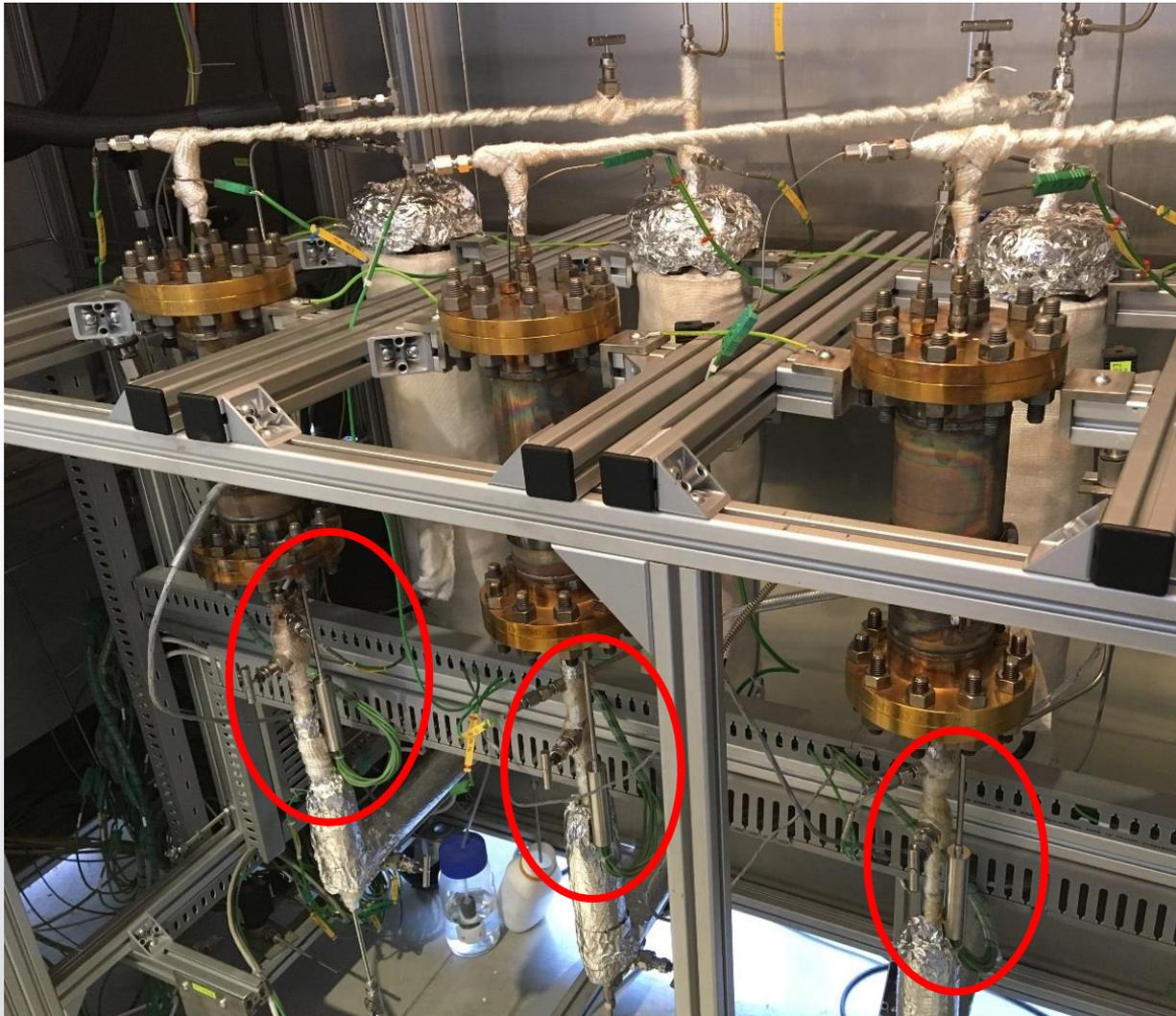
- Integration of renewable energy sources in the steelmaking process
- Reduction of CO<sub>2</sub>-emissions
- Integration of **dynamic** synthesis processes (methane, methanol)
- No interference with the steelmaking process itself



- 3 fixed-bed reactors in series
- $Q_{\max} = 50 \text{ NL/min}$
- $p = 1 - 20 \text{ bar}$
- $T_{\max} = 700 \text{ °C}$
- Meth 134®
- Honeycombs



