Demonstration of packed bed CLC of syngas using ilmenite as oxygen carrier

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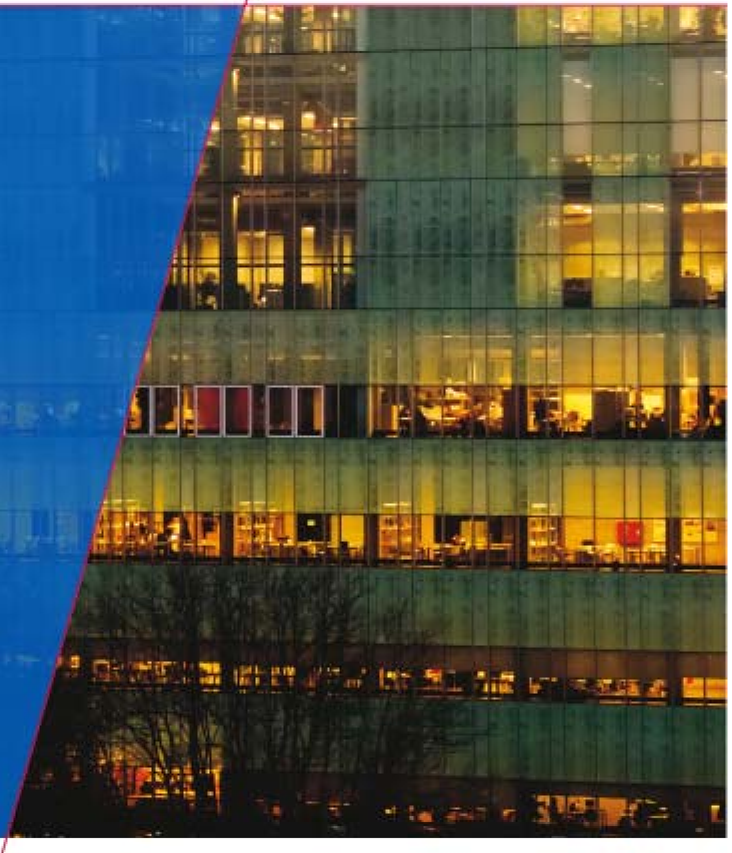

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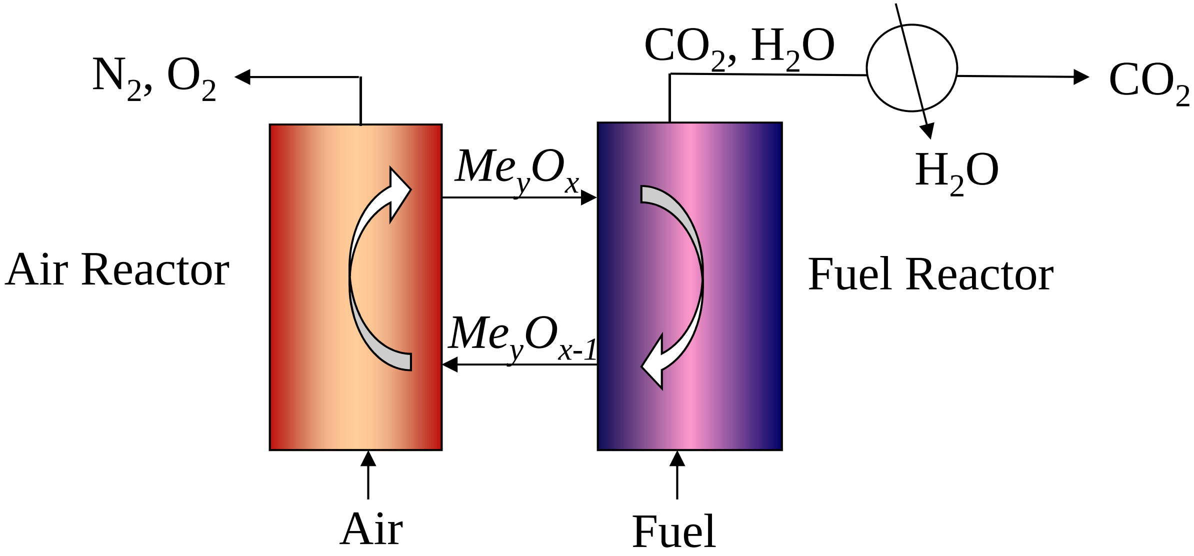
Introduction

CHEMICAL-LOOPING COMBUSTION



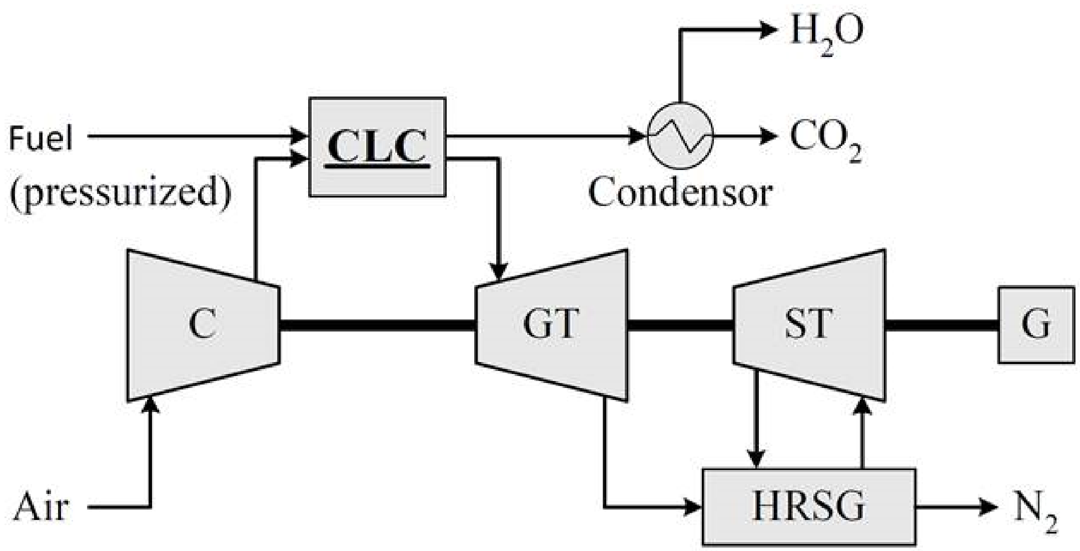
Reduction	$(CO, H_2) + 2\ MeO$	$\longrightarrow$	$2\ Me + CO_2 + H_2O$	ΔH_r
Oxidation	$O_2 + 2\ Me$	$\longrightarrow$	$2\ MeO$	ΔH_o
Total	$(CO, H_2) + O_2$	$\longrightarrow$	$CO_2 + H_2O$	$\Delta H_c = \Delta H_r + \Delta H_o$

