Process integration of packed bed Ca-Cu process for high efficiency and near-zero emission hydrogen generation

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Multiphase Reactors Group Department of Chemical Engineering & Chemistry

Outline

- Introduction on Ca-Cu looping process
- Simulations with a pseudo-homogeneous reactor model
- Integration of the process in a power plant
- Process performance results
- Conclusion

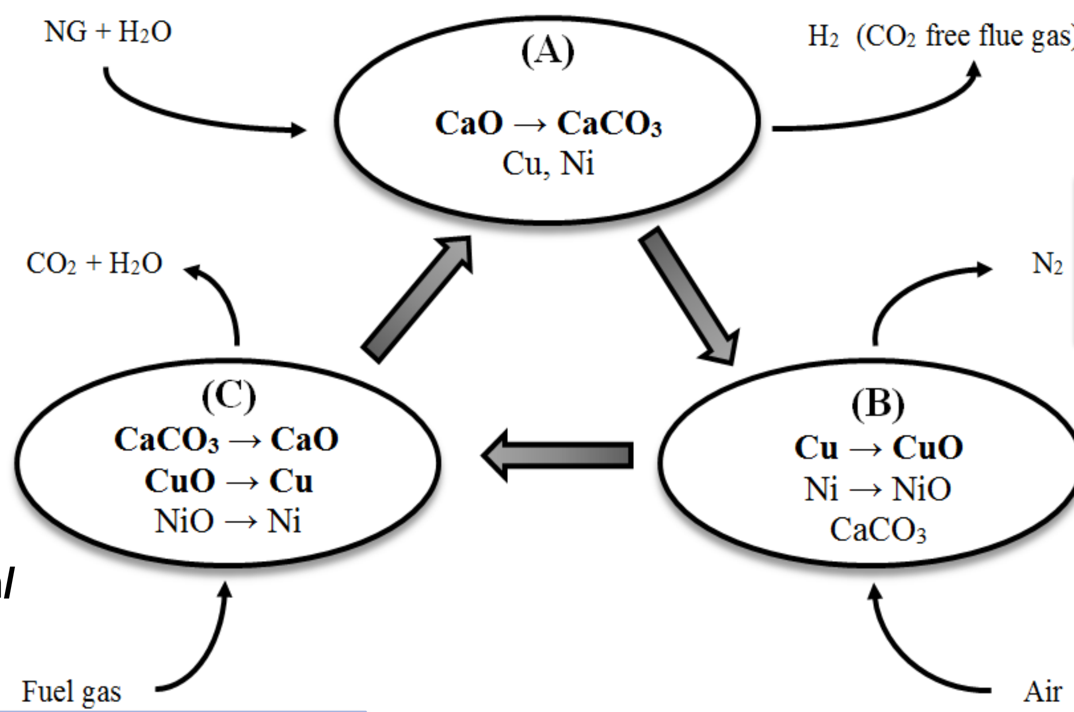
Ca-Cu looping process
Concept description

SER based process where a second chemical loop based on Cu/CuO is incorporated to solve the problem of **endothermic $CaCO_3$ calcination through CuO reduction**

SER stage

Produced at high pressure

N_2 at high pressure to limit calcination



$CaCO_3$ Calcination/ Reduction of CuO

Cu oxidation

At low pressure to avoid high calcination temperature

Process scheme

Step A
$T_{bed,in} = T_{gas,in}$ = 700 °C
P = 20 bar
Inlet gas from heated pre-reformer at 700°C (S/C=4)