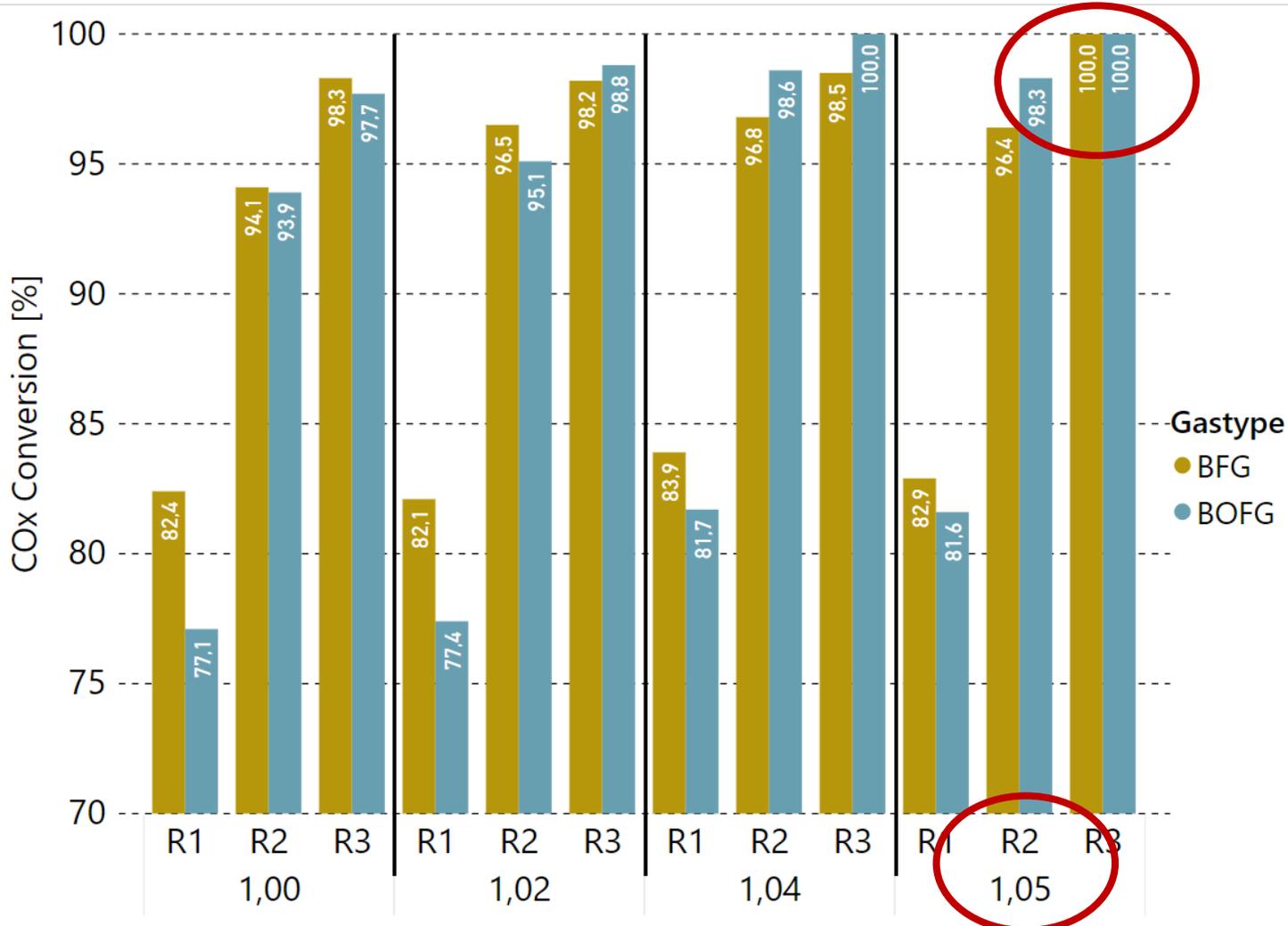
# Methanation test rig @MUL



Dynamic Methanation of By-product Gases  
from Integrated Steelworks

# ***STEADY-STATE EXPERIMENTS***

Bulk catalyst, 4 bar, 4 000 h<sup>-1</sup>, H<sub>2</sub> excess variation



BFG	[Vol.-%]
N <sub>2</sub>	~ 48
O <sub>2</sub>	-
CO <sub>2</sub>	~ 23
CO	~ 25
CH <sub>4</sub>	-
H <sub>2</sub>	~ 4
Σ C <sub>n</sub> H <sub>m</sub>	-

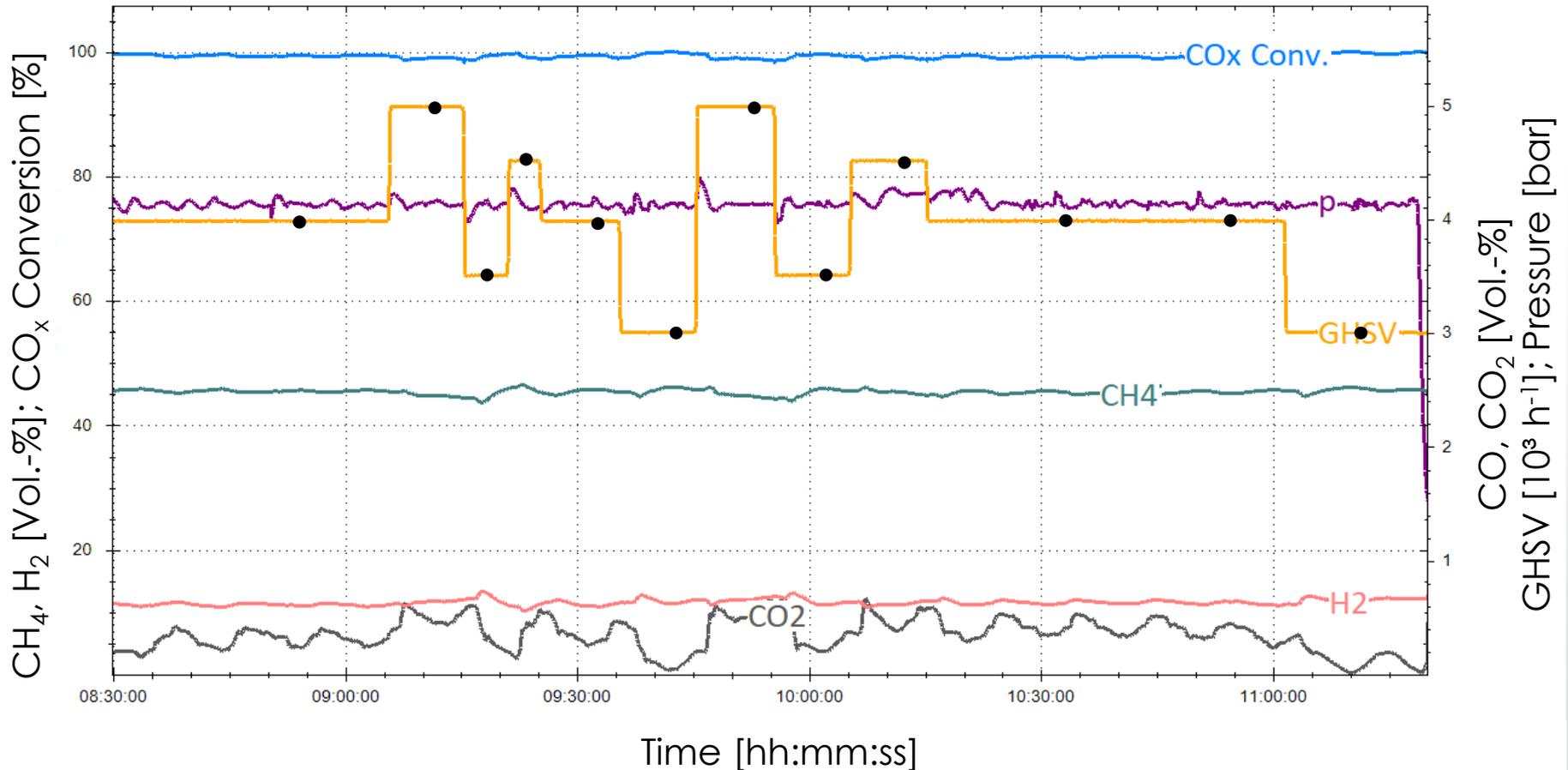
BOFG	[Vol.-%]
N <sub>2</sub>	~ 28
O <sub>2</sub>	-
CO <sub>2</sub>	~ 20
CO	~ 51
CH <sub>4</sub>	-
H <sub>2</sub>	~ 1
Σ C <sub>n</sub> H <sub>m</sub>	- 10