Introduction

CLC in power cycles

To achieve competitive energy efficiencies :

- Operating conditions of gas turbines: T=1200 °C and P=20 bar



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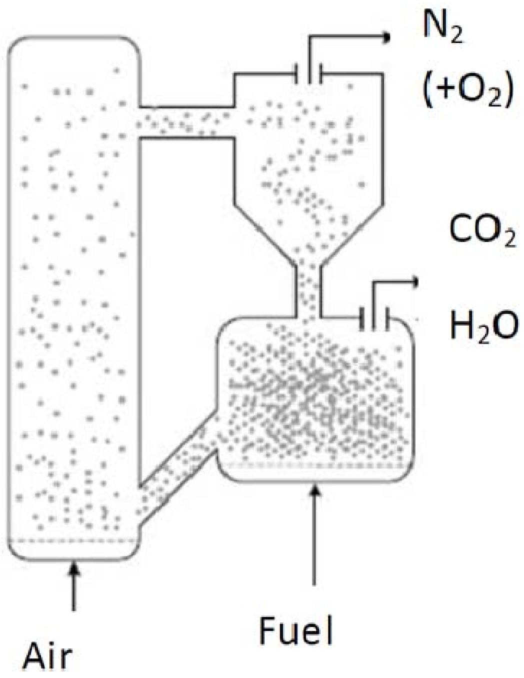
Introduction

Interconnected fluidized bed reactors

- ✓ Continues hot air production
- ✓ Proven technology
- ✘ Technological **challenging gas/particle separation and loop sealing** at high pressures
- ✘ Transport of the solid

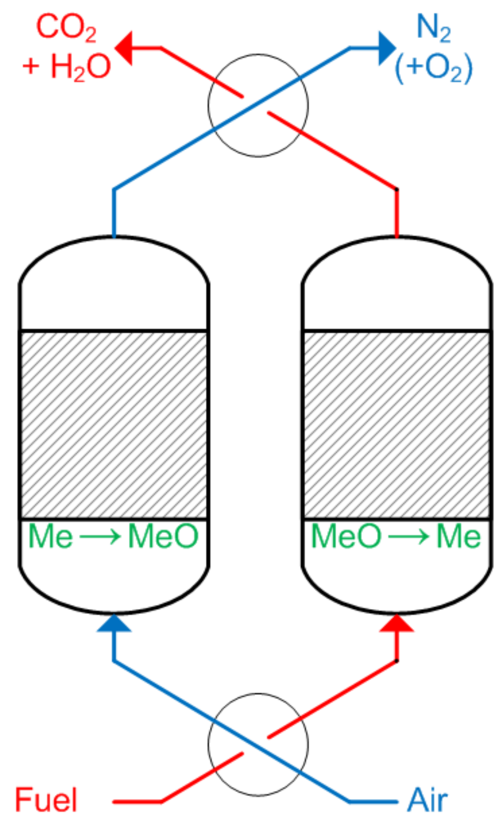


Introduction

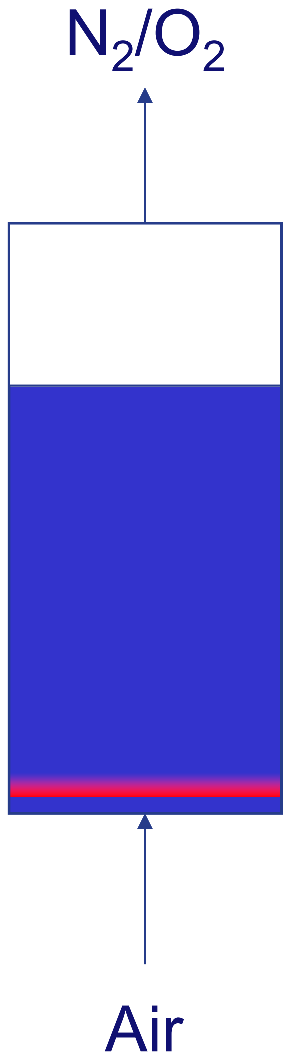
Packed bed reactors

- ✓ No transport of the solid
- ✓ No gas/particle separation
- ✗ High temperature gas switching valves

Solution for high pressure operation

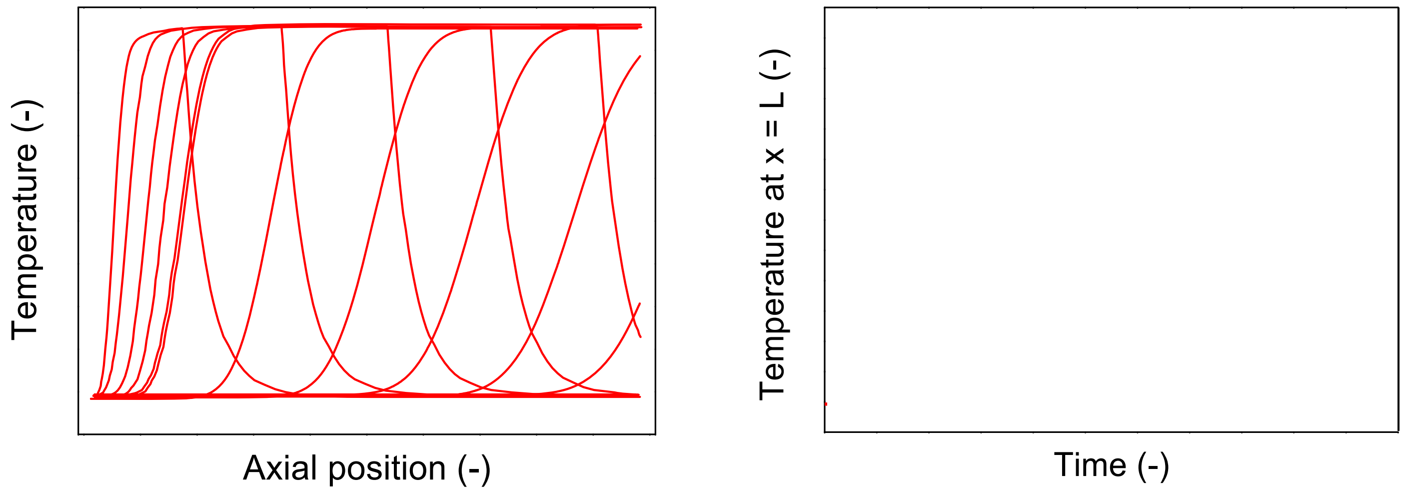


Introduction



Oxidation cycle:

- No influence of reaction kinetics or flow rate on ΔT
- Exit temperature can be controlled with oxygen carrier