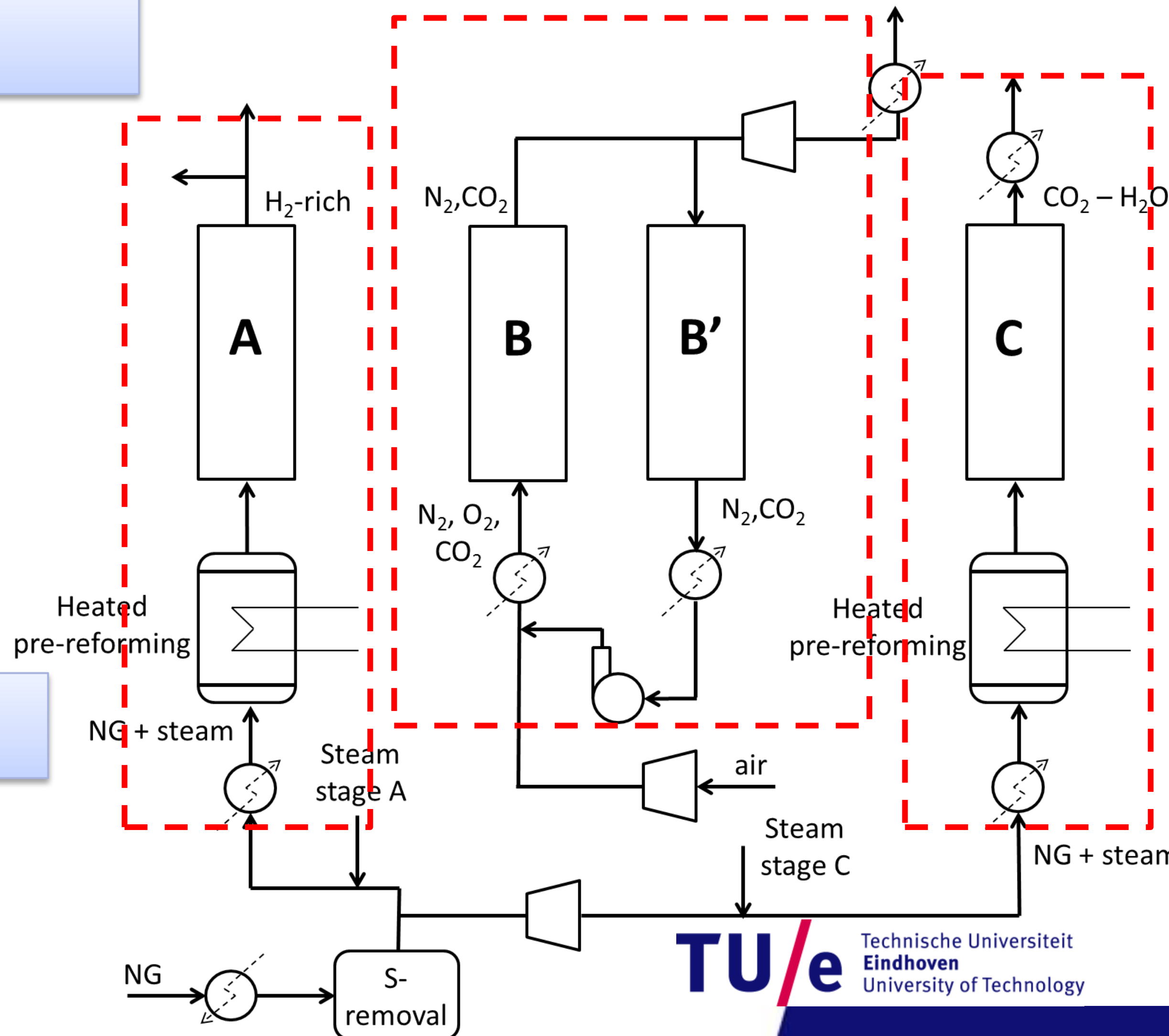
To avoid CaO hydration

Step B
$T_{bed,in}$ = 700 °C
$T_{gas,in}$ = 340 °C
P = 15 bar
3.4% O_2 in the inlet

Step B'
$T_{bed,in}$ = 340 °C
$T_{gas,in}$ ≈ 800°C
P = 15 bar

Step C
$T_{bed,in}$ ≈ 800°C
$T_{gas,in}$ = 700 °C
Inlet gas from heated pre-reformer at 700°C (S/C=1)
P = 1 bar

To avoid irregular profiles in the bed



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Pseudo-homogeneous model results

- A pseudo-homogeneous model for packed bed reactors has been used to simulate the process