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# ***DYNAMIC CONDITIONS***

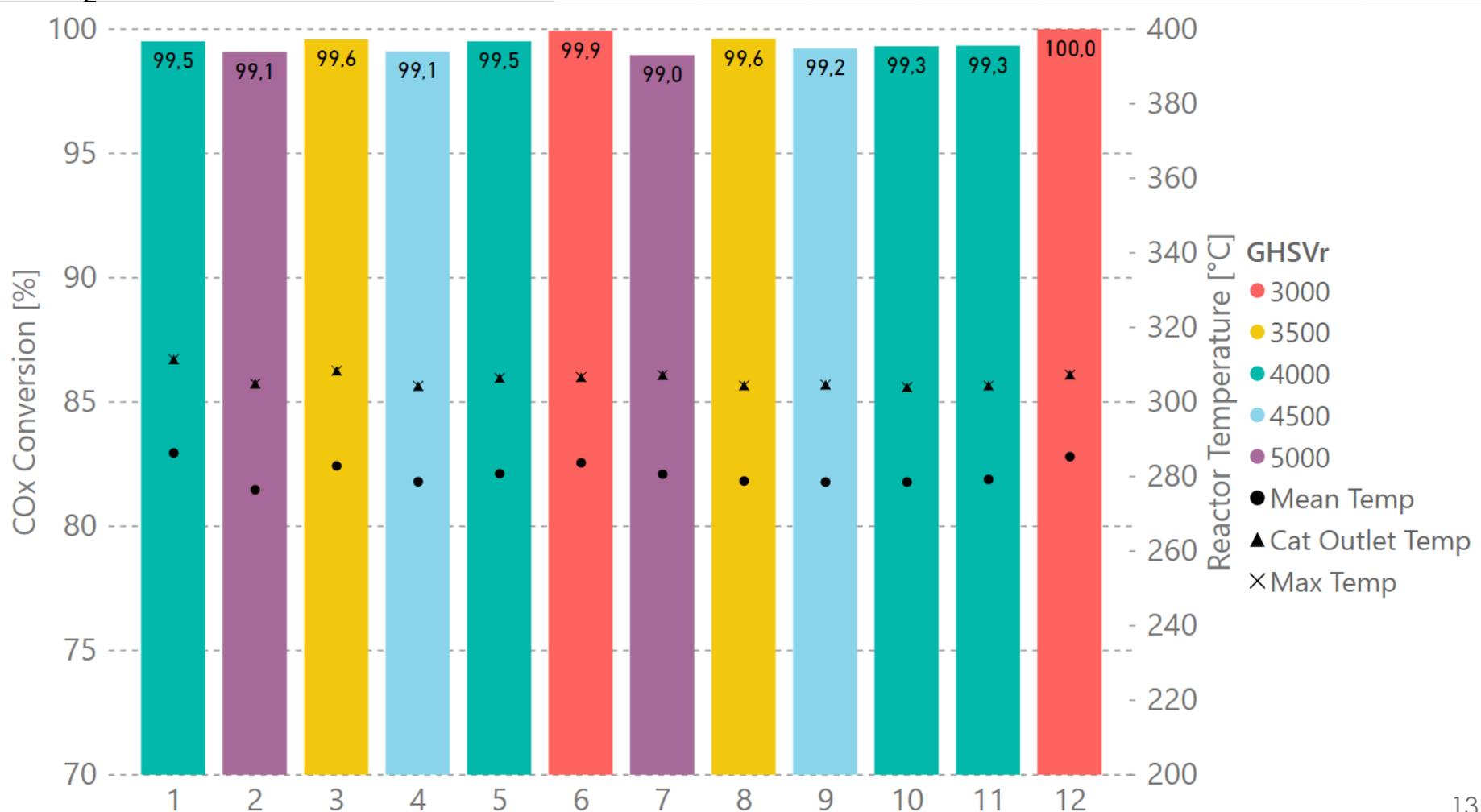
$p = 4 \text{ bar}$ , GHSV variation,  
5%  $\text{H}_2$  excess rate

BFG	$\text{N}_2$	$\text{O}_2$	$\text{CO}_2$	$\text{CO}$	$\text{CH}_4$	$\text{H}_2$	$\Sigma \text{C}_n\text{H}_m$
[Vol.-%]	~ 48	-	~ 23	~ 25	-	~ 4	-