Reduction cycle:

- Similar behavior
- Different demands: maximization of CO_2 capture efficiency, minimization of fuel slip

Objectives

To demonstrate the combustion of syngas in a packed-bed CLC reactor at elevated temperatures and pressures

- To analyze the effect of the main operating conditions, such as the syngas composition and **pressure**
- To validate a unsteady-state 1-D model developed for CLC systems

Oxygen carrier

Ilmenite

Active phase : Fe_2TiO_5 and Fe_2O_3

- Natural mineral
- Cheap material
- High conversion with syngas

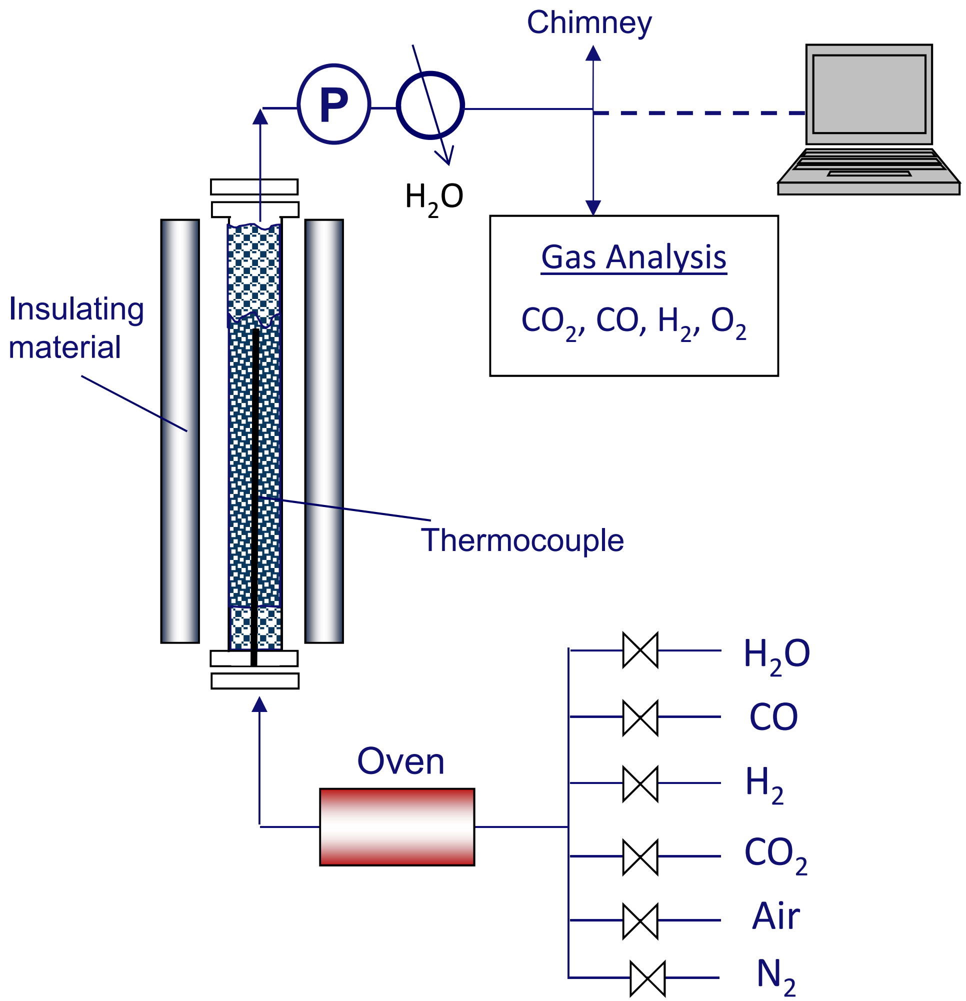
Ilmenite pellets

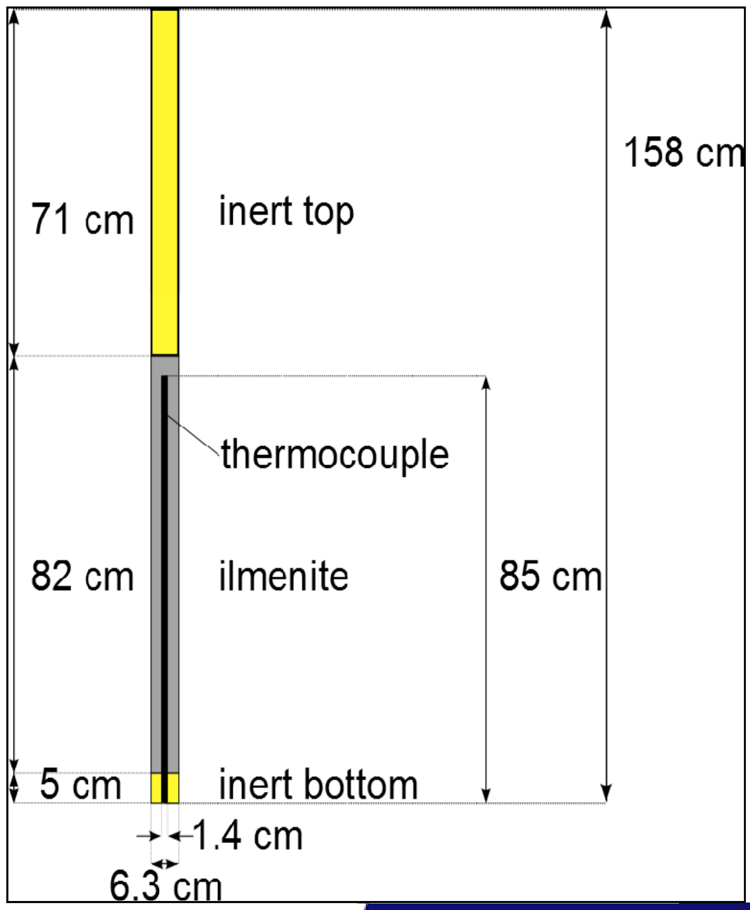
- 75% Norwegian ilmenite + 25% Mn_2O_3

Physical Properties	
Average external diameter (mm)	3,08± 0,2
Average length (mm)	6,92 ± 5,0
Density (kg/m^3)	3600
Grain Porosity (%)	15,43
Mechanical Properties	
Individual particle crushing strength (DaN/mm)	2,91
Attrition (Spence method) %	2,15

Experimental

Lab-scale packed bed reactor





Experimental

Operating Conditions

- 4 kg activated ilmenite pellets
- Flow for reaction: 40 l/min
- Flow for purge: 160 l/min

