Demonstration of cost-effective medium-size Chemical Looping Combustion through packed beds using solid hydrocarbons as fuel for power production with CO_2 capture

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Reactor design and optimization

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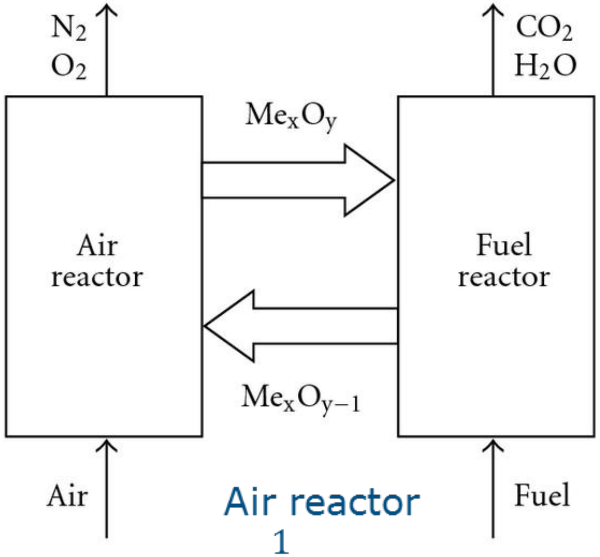
Where innovation starts

Outline

- Packed Bed Reactors (PBRs) for CLC
- Heat Management in IG-CLC
- Heat Management Strategies
- Analysis of Results
- Conclusions

PBR vs FBR



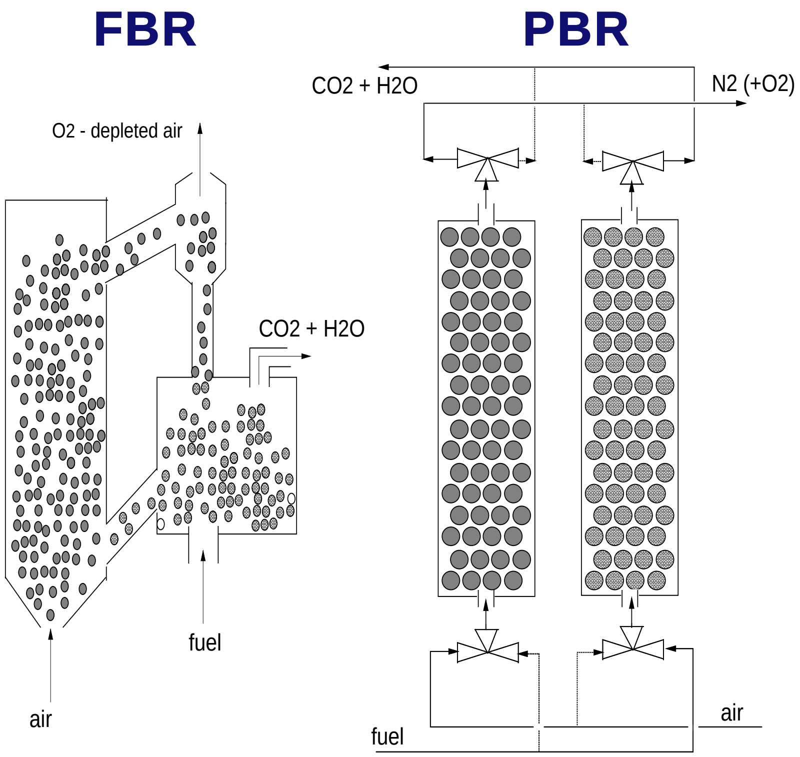
Air reactor

$$Me + \frac{1}{2}O_2 \rightarrow MeO$$

Fuel Reactor

$$MeO + H_2 \rightarrow Me + H_2O$$

$$MeO + CO \rightarrow Me + CO_2$$

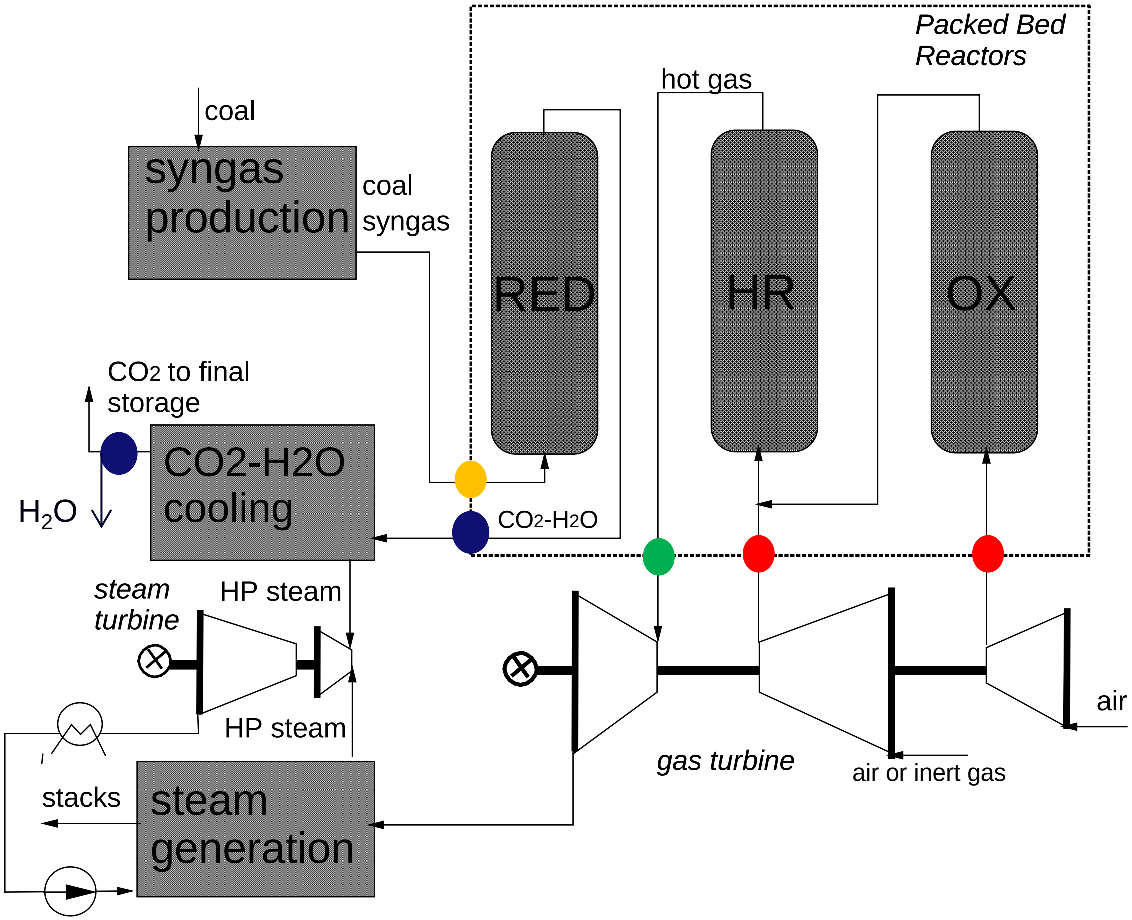


With **Ilmenite as OC ($FeTiO_3$)**
Oxidation reaction is strongly exothermic
Reduction reaction with coal syngas slightly endothermic – Low CO reaction rate

With **PBRs:**
Three main phases must be considered:

- **Solid Reduction**
- **Solid Oxidation**
- **Heat Removal**

PBR for IG – CLC: design parameters and boundary conditions



Pressurized Air/Inert gas conditions (p 20 bar and T ≈ 450°C)

HT/HP hot gas at 1200°C

CO/H_2-rich syngas at HP pressure (up to 35 bar)

Pressurized CO_2 – rich stream is cooled to ambient temperature in HEs generating HP steam

Optimization of PBR operations is connected to overall power plant performance

Input parameters

- Dry syngas composition from IGCC Puertollano

  H_2 22%, CO 60.5%, H_2O 0.3%, CO_2 2.1%, N_2 14.7%

- Steam to syngas dilution

  H_2O to dry syngas ratio (wt.) = 0.53

- Phase times are chosen to obtain 95% of solid conversion (according to the gas streams)