p = 4 bar, GHSV variation,  
5% H<sub>2</sub> excess rate

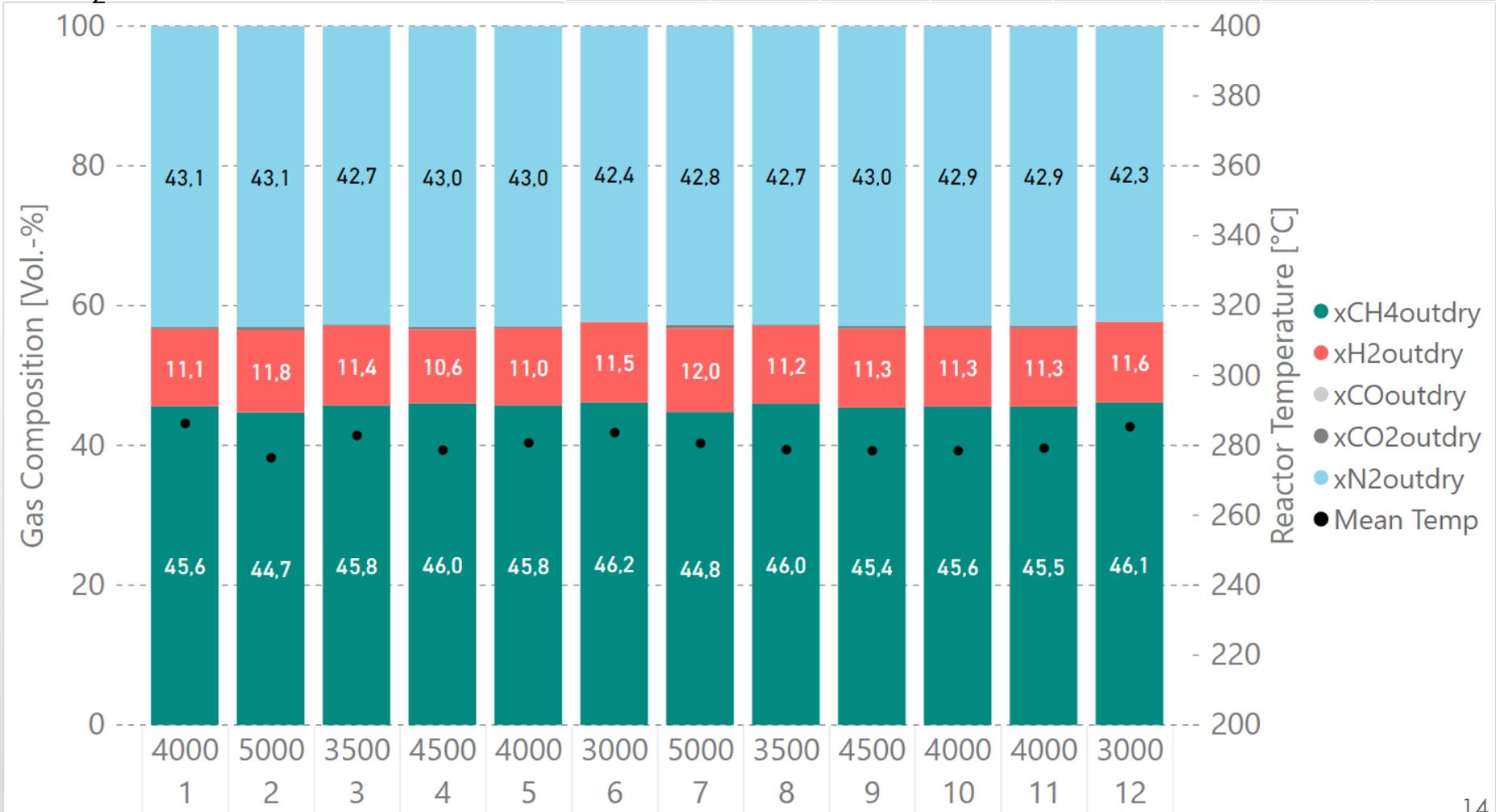
BFG	N <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	CO	CH <sub>4</sub>	H <sub>2</sub>	Σ C <sub>n</sub> H <sub>m</sub>
[Vol.-%]	~ 48	-	~ 23	~ 25	-	~ 4	-



# Dynamic tests with BFG

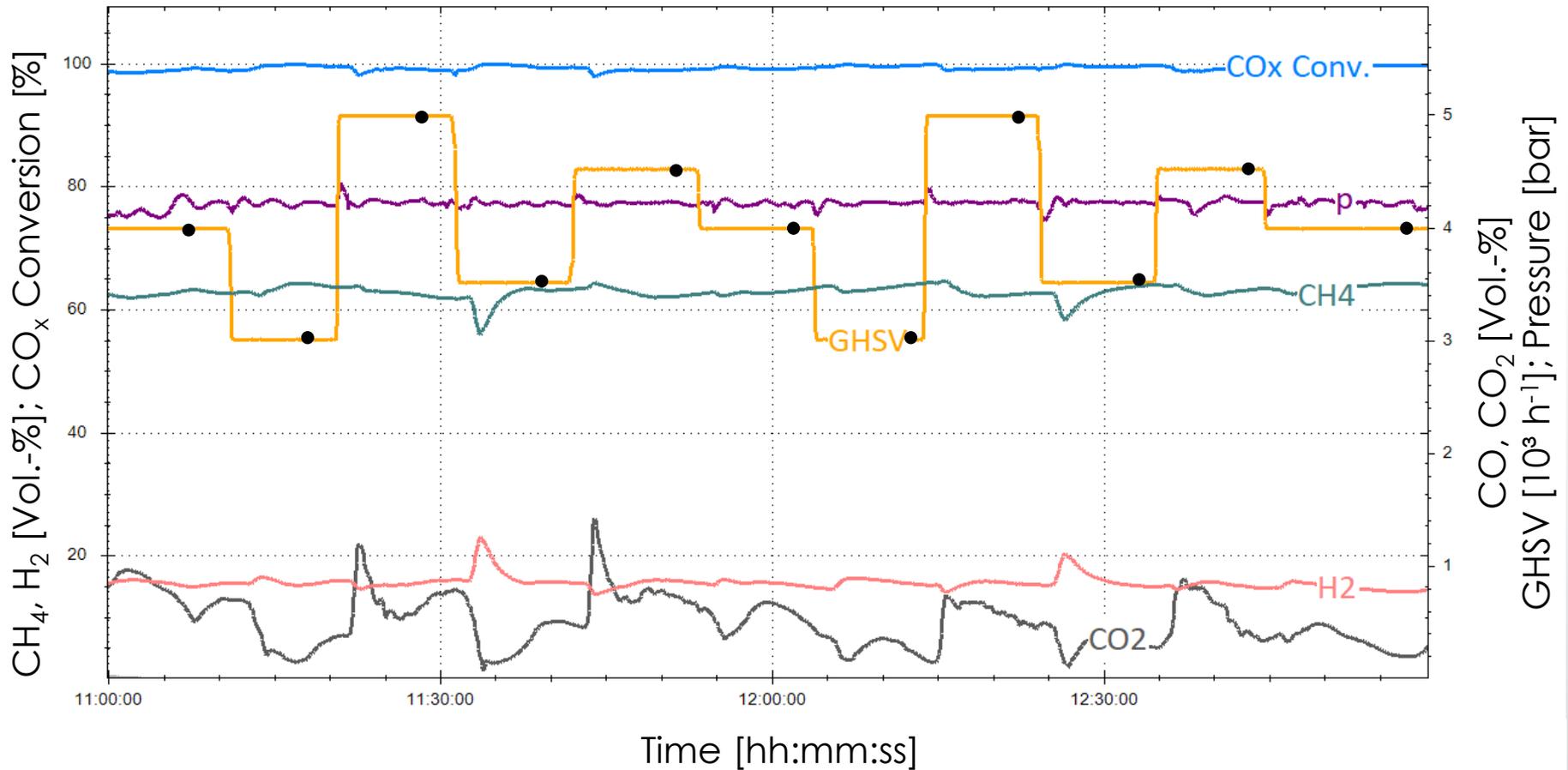
p = 4 bar, GHSV variation,  
5% H<sub>2</sub> excess rate