- Several cycles has been made in order to get a steady-state situation

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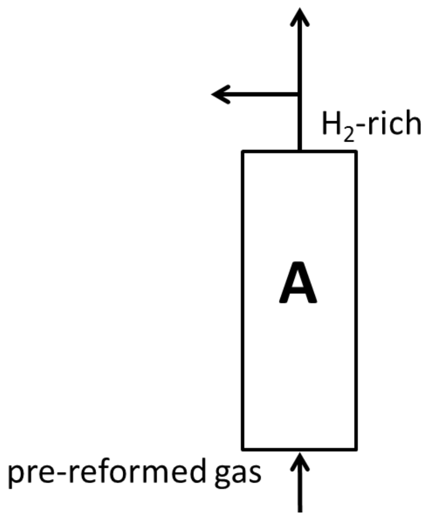
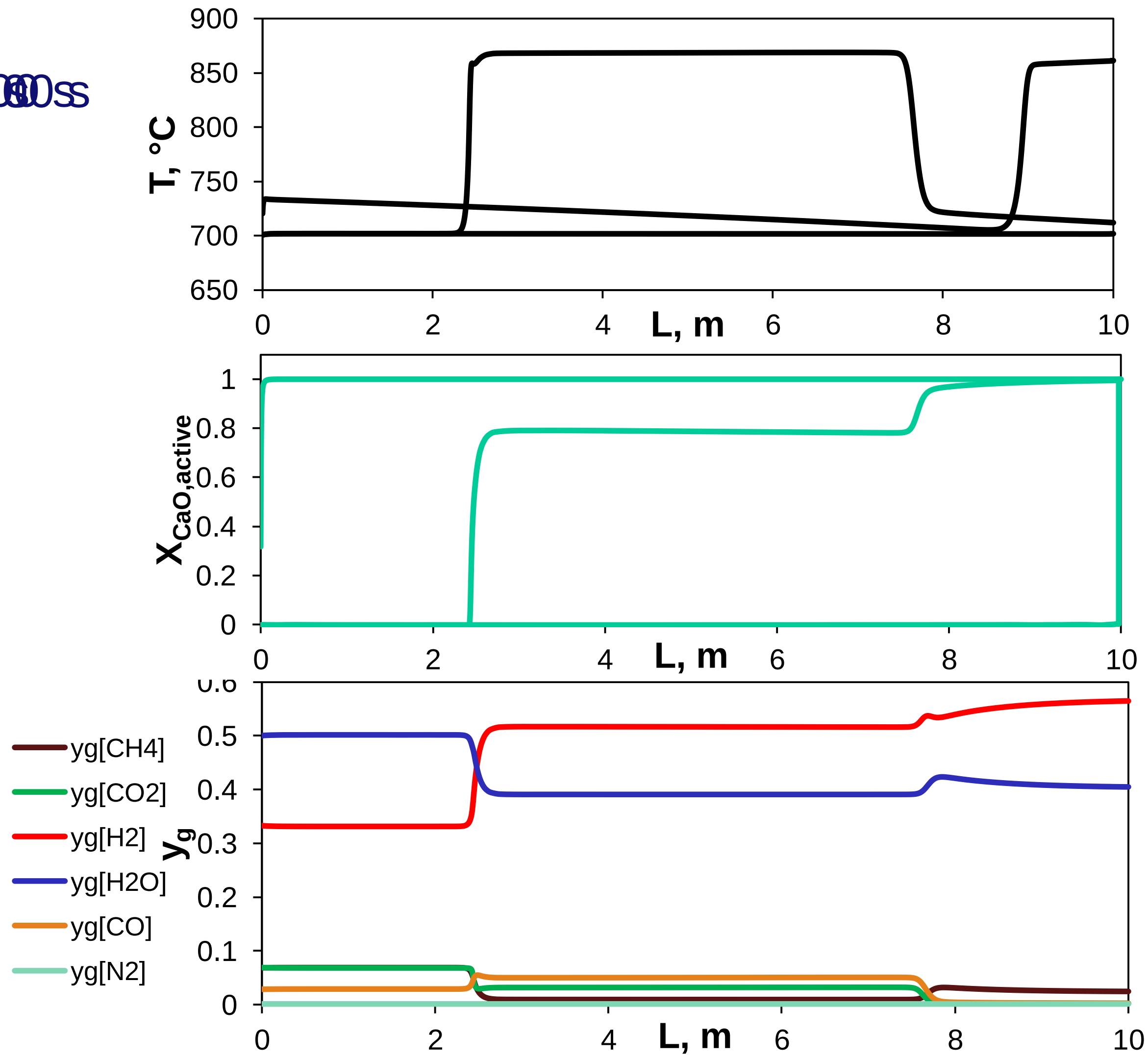
  - Temperature and composition profiles in the bed
  - Temperature and composition of the outlet stream