- Solid composition is chosen to have solid T equal to 1200°C during oxidation

- Reactor geometry: L = 2.5 m and d = 0.3 m

- Model is based on difference technique with dynamic temporal and spatial discretizetion based on T and concentrations (solid/gas) gradients

Kinetics model

- Kinetics data for the ilmenite Reduction/Oxidation are taken from Literature (*Abad et al. 2011*)

- Carbon deposition is not included

- Fe formation is not included

- Pseudo-homogeneous model

- No heat losses

Heat Management strategies

Strategy A

Reduction/Oxidation/Heat Removal

- Heat Removal phase occurs in a bed with solid at oxidized conditions
- Reduction phase occurs when the bed is at the lowest temperature (after HR phase)
- Oxidation and HR phases can be carried out in sequence (in the same reactor)
- Purge phases are needed after Reduction and Ox+HR phases

Heat Management strategies

Strategy B

Oxidation/Reduction/Heat Removal

- The solid Reduction of ilmenite is almost iso-thermal using coal syngas

- The reduction reaction occurs when the bed is at the maximum temperature (at 1200°C H_2-CO oxidation with ilmenite is very fast and solid conversion is properly accomplished)

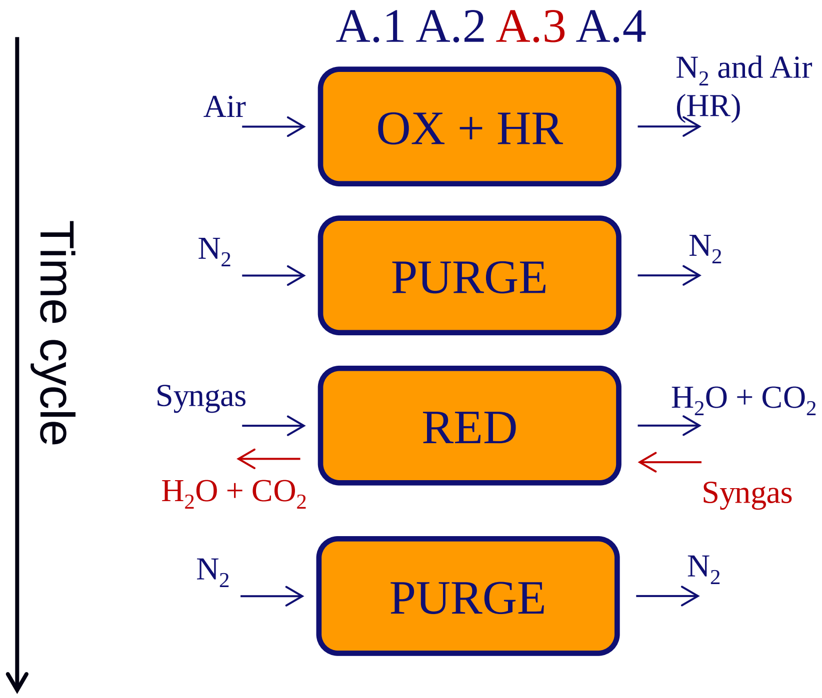
- The heat stored in the bed can be removed after the Reduction phase with constant high temperature and mass flow rate gas production (air can NOT be used)

- The N_2 mass flow rate is higher than air and syngas (a future plant must be consider this different layout in terms of turbomachines design and gas management)

- HR phase acts also as purge phase (only 1 purge phase is required)

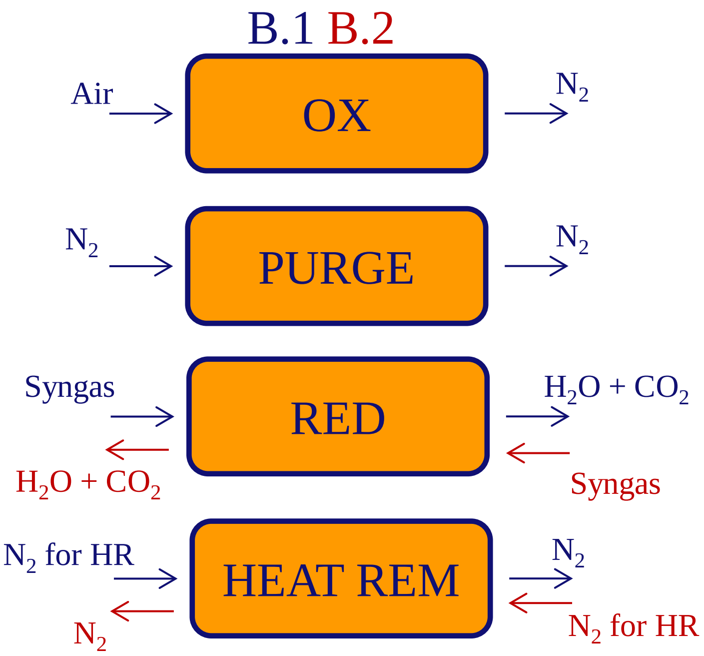
Heat Management strategies

Strategy A
Reduction/Oxidation/Heat Removal



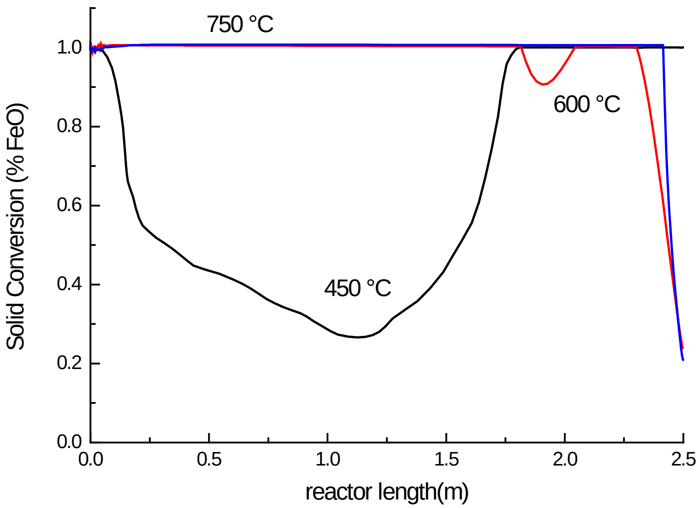
- Effect of T_air (Heat removal cycle) – A1
- Effect of solid active weight – A2
- Effect of WGS (equilibrium approach) A4

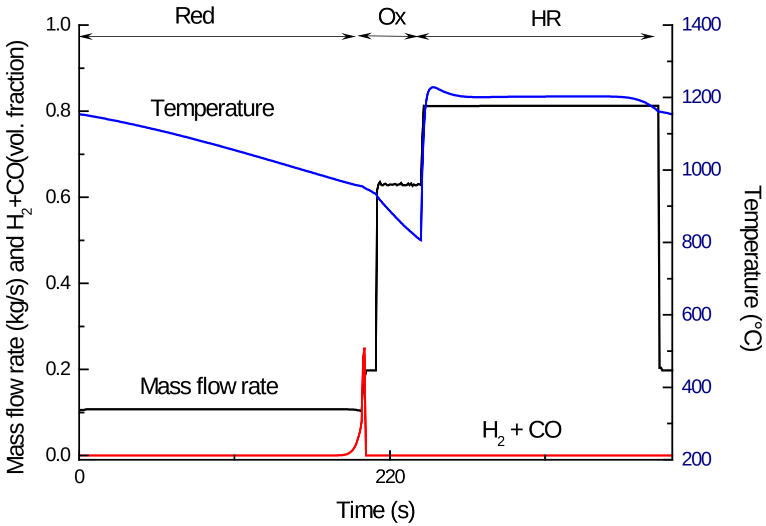
Strategy B
Reduction/Heat Removal/Oxidation



- Effect gas feeding B1 vs B2
- Effect of CO reaction rate (rr B2)