BFG	N <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	CO	CH <sub>4</sub>	H <sub>2</sub>	Σ C <sub>n</sub> H <sub>m</sub>
[Vol.-%]	~ 48	-	~ 23	~ 25	-	~ 4	-



p = 4 bar, GHSV variation,  
5% H<sub>2</sub> excess rate

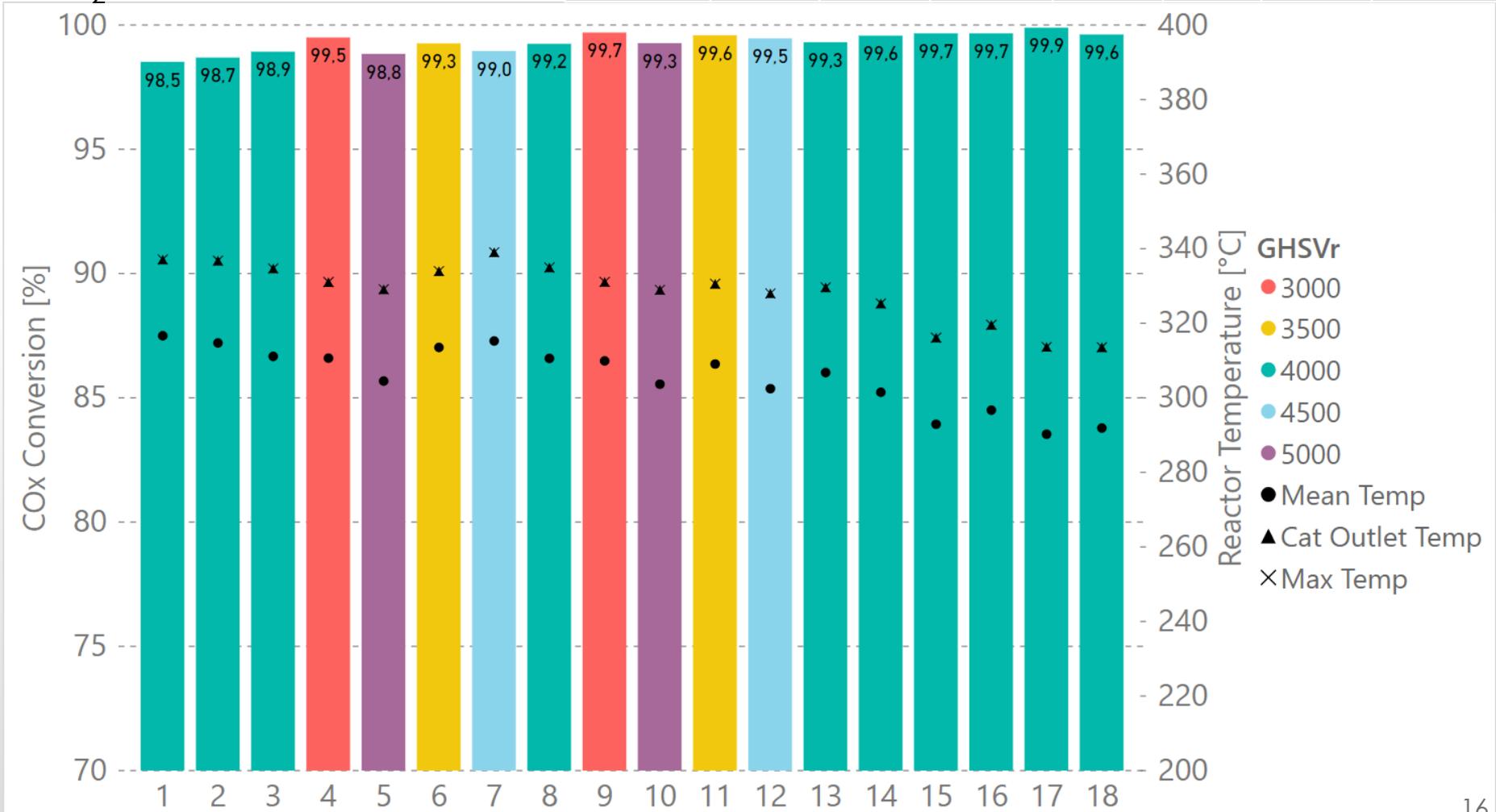
BOFG	N <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	CO	CH <sub>4</sub>	H <sub>2</sub>	Σ C <sub>n</sub> H <sub>m</sub>
[Vol.-%]	~ 28	-	~ 20	~ 51	-	~ 1	-