Reduction

- Fuel: CO+ CO_2 ,H_2 +H_2O and syngas
- T = 800 ºC
- Time : 60 min

Oxidation

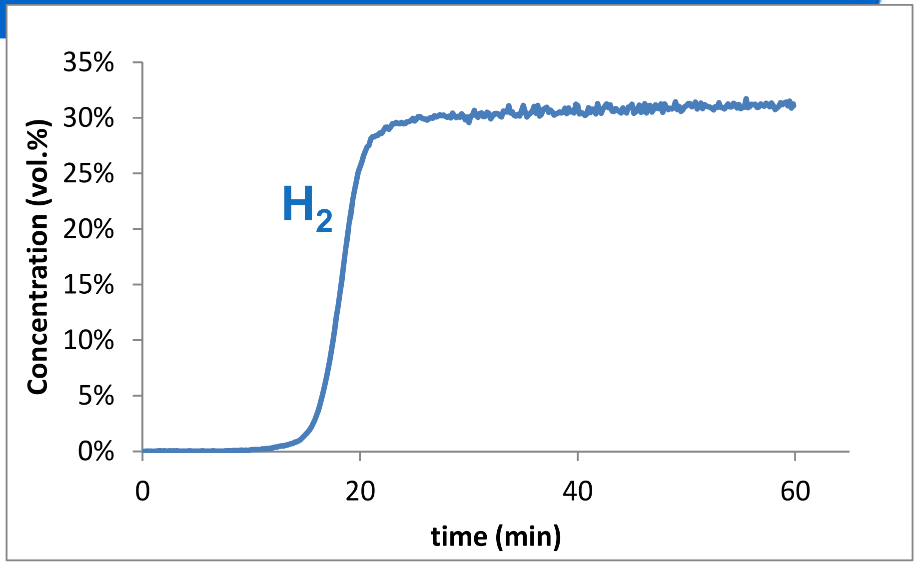
- 100 % Air
- T = 600ºC
- Time : 17 min

Results

Fuel composition

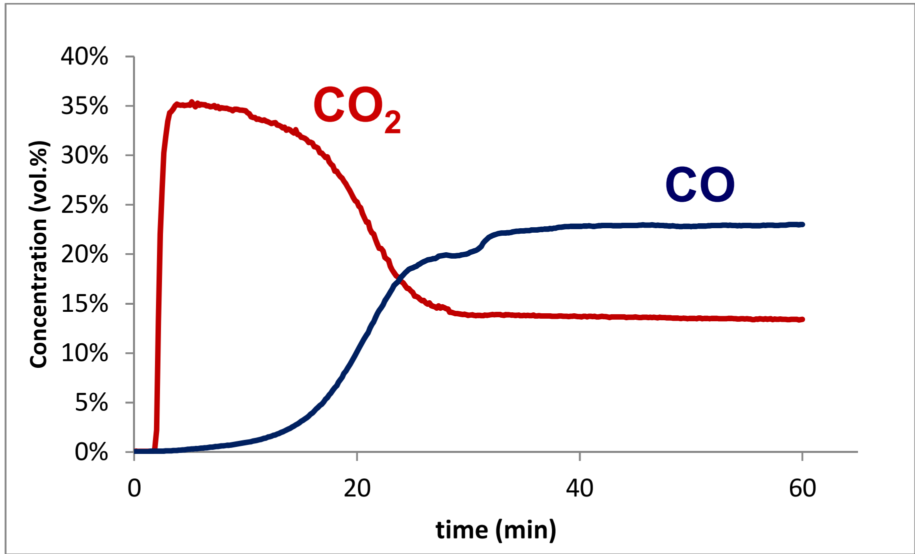
Reduction with H_2

30% H_2, 15% H_2O, 55% N_2
Pressure 4 bar



Reduction with CO

30% CO, 15% CO_2, 55% N_2
Pressure 4 bar



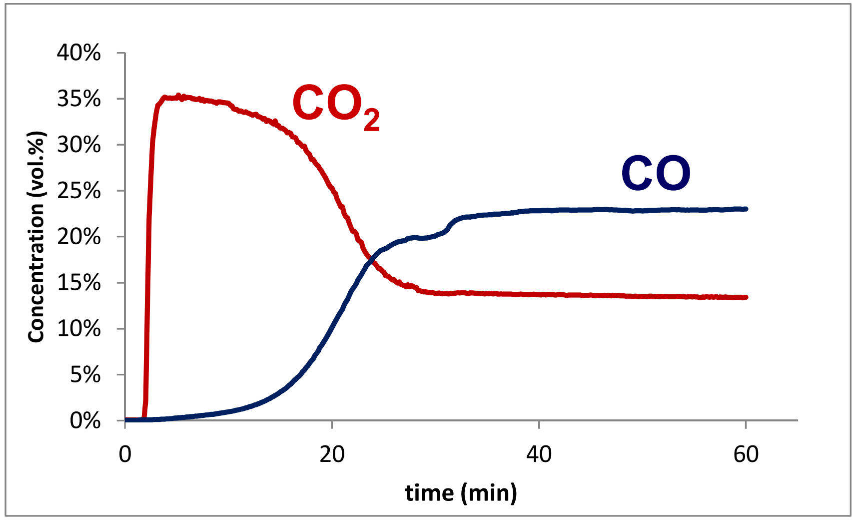
Results

Reduction with CO

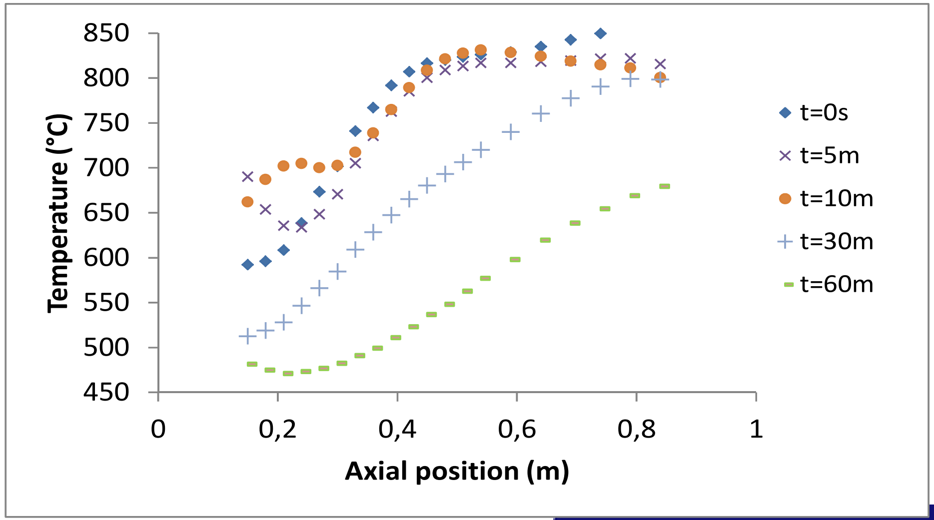
30% CO, 15% CO_2, 55% N_2
Pressure 4 bar