Solid conversion with different inlet air temperature: 750/600/450 °C – A1



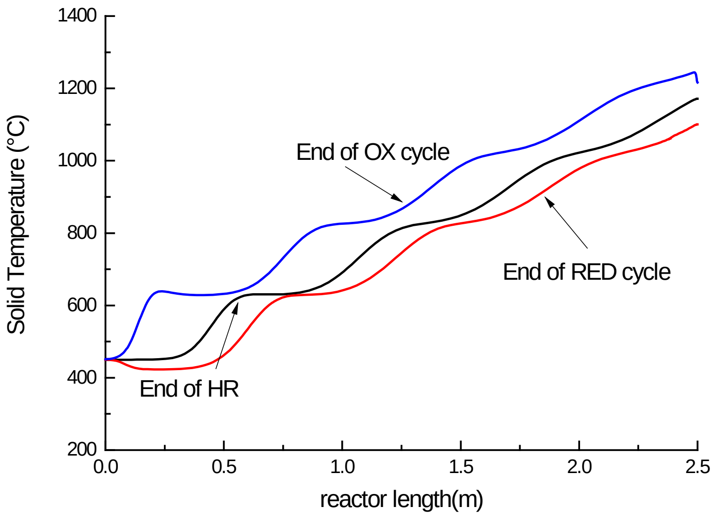


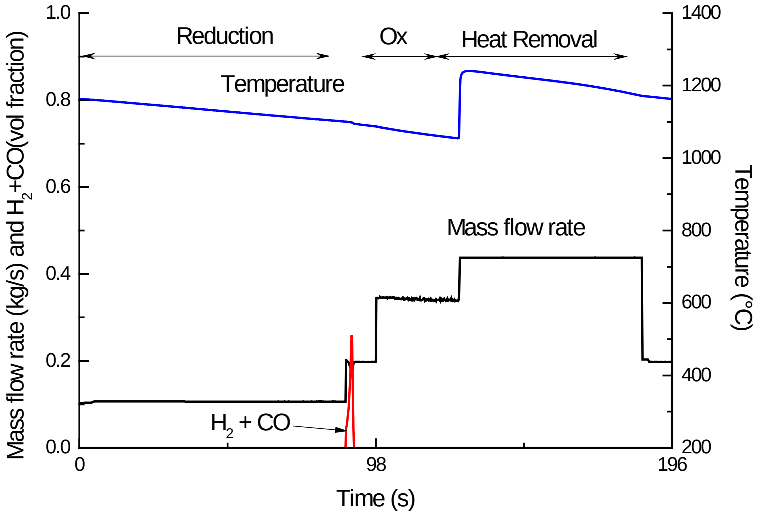
Strategy A1 is useful for the PBR heat management if air is heated up to HT (otherwise CO kinetic is not fast enough)

Air pre-heating leads to some very high penalty efficiencies if it is not carried out properly and reduces the positive effect of ΔT through the exothermic reaction of solid oxidation

If air temperature is 750°C solid conversion is almost complete and the HR phase provides a constant air mass flow rate at constant temperature.

Solid conversion with low active weight content: inlet air T 450 °C – A2



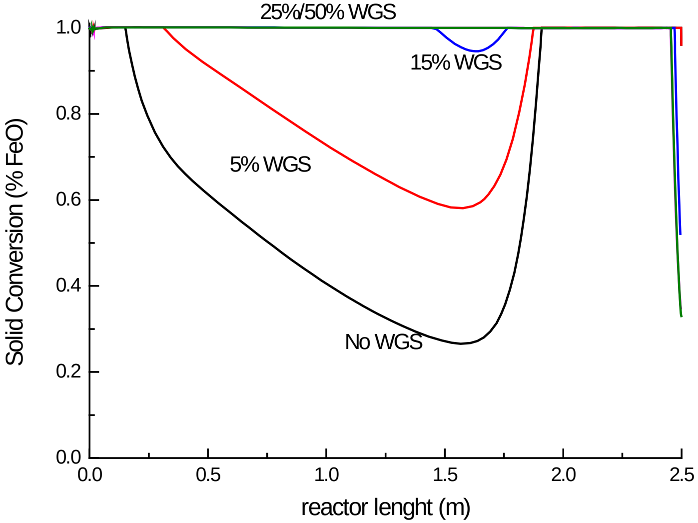


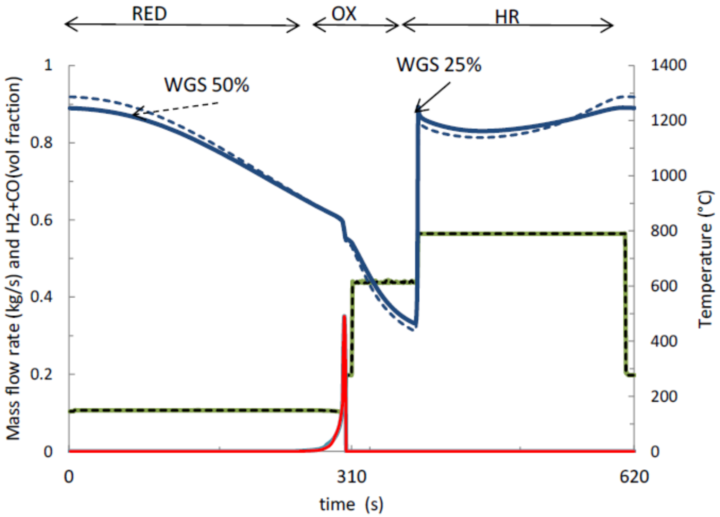
time cycle are shorter than strategy A1 (low solid material to be converted)

If air temperature is 450°C solid conversion is almost complete and the HR phase provides a constant air mass flow rate at almost constant temperature. The same effect occurs in case of exhaust gases from reduction reactor with positive effect in the steam cycle behavior

Solid temperature is not under strong transient conditions (maximum ΔT equal to 150°C)

Effect of WGS with inlet air T 450°C – strategy A4





According to Schwebel et al.(2011) WGS can occurs during the Reduction phase (better if catalyzed with CaO)

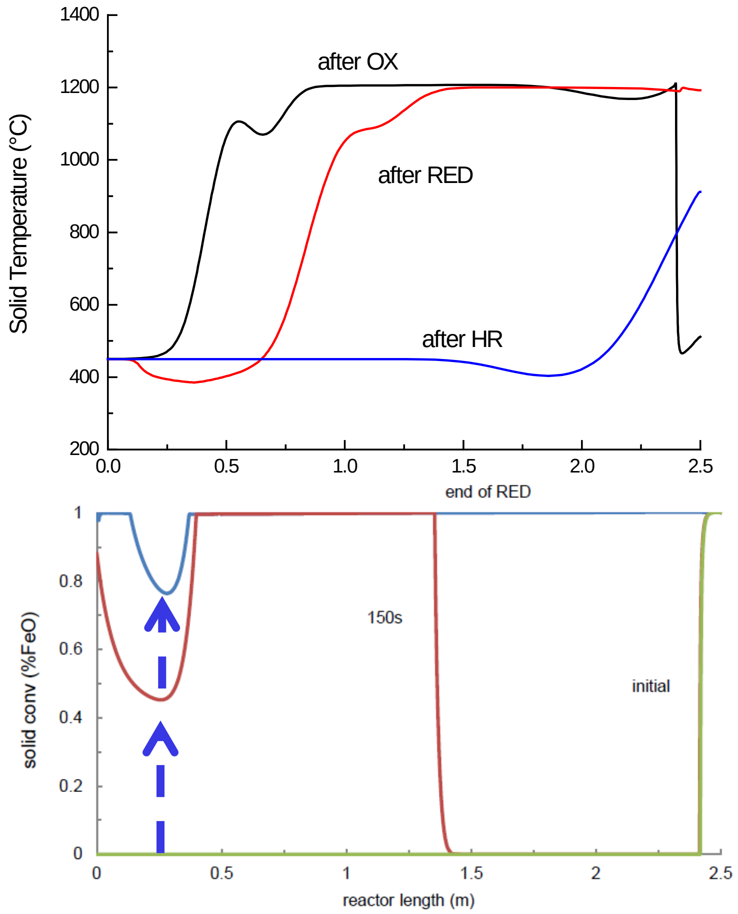
The analysis is carried out assuming a WGS reaction rate as a fraction of the conversion at chemical equilibrium. WGS kinetics is required

It is possible to reach a complete solid conversion

The results change if a CO_2-rich syngas is used (less H_2O and N_2) as expected in IG-CLC plant