# Dynamic tests with BOFG

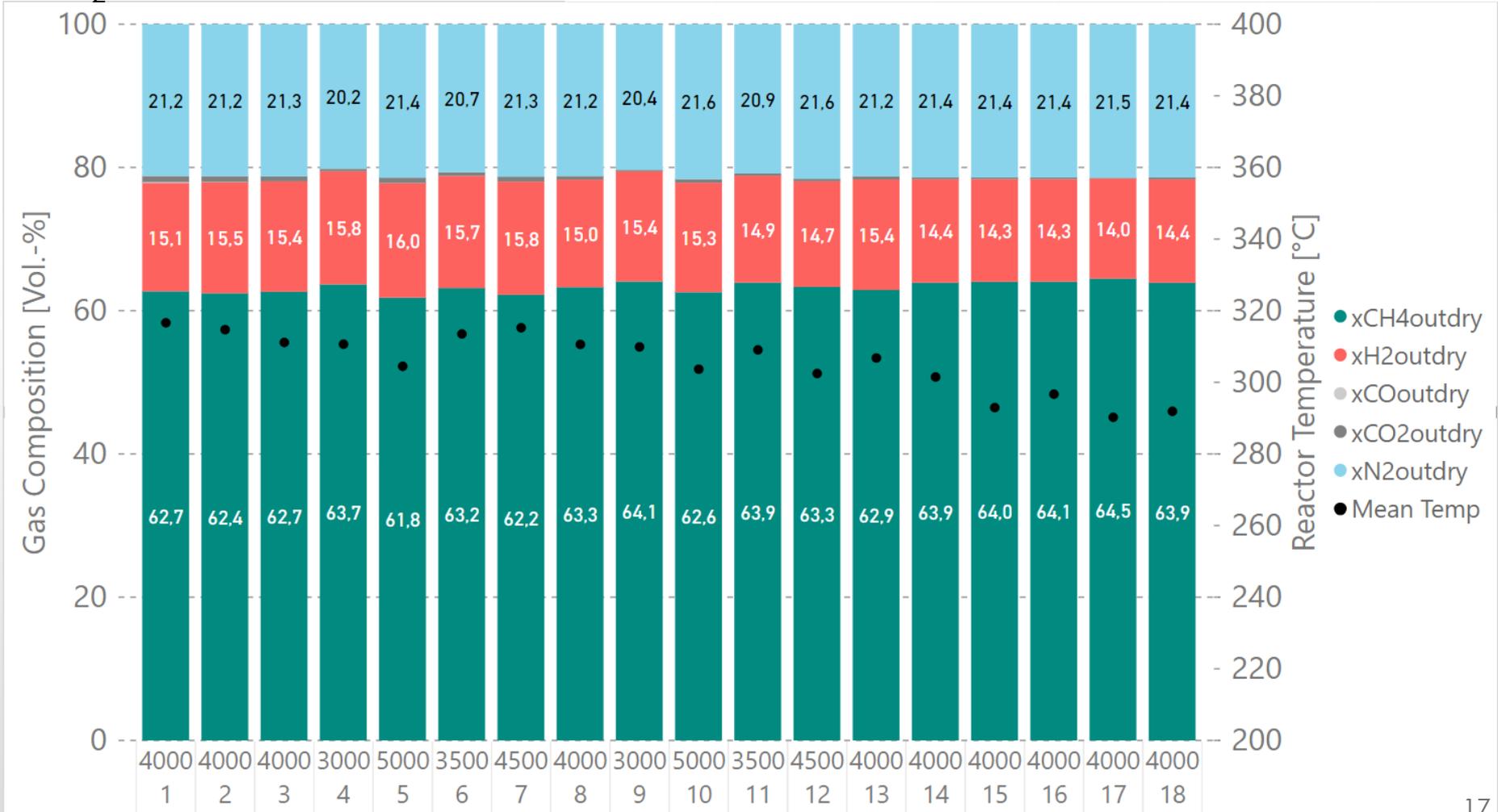
p = 4 bar, GHSV variation,  
5% H<sub>2</sub> excess rate

BOFG	N <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	CO	CH <sub>4</sub>	H <sub>2</sub>	Σ C <sub>n</sub> H <sub>m</sub>
[Vol.-%]	~ 28	-	~ 20	~ 51	-	~ 1	-