- Delayed breakthrough of CO, so operation without fuel slip possible
- Temperature decrease
- Heat front visible

Gas concentration



Temperature profile



Results

Oxidation

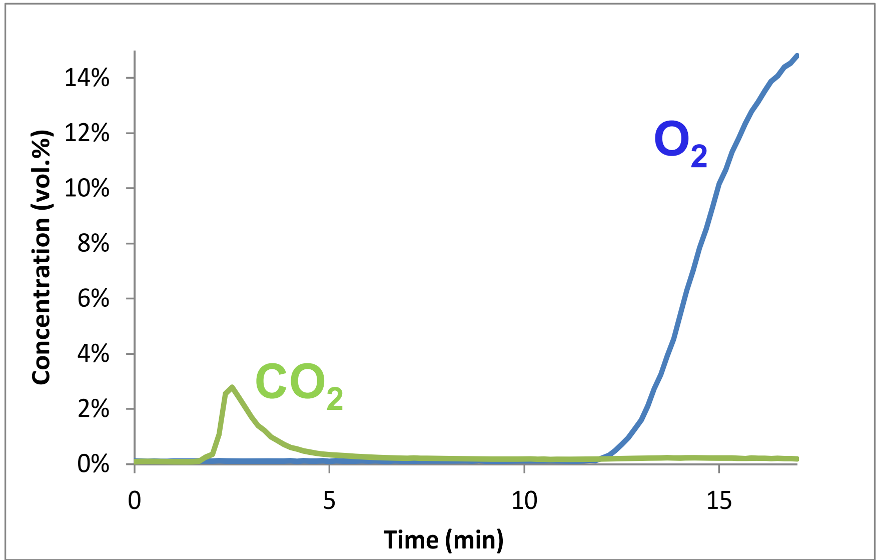
17 min oxidation with 100% Air

Pressure 4 bar

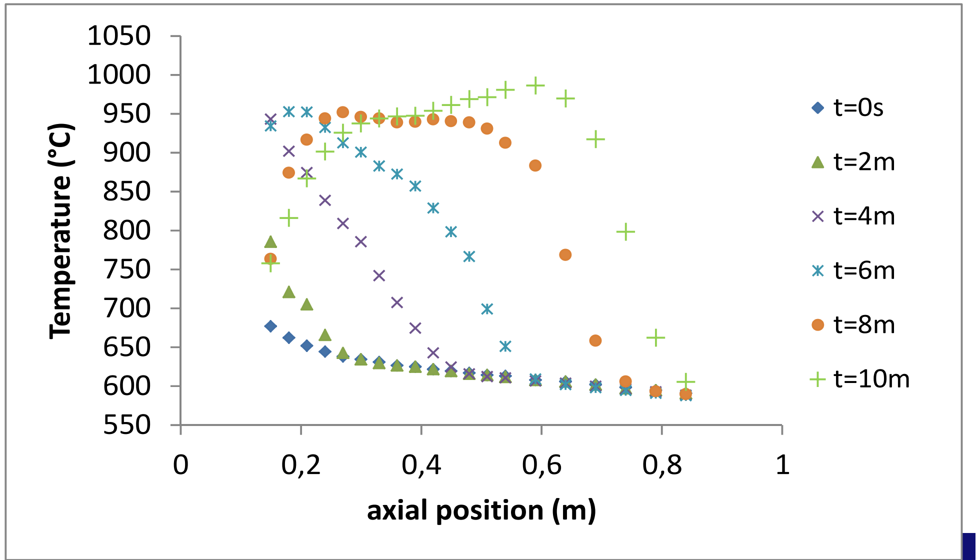
40 L/min

- Small CO_2 peak: carbon deposition
- Temperature increase
- Reaction front visible
- After 12 min O_2 breakthrough which is comparable to reaction front