Pseudo-homogeneous model results
Step A

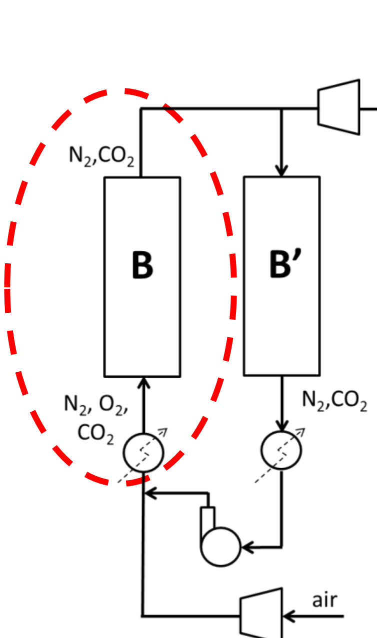


t = [illegible] s

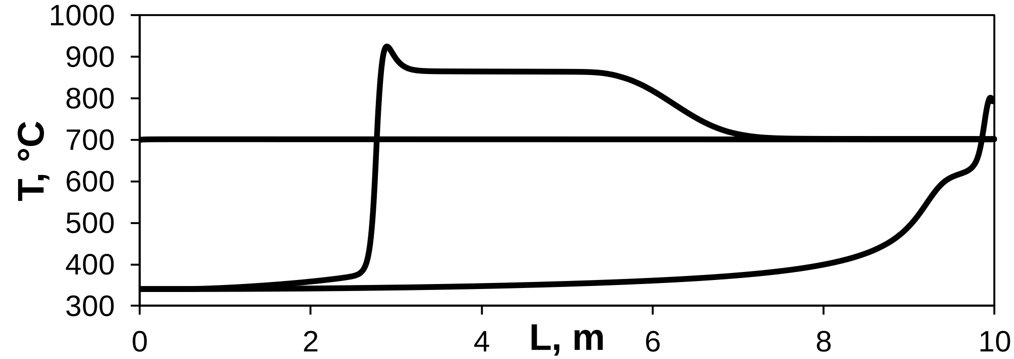
	inlet	outlet
T_{gas}, °C	700	845
y_{CH4}	0.0679	0.0153
y_{H2}	0.3334	0.5302
y_{CO}	0.0284	0.0333
y_{CO2}	0.0686	0.0224
y_{H2O}	0.5003	0.3955
y_{N2}	0.0014	0.0032