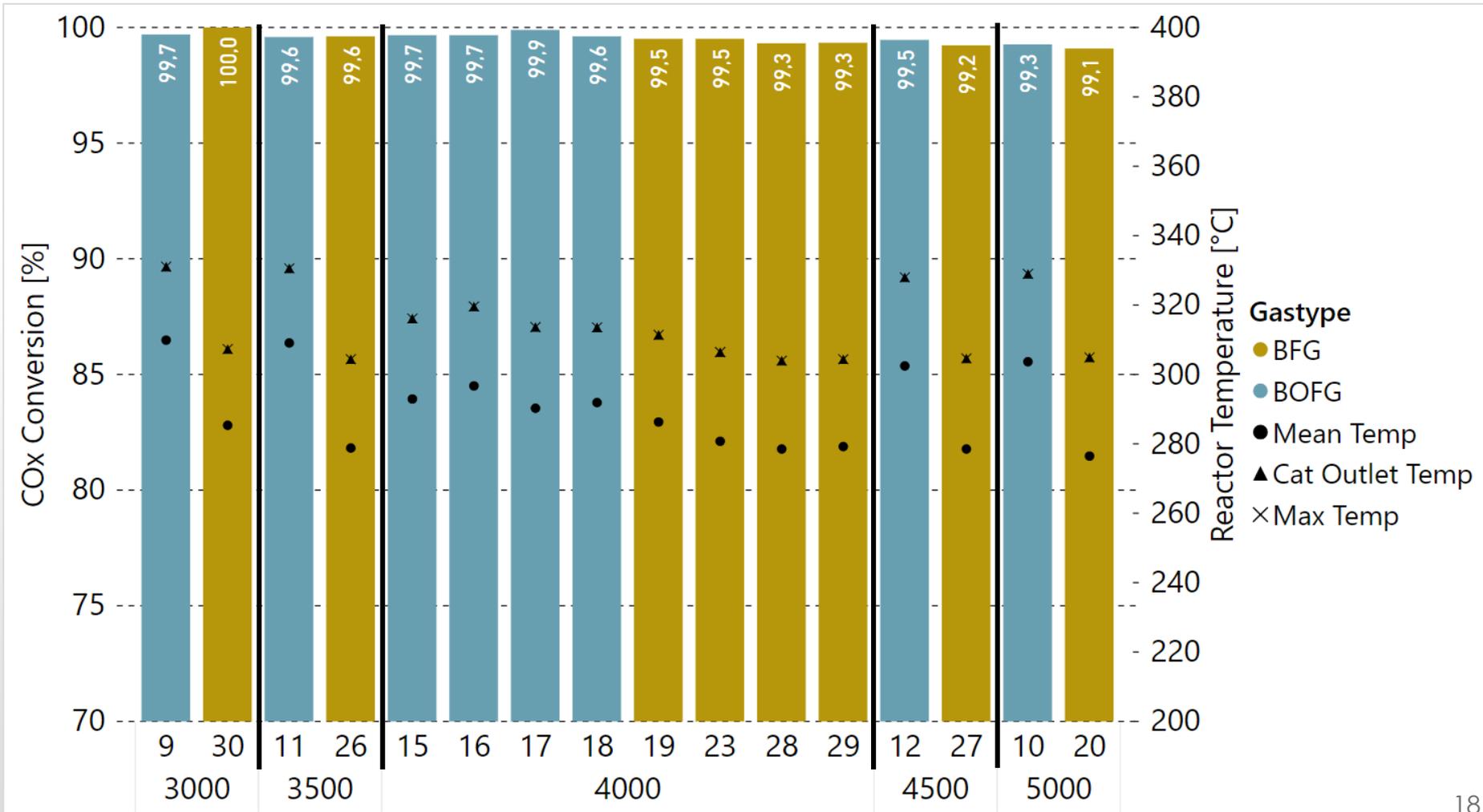


p = 4 bar, GHSV variation,  
5% H<sub>2</sub> excess rate

BOFG	N <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	CO	CH <sub>4</sub>	H <sub>2</sub>	Σ C <sub>n</sub> H <sub>m</sub>
[Vol.-%]	~ 28	-	~ 20	~ 51	-	~ 1	-



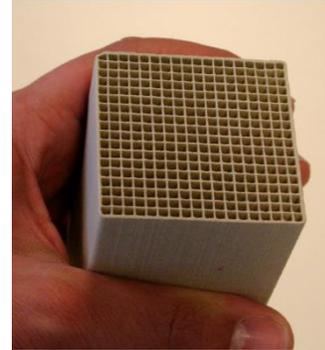
Bulk catalyst, 4 bar, GHSV variation, 5% H<sub>2</sub> excess rate



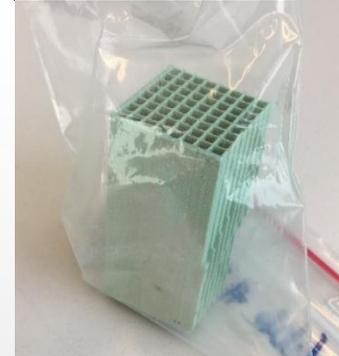
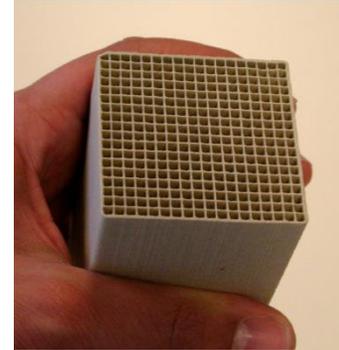
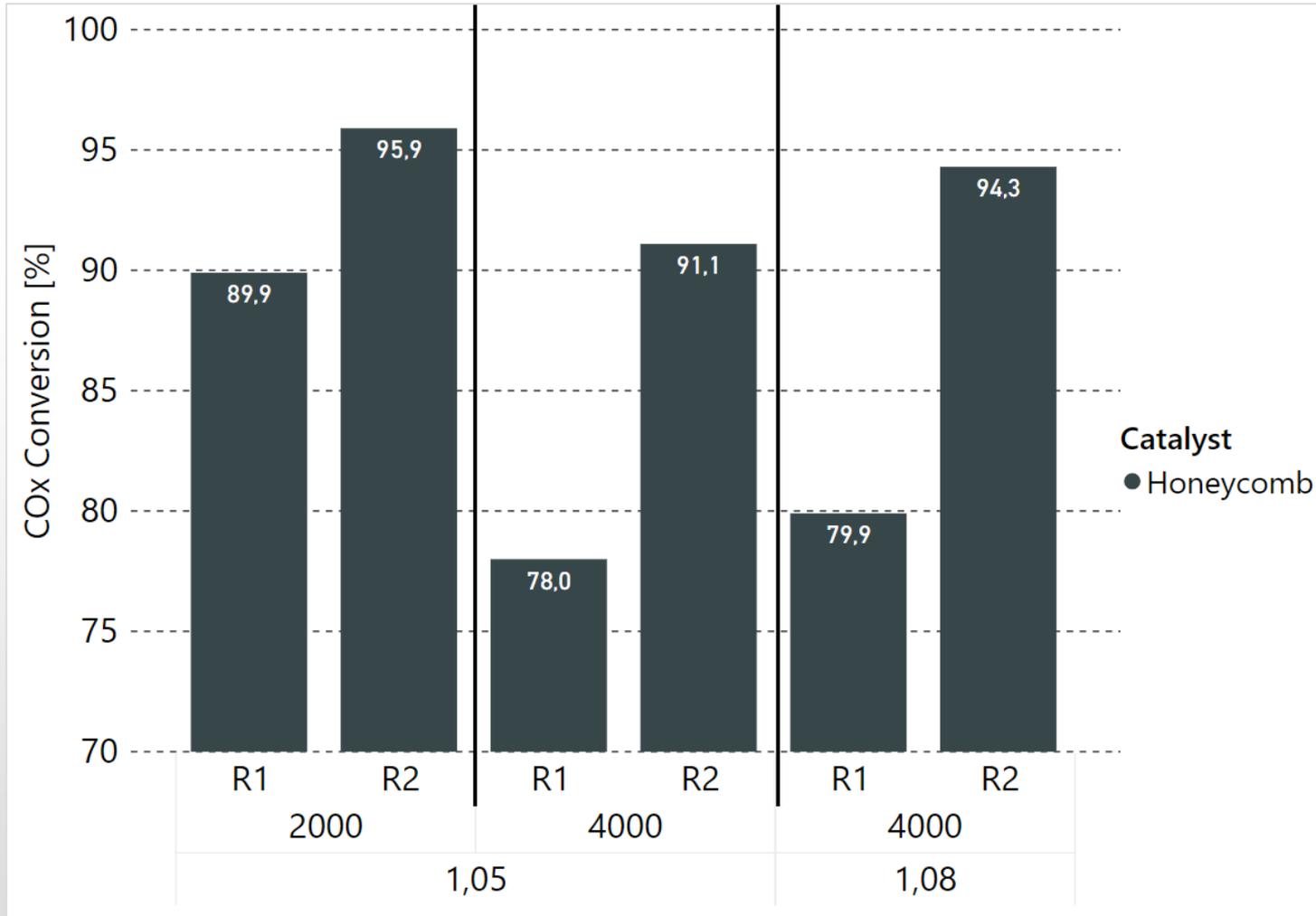
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# ***CATALYST COMPARISON BULK VS. HONEYCOMBS***