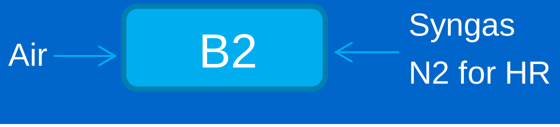
Gas streams are fed from the same side – strategy B1

Air
Syngas → B1
N2 for HR



- After Pure Oxidation phase the heat front is in the first 10% of the reactor length
- At the end of Reduction phase the heat front is almost at first 60% of the reactor length (enough heat is still stored in the bed)
- During the Reduction phase (from initial to 150s to 300s) the solid conversion occurs sequentially (except for the first part which is the coldest)
- Solid conversion is almost completed at the end of the Reduction phase

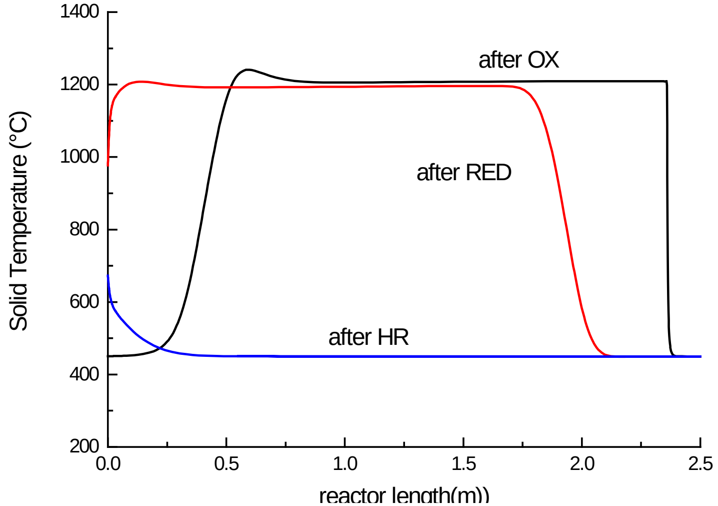
N_2 and syngas are fed in the opposite side – strategy B2

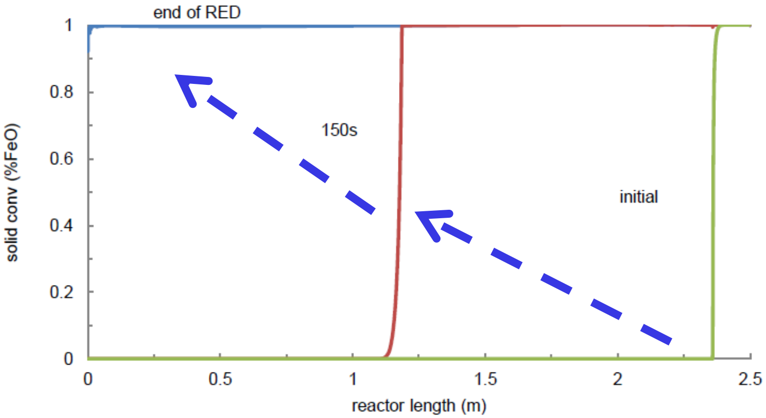

Air

B2

Syngas

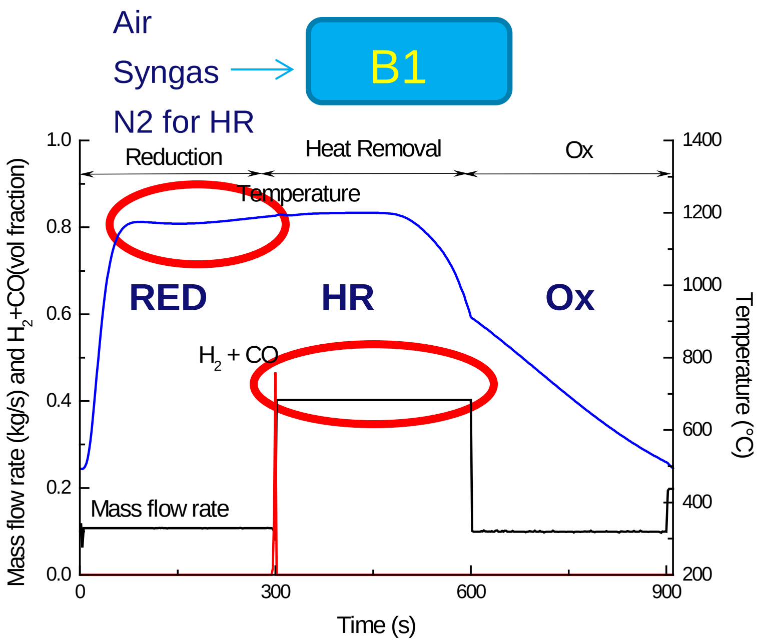
N2 for HR

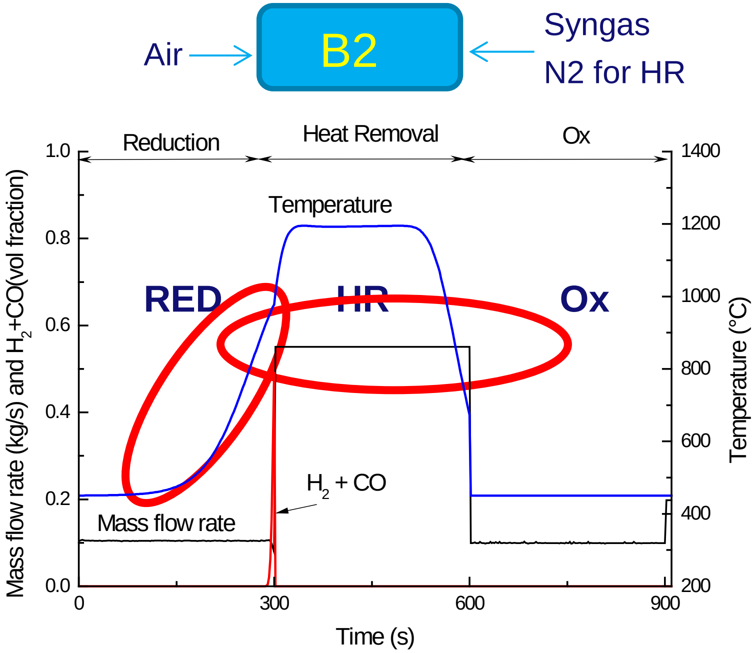




- After Pure Oxidation phase (reaction front at the end of reactor) the heat front is in the first 10% of the reactor length (same than case B1)
- At the end of Reduction phase more than 65-70% of bed is at high temperature(enough heat is still stored in the bed)
- During the reduction phase (from initial to 130s to 260s) the solid conversion occurs sequentially from the end of reactor to the initial part
- Solid conversion is complete

Outlet flows conditions: comparison between strategies B1 & B2





In B1 CO_2/H_2O are produced at the maximum temperature while in the in B2 the temperature is variable (from 450 to 1100°C) with a different effects for the stream management (in case B1 more heat is available for the steam cycle)

In case B2, the amount of N_2 for the heat removal is 27% higher than in case B1: more gas is used in the GT and the power electricity is switched from the steam cycle (CO_2-H_2O & N_2 from pure oxidation cooling) to GT (N_2 from HR)