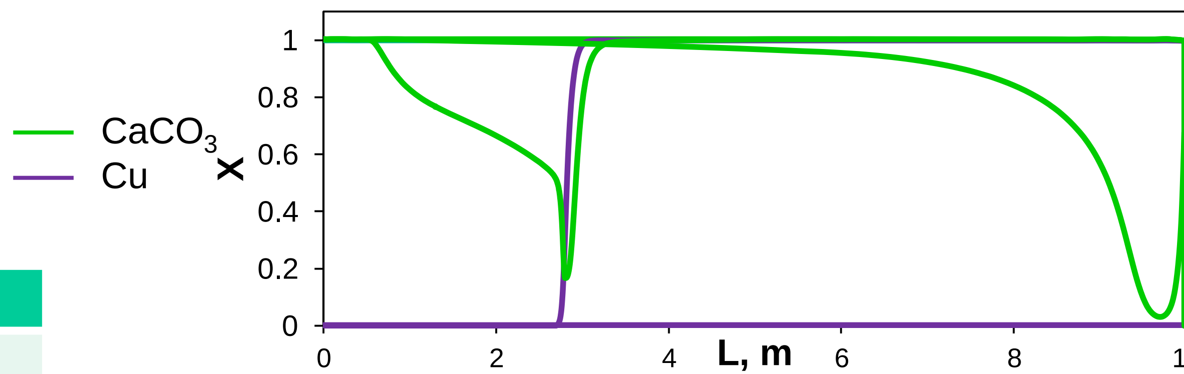


Pseudo-homogeneous model results
Step B

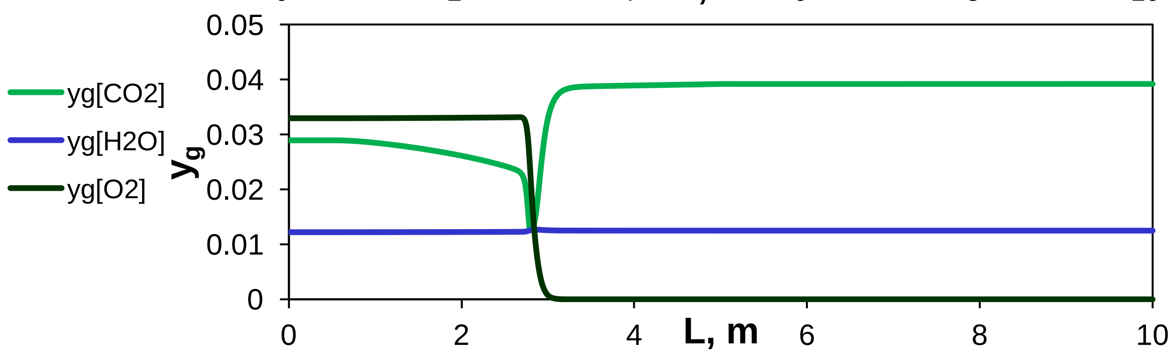


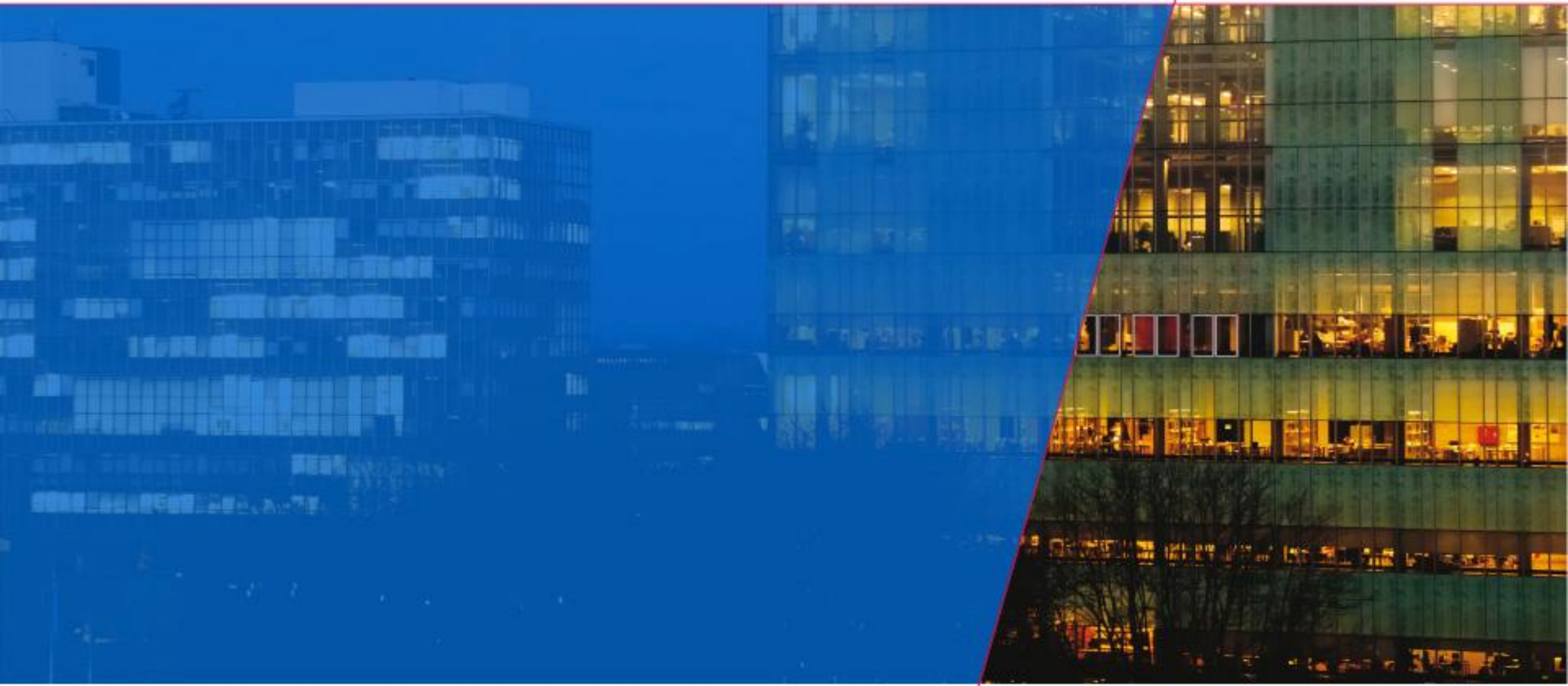
t = 2000 s





	inlet	outlet
T_{gas}, °C	340	790
y_{O2}	0.033	0.0
y_{CO2}	0.029	0.033
y_{H2O}	0.0123	0.0126
y_{N2}	0.9257	0.9544