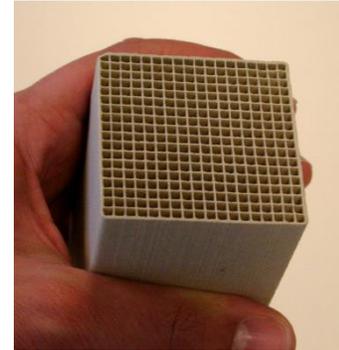
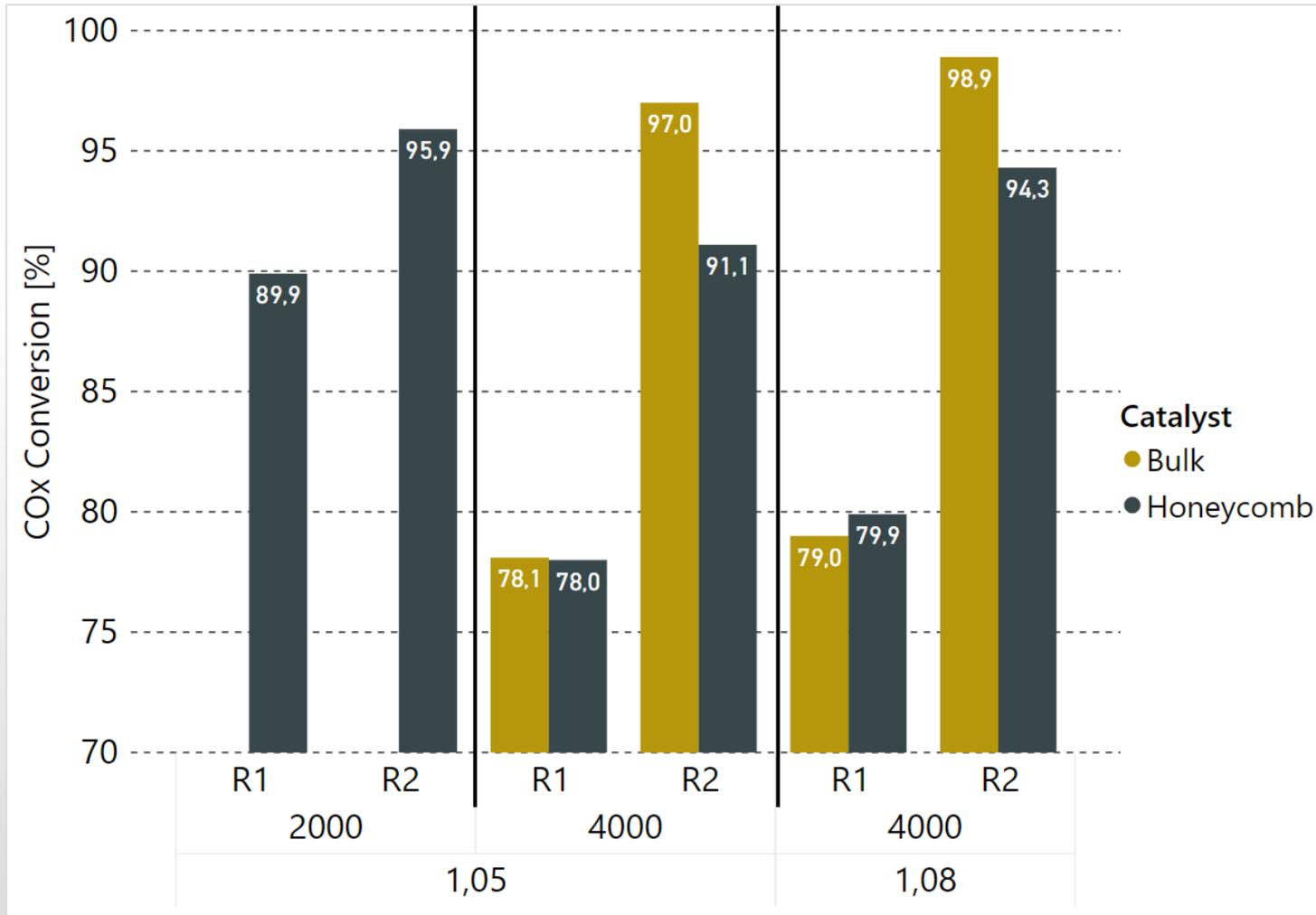
- Ceramic monoliths (Cordierite)
- Wash-coats w/ Boehmite & Ni-nitrate
- Advantages:
  - Load flexibility,  $\Delta p$ , thermal management
  - Scalability, stand-by behaviour
- Catalytic activity tested for
  - H<sub>2</sub> excess rates of 5 & 8%
  - GHSV = 2 000; 4 000 h<sup>-1</sup>
  - p = 4 bar



4 bar, 2 reactors, BFG



4 bar, 2 reactors, BFG



- Dynamic methanation
  - + Full/high CO<sub>x</sub> conversion for BFG & BOFG
  - + 5% H<sub>2</sub> excess rate required
  - + Only minor changes in CO<sub>x</sub> conv. & prod. gas composition
  - + Temperature control essential
  - Further dynamic experiments/load changes
- Wash-coated honeycomb catalyst
  - + Catalytically active
  - Improved coating process
  - Dynamic experiments



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