Performance

Energy loss because of fuel slip

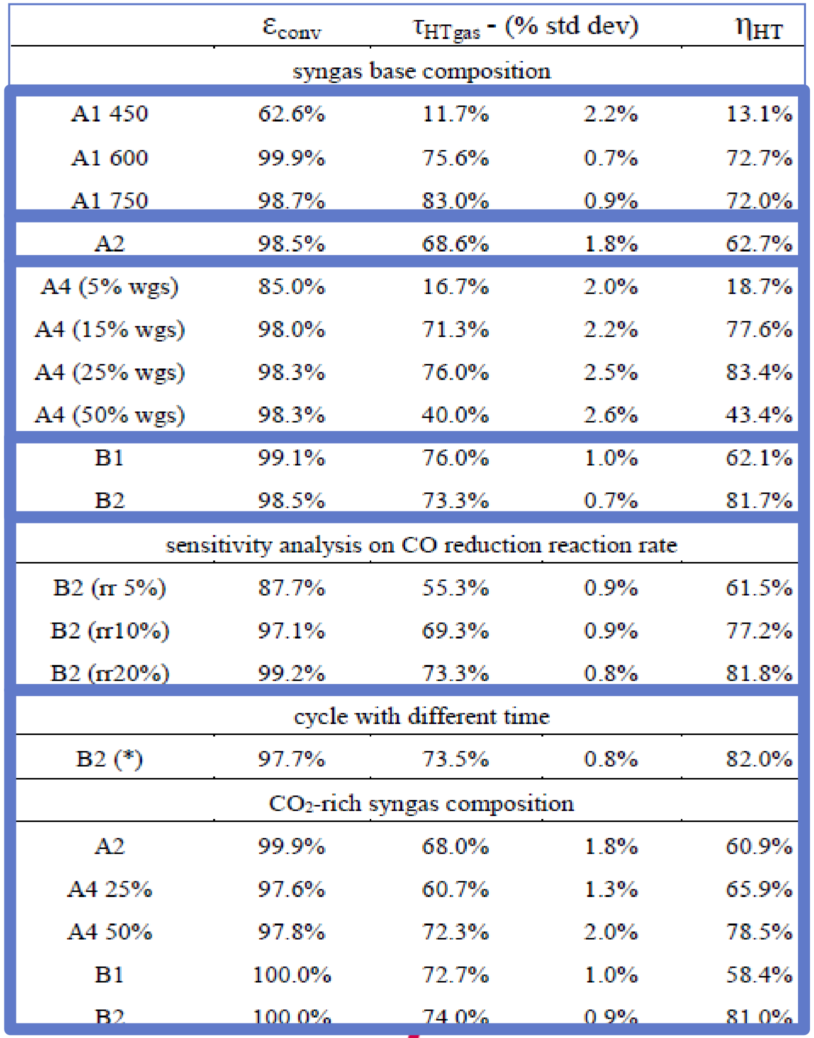
$$\varepsilon_{conv} = 1 - \frac{\int_{t\,red=0s}^{t\,red=end} (\dot{m}_{H2}^{out} \cdot LHV_{H2} + \dot{m}_{CO}^{out} \cdot LHV_{CO})dt}{\dot{m}_{syngas}^{in} \cdot LHV_{syngas}^{in} \Delta t_{red\ cycle}}$$

Capacity to have gas (air or N_2) at temperature in the range 1150°C - 1250°C respect to the complete time cycle

$$\tau_{HT_{gas}} = \frac{t_{HT_{gas}}}{t_{cycle}}$$

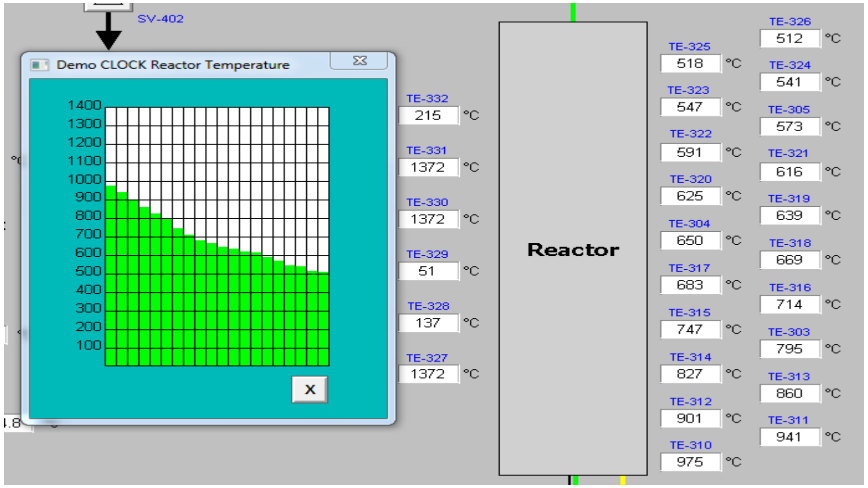
Capacity to convert the syngas LHV in heat useful for a gas turbine (quality of energy conversion)

$$\eta_{HT} = \frac{\dot{m}_{HT\ gas\ stream}\left(h_{i,T\_out} - h_{i,T\_in}\right)}{\dot{m}_{syngas} LHV_{fuel}} \tau_{HT_{gas}}$$

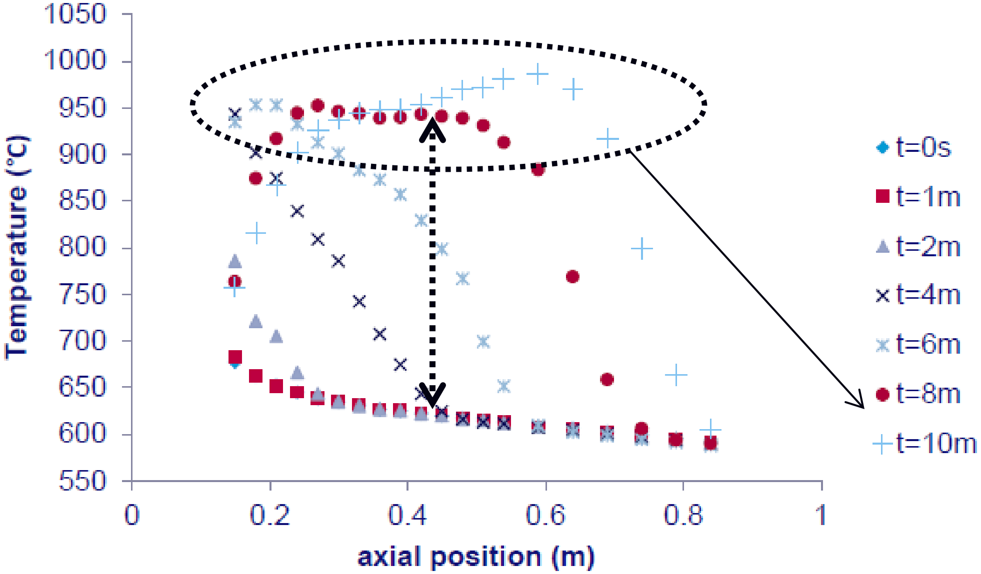


	ε_{conv}	$\tau_{HT\,gas}$ -	(% std dev)	η_{HT}
syngas base composition				
A1 450	62.6%	11.7%	2.2%	13.1%
A1 600	99.9%	75.6%	0.7%	72.7%
A1 750	98.7%	83.0%	0.9%	72.0%
A2	98.5%	68.6%	1.8%	62.7%
A4 (5% wgs)	85.0%	16.7%	2.0%	18.7%
A4 (15% wgs)	98.0%	71.3%	2.2%	77.6%
A4 (25% wgs)	98.3%	76.0%	2.5%	83.4%
A4 (50% wgs)	98.3%	40.0%	2.6%	43.4%
B1	99.1%	76.0%	1.0%	62.1%
B2	98.5%	73.3%	0.7%	81.7%
sensitivity analysis on CO reduction reaction rate				
B2 (rr 5%)	87.7%	55.3%	0.9%	61.5%
B2 (rr10%)	97.1%	69.3%	0.9%	77.2%
B2 (rr20%)	99.2%	73.3%	0.8%	81.8%
cycle with different time				
B2 (*)	97.7%	73.5%	0.8%	82.0%
CO_2-rich syngas composition				
A2	99.9%	68.0%	1.8%	60.9%
A4 25%	97.6%	60.7%	1.3%	65.9%
A4 50%	97.8%	72.3%	2.0%	78.5%
B1	100.0%	72.7%	1.0%	58.4%
B2	100.0%	74.0%	0.9%	81.0%

Pressurized packed bed Reactor model (lab scale)



TE-332 215 °C
TE-331 1372 °C
TE-330 1372 °C
TE-329 51 °C
TE-328 137 °C
TE-327 1372 °C
TE-325 518 °C
TE-323 547 °C
TE-322 591 °C
TE-320 625 °C
TE-304 650 °C
TE-317 683 °C
TE-315 747 °C
TE-314 827 °C
TE-312 901 °C
TE-310 975 °C
TE-326 512 °C
TE-324 541 °C
TE-305 573 °C
TE-321 616 °C
TE-319 639 °C
TE-318 669 °C
TE-316 714 °C
TE-303 795 °C
TE-313 860 °C
TE-311 941 °C