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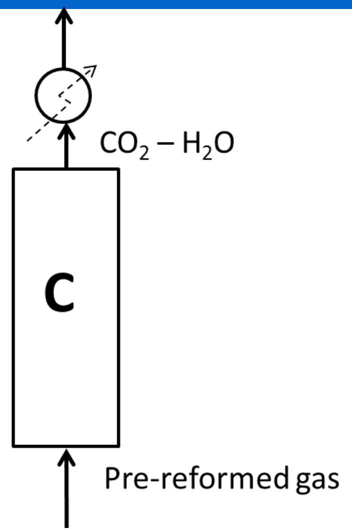
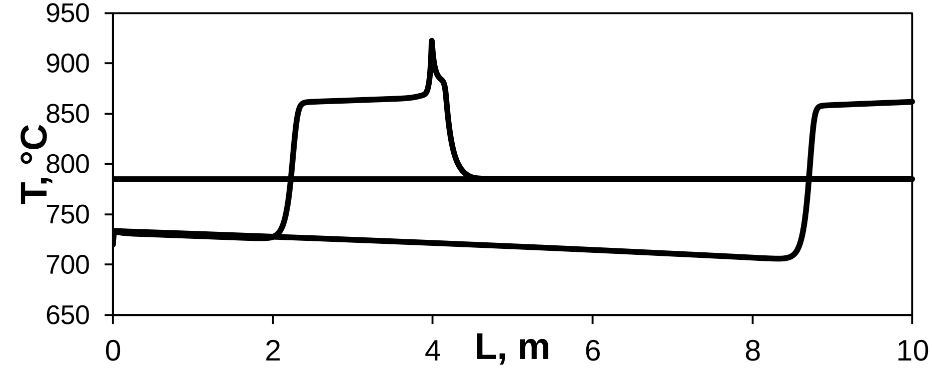
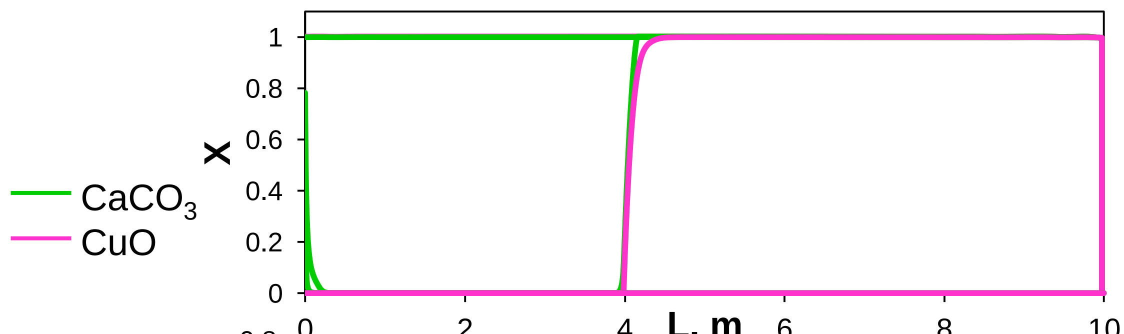
Pseudo-homogeneous model results
Step C