Gas concentration



Temperature profile



Effect of the pressure

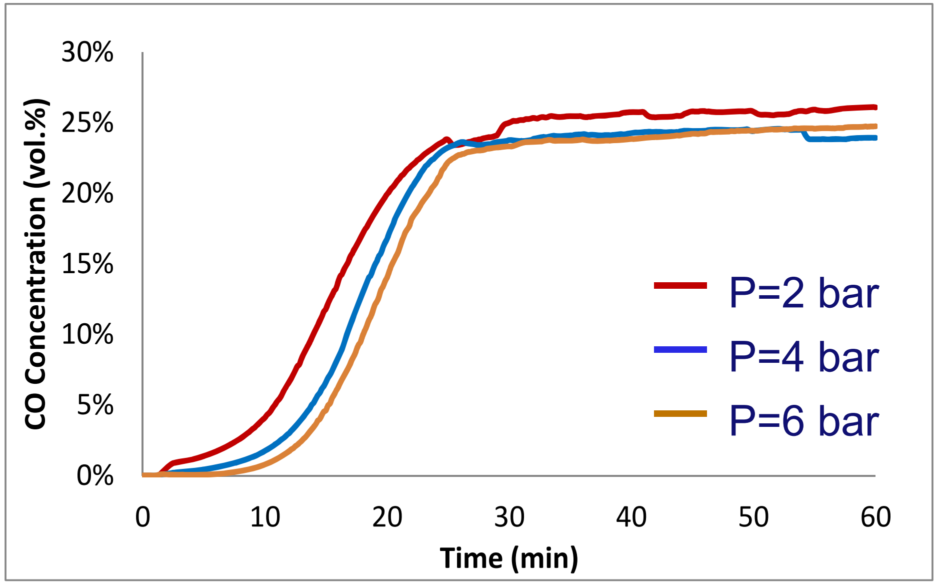
Pressure 2, 4 and 6 bar

Reduction 30% H_2 + 40% CO_2

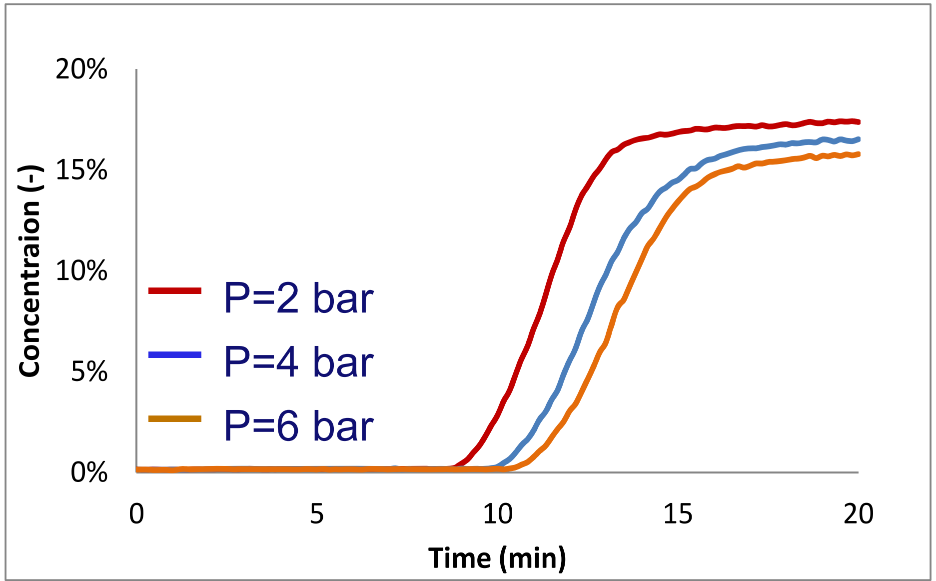
Oxidation 100% Air

- Higher pressure later breakthrough of CO
- Increase reaction rate

Reduction with CO



Oxidation



Results
Pressure influence

20 min oxidation

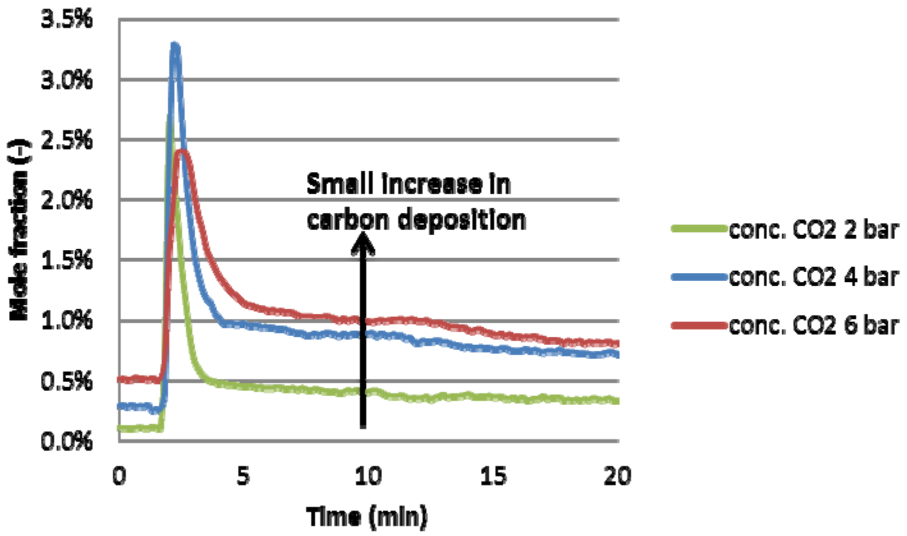
Pressure 2, 4 and 6 bar

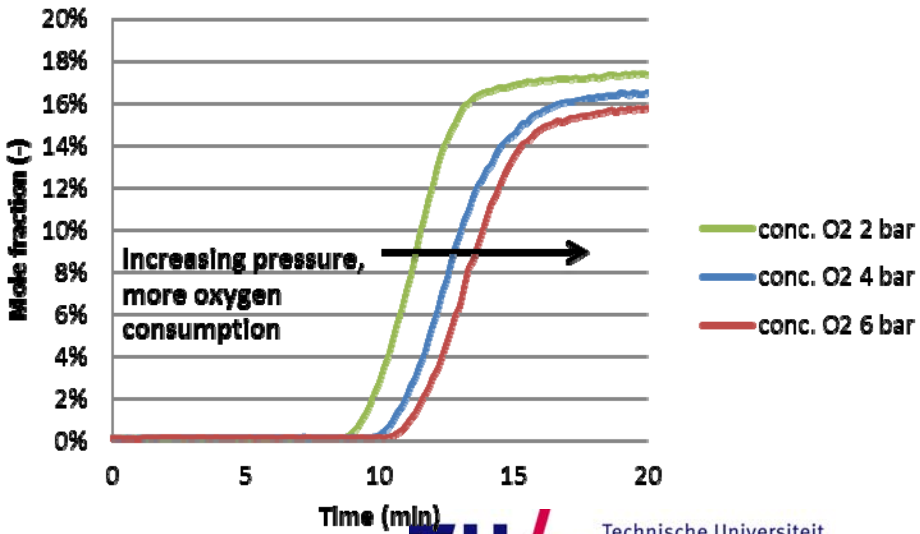
40 L_n/min air

Observations:

Small increase in carbon deposition

Increased O_2 consumption due to higher degree of reduction





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Results

Reduction with syngas

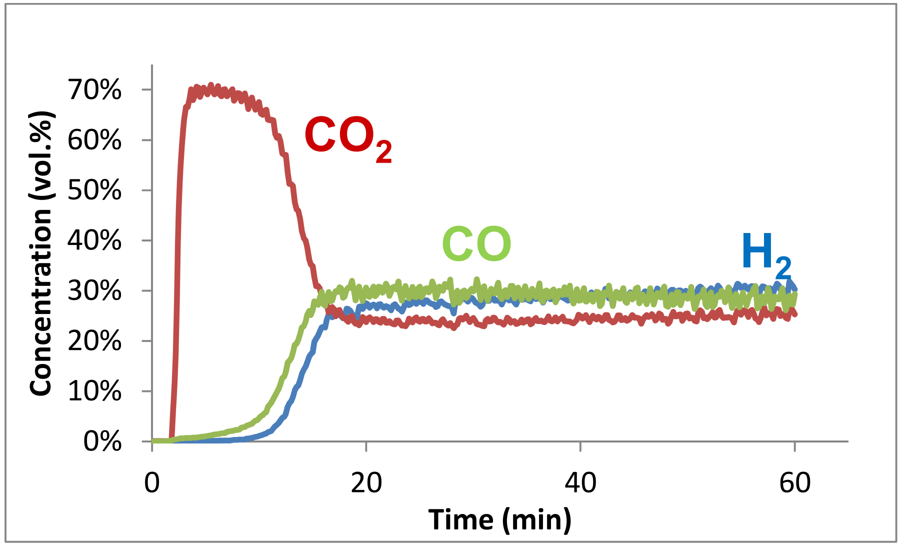
Pressure 2 bar

Syngas composition: 60,7% CO, 22% H_2, 14,6% N_2 and 2,7% CO_2

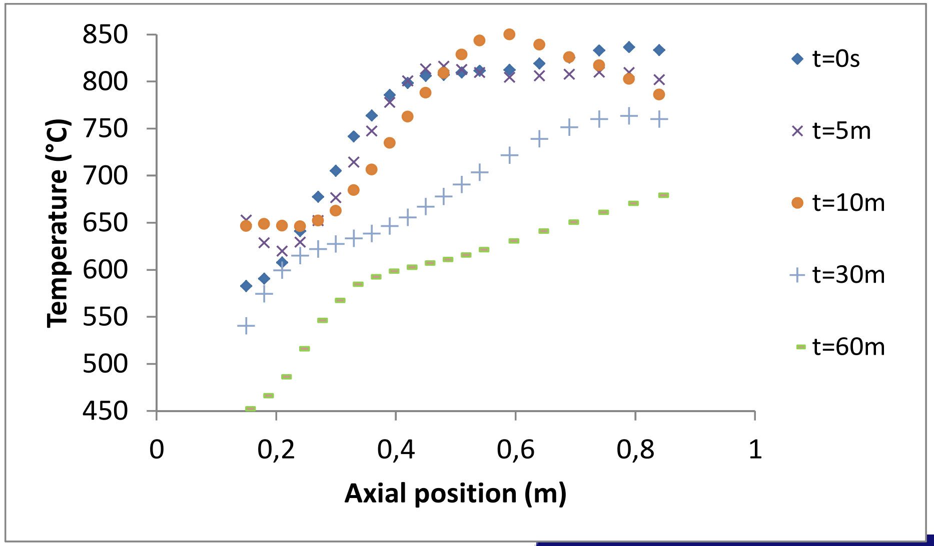
S/C = 1,5

- Delayed breakthrough curves, so operation without fuel slip possible
- Temperature decrease
- Heat front visible

Gas concentration



Temperature profile



Results

Oxidation

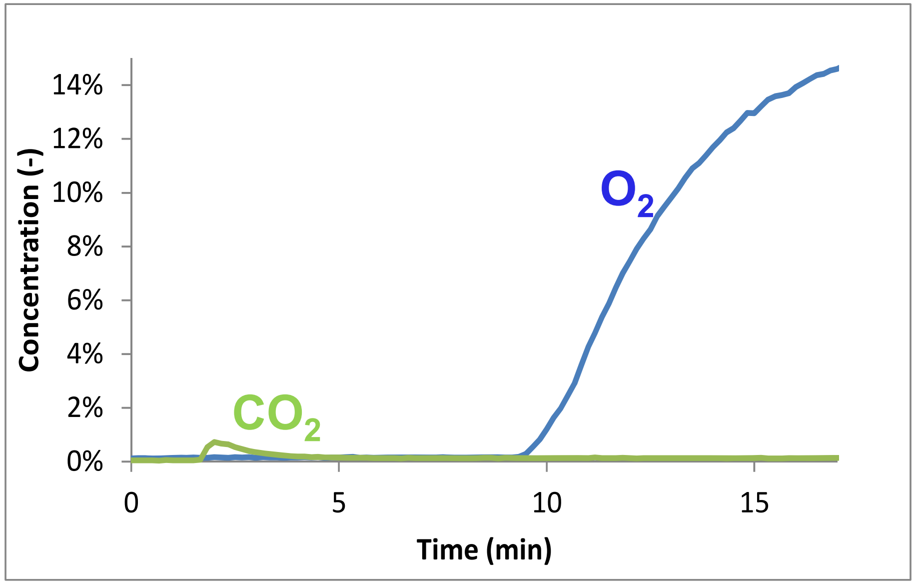
17 min oxidation with 100% Air

Pressure 4 bar

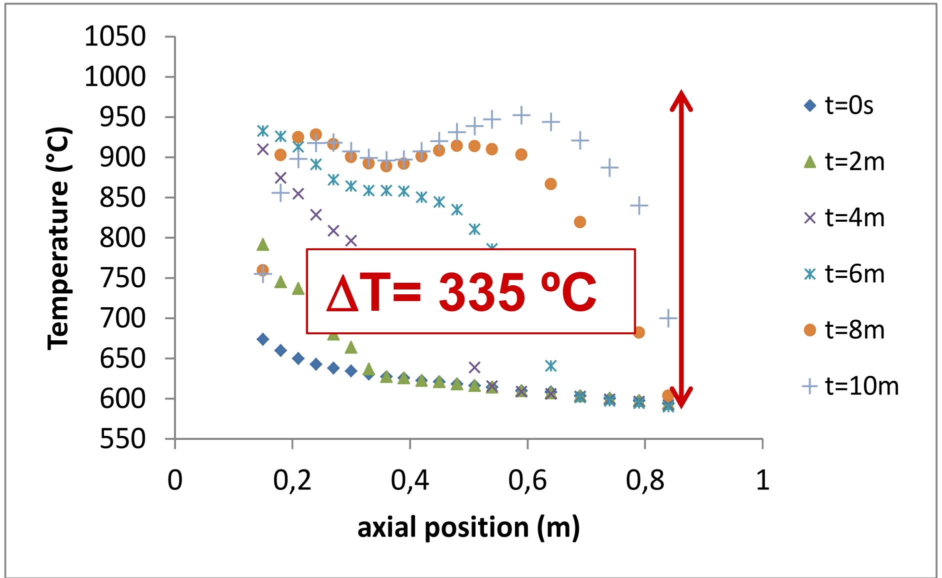
40 L/min

- After 8.5 min O_2 breakthrough which is comparable to reaction front
- Maximum temperature rise = 335ºC

Gas concentration



Temperature profile



Temperature rise during oxidation

- Theoretical temperature rise

$$\Delta T = \frac{(-\Delta H_{R,i})}{\frac{c_{p,s} M_{act}}{\omega_{act}^{0} \zeta} - \frac{c_{p,g} M_{g,i}}{\omega_{g,i}^{in}}}$$

Theoretical ΔT Ilmenite pellets = 811 ºC

- Calculation should include heat capacity of the Inconel liner and thermocouple

$$\Delta T = \frac{(-\Delta H_{R,i})}{\frac{M_{act}}{\omega_{act}^{0} \zeta}\left(c_{p,s} + \frac{V_{liner} \rho_{l}}{V_{s} \rho_{s}} c_{p,liner}\right) - \frac{c_{p,g}}{\omega_{g,i}^{in}} M_{g,i}}$$

Theoretical ΔT Ilmenite + liner = 330 ºC
Theoretical ΔT Ilmenite + liner + thermocouple = 300 ºC

Results
Numerical 1D model

- Assumptions:
  - No radial temperature or concentration profiles
  - No temperature difference between solids and gas (pseudo-homogeneous)
  - Heat losses through insulation material of cylindrical wall (heat transfer coefficient)
  - Heat capacity of liner and thermocouple are included