Design conditions

- Pressure: 10 bar
- T max: 1150°C
- D_{int} = 6.3 cm
- Vol flow: 200 l/min (≈20-30 kW_{TH})

Conclusions

- Strategy A operated with air at 450°C is feasible if low active weight content (A2) is present in the solid material:
    - good temperature stability (MAX ΔT equal to 150°C)
    - short time phases (95 sec. vs 300 sec.)
- If WGS occurs (A4):
    - CO oxidation through H_2 conversion
    - investigation on kinetics with ilmenite (or other catalysts)
- The other configurations (strategy A1 & A3) need air temperature higher than 600°C which can strongly affects the plant efficiency
- Strategies B appears very interesting for CLC application in PBR using ilmenite as OC (or other OC which are not extremely reactive with CO).
    - solid conversion is almost complete if working with gas at 450°C
    - high N_2 mass flow rate must be used for heat removal in the reduced bed

Future improvements

- Analysis of the HM strategies with a different kinetics:
  - a new set of kinetic equations have been developed for the ilmenite with TGA analysis
  - WGS reaction rate has been provided
- Experimental activity at Lab-scale (20-30 kW_{th}) and Demo-scale (500 kW_{th}):
  - Lab reactor operating at 10 bar and 1150°C is now working @TUe
  - Demo reactor will start operation in Puertollano in the next months
- Tests will be carried out with different OCs
- Design and reactors behavior analysis for PBR used in large scale power plant (hundreds MW)

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 268112 (Project acronym DEMOCLOCK).

Thank you!

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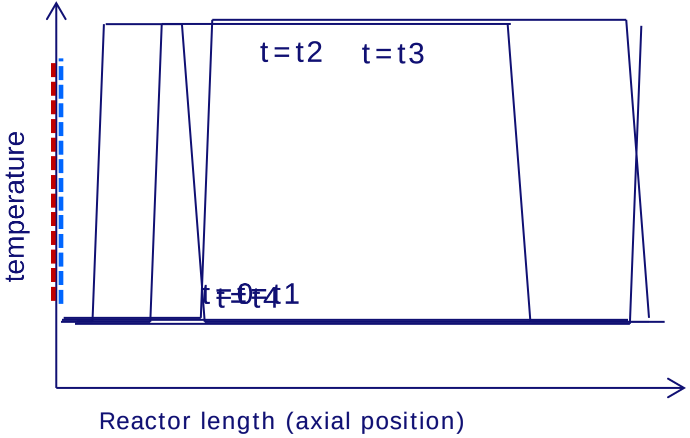
Ref. paper:
Spallina et al. ”Investigation of Heat Management for CLC of syngas in Packed Bed Reactors”, Chemical Engineering Journal 225 (2013) 174 - 191

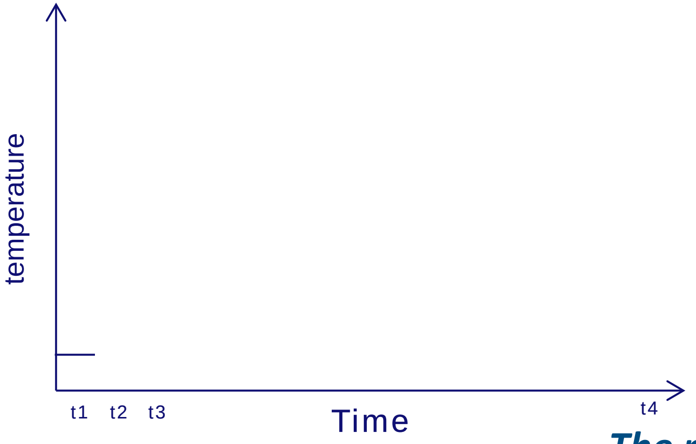
Backup slides

PBR for CLC

Temperature profile along the reactor



Gas T at the reactor outlet

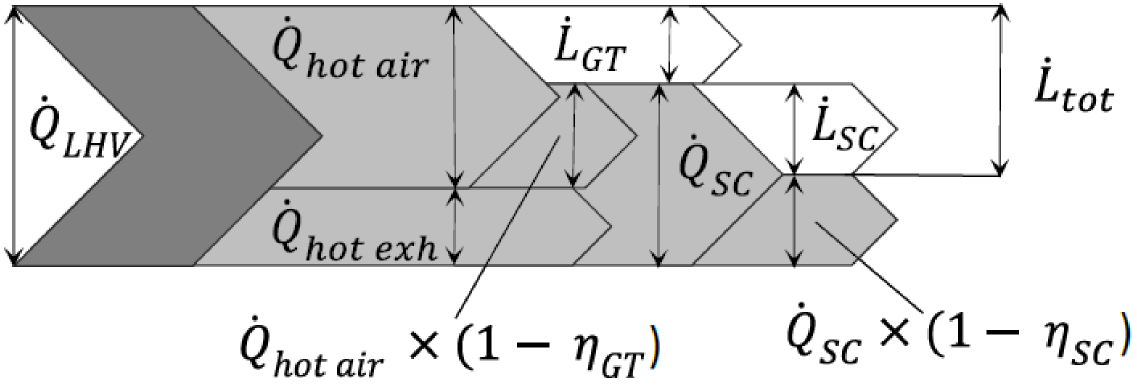


- Oxidation / Reduction phases stop when the reaction front reaches the end of reactor
- Heat removal phase stops when the heat front reaches the end of the reactor and the temperature of the reactor is at the minimum value.

The model description is reported in:

Noorman et al., Chem. Eng. J., 167 (1) (2011) 369-376
Noorman et al., Ind. Eng. Chem. Res. 49 (20) (2010) 9720-9728
Noorman et al., Ind. Eng. Chem. Res. 50 (4) (2011) 1968-1980

IG-CLC simplified energy balance



$$\dot{Q}_{LHV} = \dot{Q}_{hot\ air} + \dot{Q}_{hot\ exh}$$

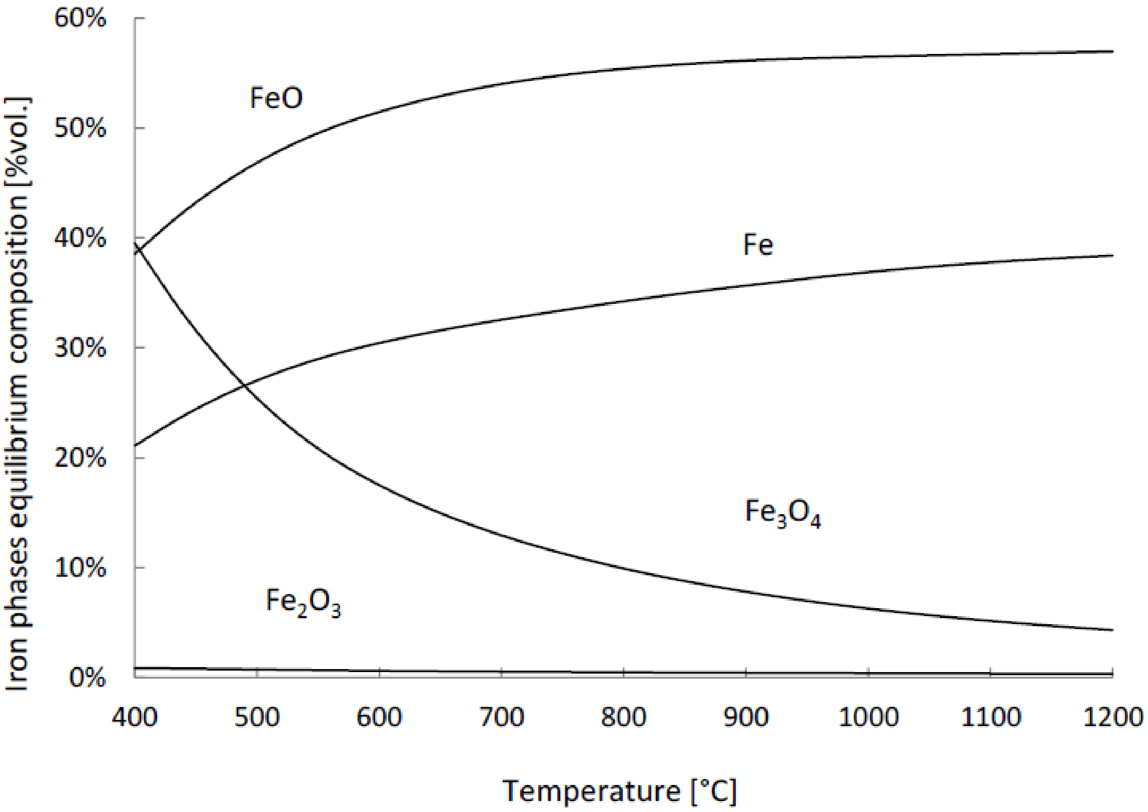
$$\dot{L}_{GT} = \dot{Q}_{hot\ air} \times \eta_{GT}$$

$$\dot{L}_{SC} = \underbrace{(\dot{Q}_{hot\ air} \times (1 - \eta_{GT}) + \dot{Q}_{hot\ exh})}_{\dot{Q}_{SC}} \times \eta_{SC}$$