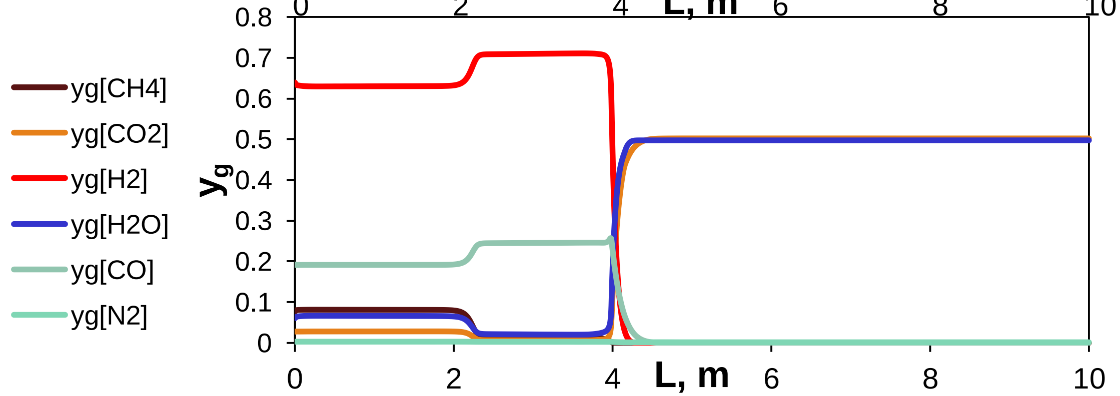


t = 2000 s

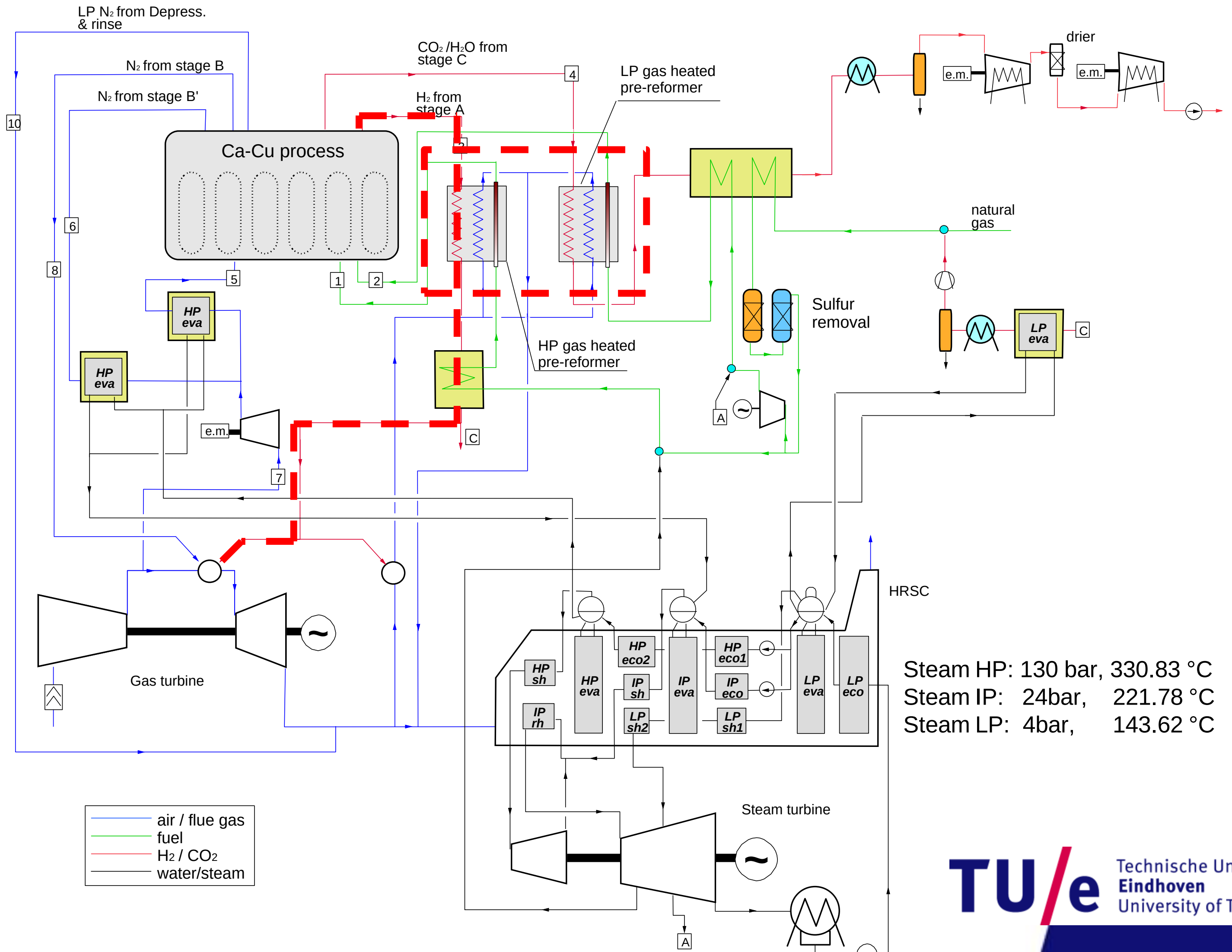
	inlet	outlet
T_{gas}, °C	700	790
y_{CH4}	0.0679	0.0
y_{H2}	0.6385	0.0
y_{CO}	0.1897	0.0
y_{CO2}	0.0292	0.500
y_{H2O}	0.0610	0.499
y_{N2}	0.0024	0.001