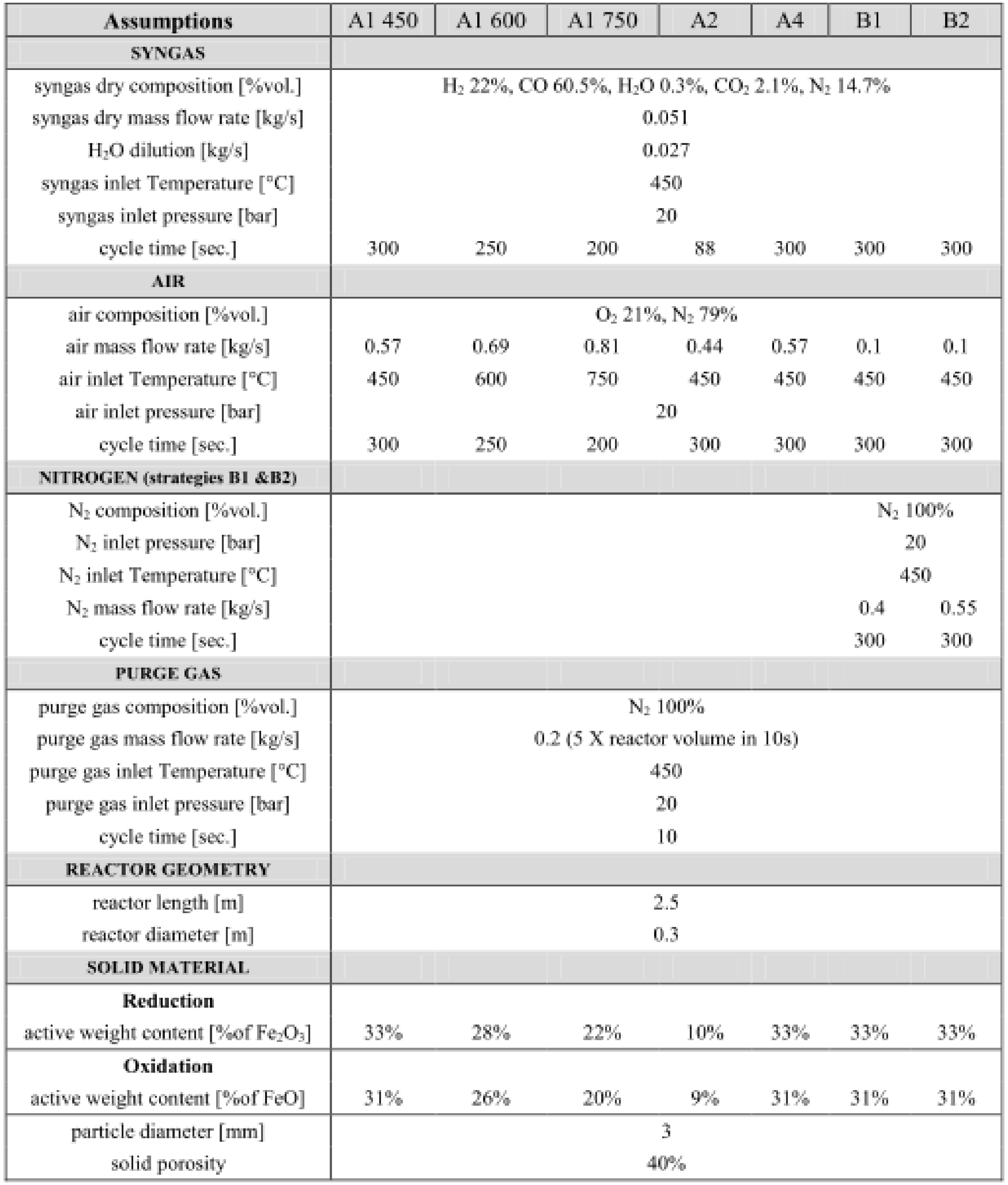
$$\dot{L}_{tot} = \dot{L}_{GT} + \dot{L}_{SC} = \dot{Q}_{hot\ air} \times \overbrace{(\eta_{GT} + (1 - \eta_{GT}) \times \eta_{SC})}^{\eta_{CC}} + \dot{Q}_{hot\ exh} \times \eta_{SC}$$

$$\eta_{CC} > \eta_{SC}$$

Iron phases equilibrium during reduction with the syngas considered

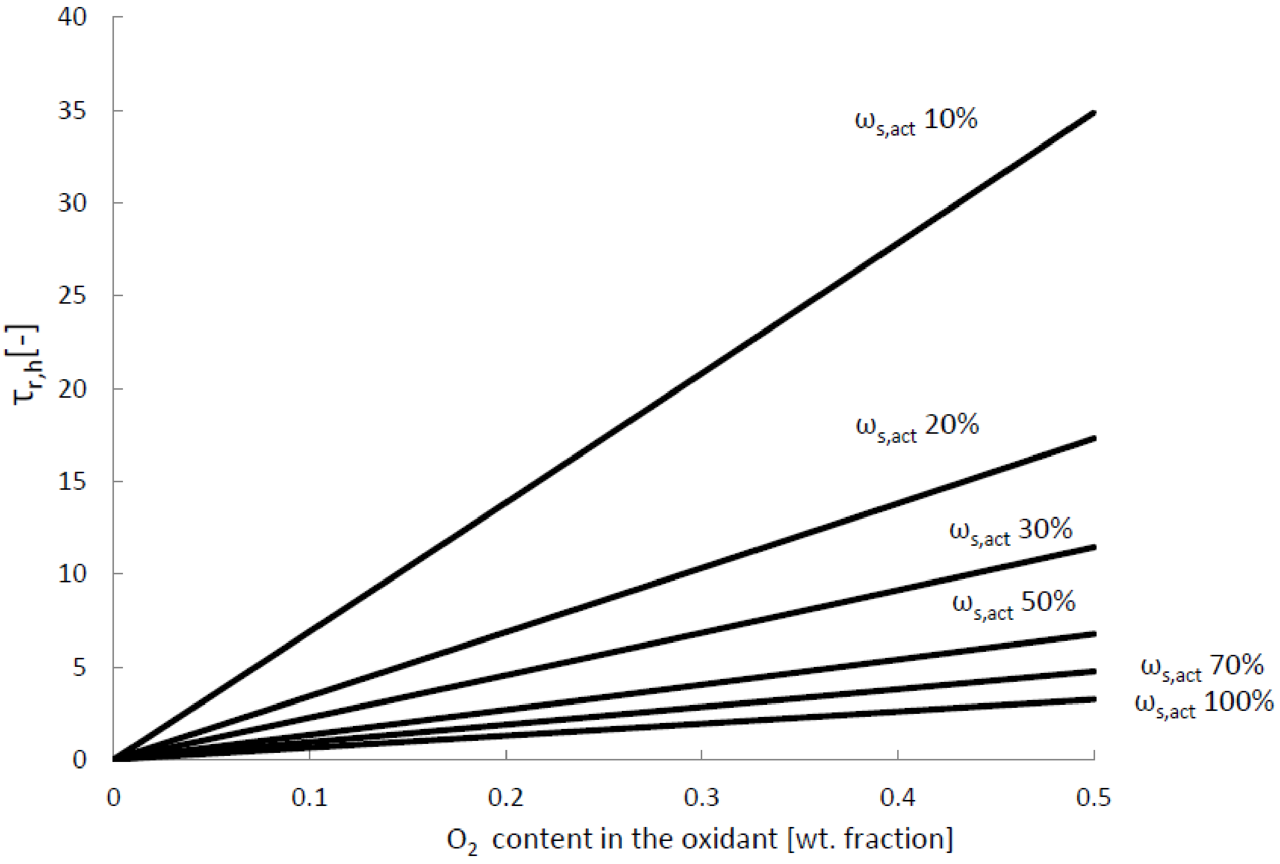


Assumptions

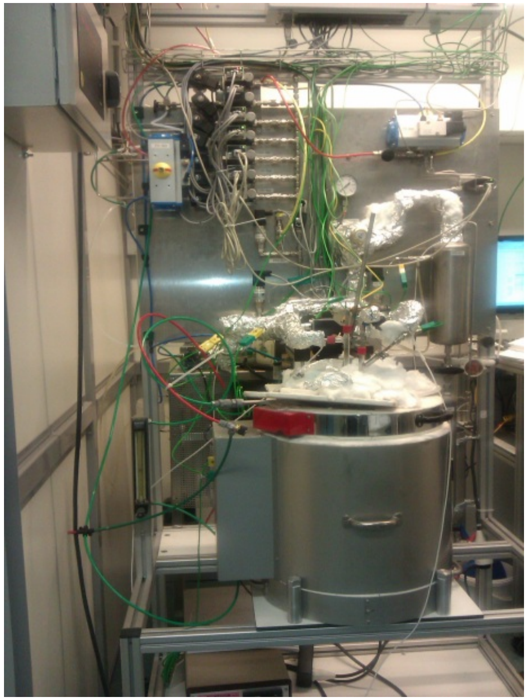


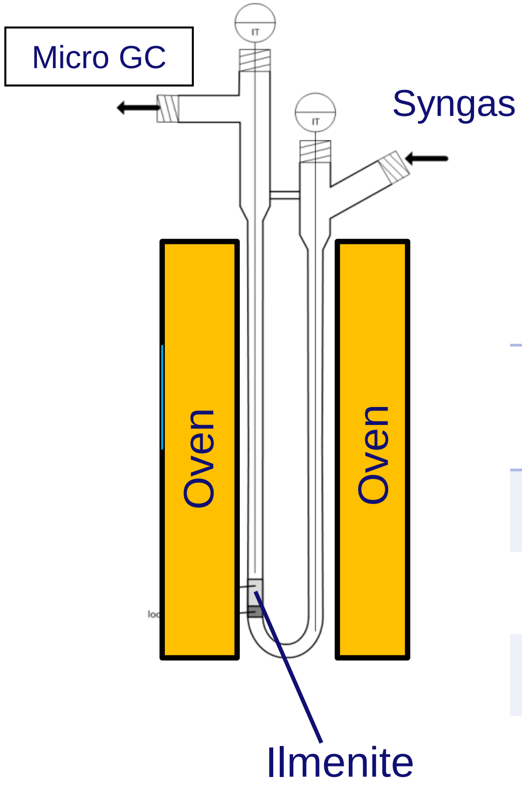
Assumptions	A1 450	A1 600	A1 750	A2	A4	B1	B2
SYNGAS							
syngas dry composition [%vol.]	H_2 22%, CO 60.5%, H_2O 0.3%, CO_2 2.1%, N_2 14.7%						
syngas dry mass flow rate [kg/s]	0.051						
H_2O dilution [kg/s]	0.027						
syngas inlet Temperature [°C]	450						
syngas inlet pressure [bar]	20						
cycle time [sec.]	300	250	200	88	300	300	300
AIR							
air composition [%vol.]	O_2 21%, N_2 79%						
air mass flow rate [kg/s]	0.57	0.69	0.81	0.44	0.57	0.1	0.1
air inlet Temperature [°C]	450	600	750	450	450	450	450
air inlet pressure [bar]	20						
cycle time [sec.]	300	250	200	300	300	300	300
NITROGEN (strategies B1 &B2)							
N_2 composition [%vol.]						N_2 100%	
N_2 inlet pressure [bar]						20	
N_2 inlet Temperature [°C]						450	
N_2 mass flow rate [kg/s]						0.4	0.55
cycle time [sec.]						300	300
PURGE GAS							
purge gas composition [%vol.]	N_2 100%						
purge gas mass flow rate [kg/s]	0.2 (5 X reactor volume in 10s)						
purge gas inlet Temperature [°C]	450						
purge gas inlet pressure [bar]	20						
cycle time [sec.]	10						
REACTOR GEOMETRY							
reactor length [m]	2.5						
reactor diameter [m]	0.3						
SOLID MATERIAL							
Reduction							
active weight content [%of Fe_2O_3]	33%	28%	22%	10%	33%	33%	33%
Oxidation							
active weight content [%of FeO]	31%	26%	20%	9%	31%	31%	31%
particle diameter [mm]	3						
solid porosity	40%						

reaction/heat front velocity ratio



Micro – reactor for WGS kinetics





Vol flow: 500 ml/min

Diameter = 1 mm

T = 600 - 800 C

300 mg ilmenite

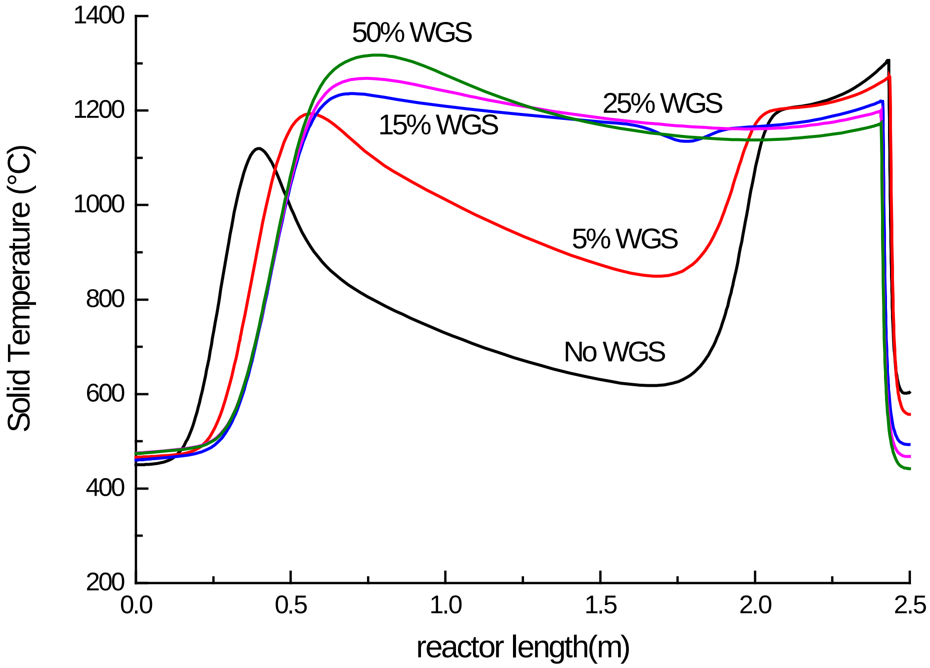
Gas	Inlet (%vol.)	Outlet (%vol.) 800	Outlet (%vol.) 700	Outlet (%vol.) 600
CO	30.1	26.7	29.2	29.9
CO_2	1.3	4.7	2.3	1.6
H_2O	50.4	46.9	49.4	50.1
H_2	10.9	14.3	11.8	11.2
N_2	7.3	7.3	7.3	7.3

Some WGS occurs!!!

WGS kinetics with ilmenite

- HT WGS with $FeTiO_3$
- Effect of T
- Effect of exhaust dilution (H_2O/CO_2)

Strategy A4: Solid temperature at different WGS conversion



Strategy A1: Solid temperature at different inlet air temperature