Power plant scheme



Steam HP: 130 bar, 330.83 °C
Steam IP: 24bar, 221.78 °C
Steam LP: 4bar, 143.62 °C

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Process performance results

	NGCC w/o CO2 capture	ATR+MDEA	Ca-Cu looping process
Gas turbine gross power (MW)	273.2	291.3	292.10
Gas turbine auxiliaries (MW)	-1.09	-1.17	-1.17
Steam turbine gross power (MW)	147.1	119.74	185.90
Steam cycle pumps power (MW)	-1.79	-3.41	-3.30
Auxiliaries for condenser heat rejection (MW)	-1.86	-1.09	-1.65
Rich N2 gas cycle fan consumption (MW)	-	-	-9.555
Air fan concumption (MW)	-	-	-0.929
Other auxiliaries (MW)	-	-1.25	-
CO_2 compressor power		-14.73	-11.086
Net power, MWe	415.6	373.3	450.54
Thermal imput, MW_{LHV}	711.3	792.2	899.57
Net electric efficiency, $\%_{LHV}$	58.42	47.12	50.08
Carbon Capture ratio, %	-	91.56	52.98
CO_2 Specific emission, kg_{CO2}/MWh	350.6	36.66	82.04
SPECCA, MJ_{LHV}/kg_{CO2}		4.71	3.82

Process performance results

- **Problem: Large plateau at high temperature in step A**

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2 strategies:

A) Decrease $T_{gas,in}$ of step A and C to 650°C

B) Increase the amount of inert in the bed

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Process performance results

	NGCC w/o CO2 capture	ATR+MDEA	Ca-Cu	Ca-Cu Case A	Ca-Cu Case B
Gas turbine gross power (MW)	273.2	291.3	292.10	299.88	292.12
Gas turbine auxiliaries (MW)	-1.09	-1.17	-1.17	-1.20	-1.17
Steam turbine gross power (MW)	147.1	119.74	185.90	179.64	185.81
Steam cycle pumps power (MW)	-1.79	-3.41	-3.30	-3.21	-3.29
Auxiliaries for condenser heat rejection (MW)	-1.86	-1.09	-1.65	-1.59	-1.64
Rich N2 gas cycle fan consumption (MW)	-	-	-9.555	-9.55	-9.56
Air fan consumption (MW)	-	-	-0.93	-0.93	-0.93
Other auxiliaries (MW)	-	-1.25	-	-	-
CO_2 compressor power		-14.73	-11.086	-12.14	-11.21
Net power, MWe	415.6	373.3	450.54	451.18	450.35
Thermal imput, MW_{LHV}	711.3	792.2	899.57	899.57	899.57
Net electric efficiency, $\%_{LHV}$	58.42	47.12	50.08	50.16	50.06
Carbon Capture ratio, %	-	91.56	52.98	62.9	57.35
CO_2 Specific emission, kg_{CO2}/MWh	350.6	36.66	82.04	70.08	79.24
SPECCA, MJ_{LHV}/kg_{CO2}		4.71	3.82	3.62	3.79

Conclusions

- **Ca-Cu process has been simulated with a pseudo-homogeneous reactor model**
  - **The operative conditions have been chosen in order to have uniform temperature and composition profiles and to avoid the hydration of CaO**
  - **A stable operation of the Ca-Cu reactors has been achieved**

- **A detailed integration of this H_2 production process into a combined cycle for power production has been carried out**
  - **Net electric efficiencies achieved are at around 50 % (higher than other pre-combustion schemes)**
  - **Medium CO_2 capture performance is achieved due to the large CO_2 emissions associated to stage A in the Ca-Cu process**

- **Future work**
  - **The rather low CCR achieved should be optimized by carrying out changes in the layout or modifying some of the operating conditions**
  - **Design the scheduling of the whole process**

Thank you for your attention

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