Numerical model	
Gas phase:	$\epsilon_g \rho_g \frac{\partial \omega_{g,i}}{\partial t} = -\rho_g v_g \frac{\partial \omega_{g,i}}{\partial x} + \frac{\partial}{\partial x} \rho_g D_{ax} \frac{\partial \omega_{g,i}}{\partial x} + \epsilon_g r_i M_i$
Solid phase:	$\epsilon_s \rho_s \omega_{act}^0 \frac{\partial \omega_{g,j}}{\partial t} = \epsilon_g r_j M_j$
Energy balance:	$\left(\epsilon_g \rho_g C_{p,g} + \epsilon_s \rho_s C_{p,s} + \epsilon_{liner} \rho_{liner} C_{p,liner}\right) \frac{\partial T}{\partial t} = - \rho_g v_g C_{p,g} \frac{\partial T}{\partial x} + \frac{\partial}{\partial x} \lambda_{eff} \frac{\partial T}{\partial x} + \epsilon_g r_i \Delta H_{R,i} - \alpha \frac{4}{d_r} (T - T_{env})$
Reaction rate:	Based on TGA experiments

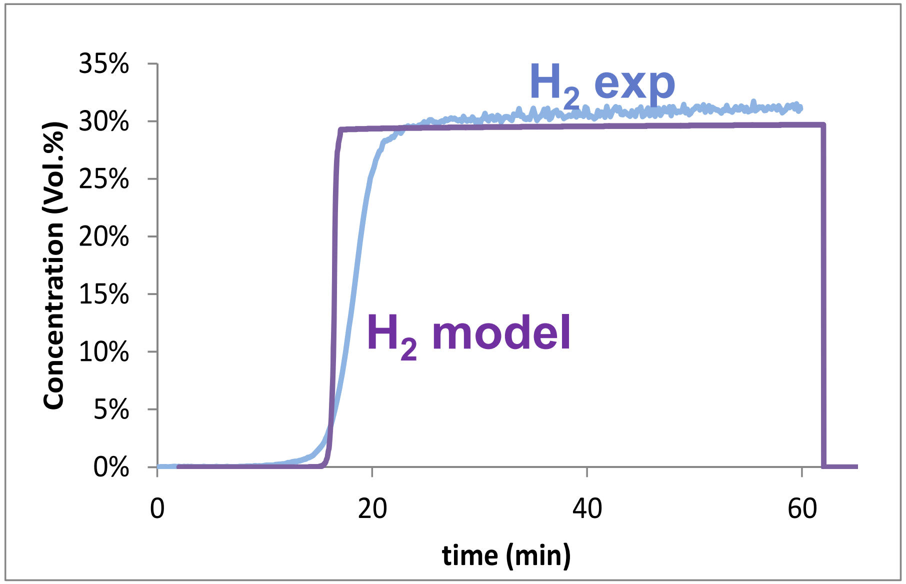
Model results

Pressure 4 bar

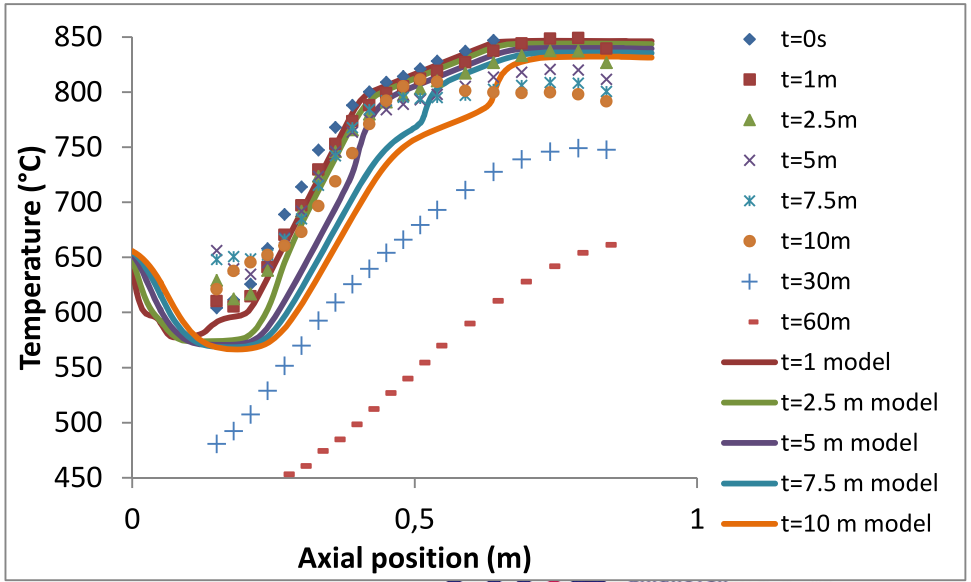
Reduction 30% H_2 + 15% H_2O

- Good description of H_2 breakthrough
- Faster cooling down predicted by model

Gas concentration



Temperature profile



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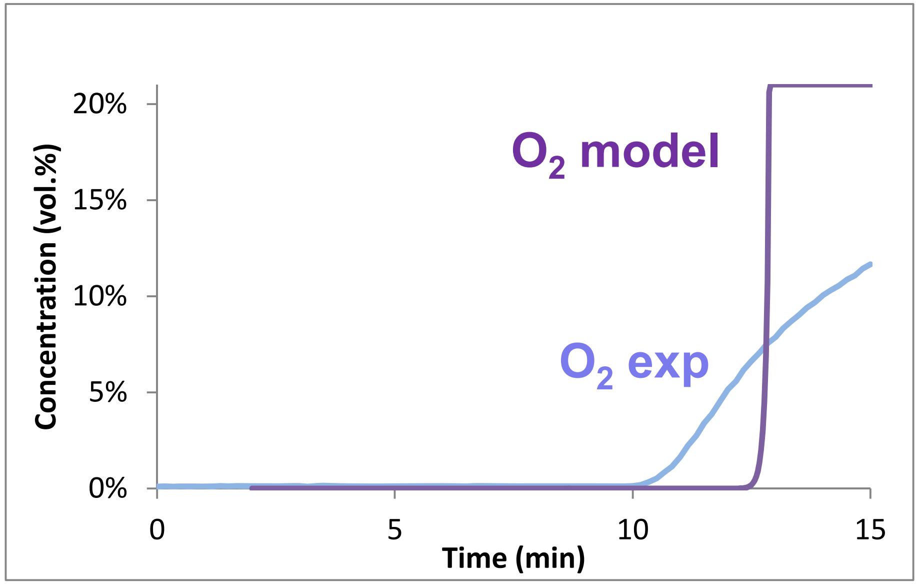
Model results

Oxidation 100% Air

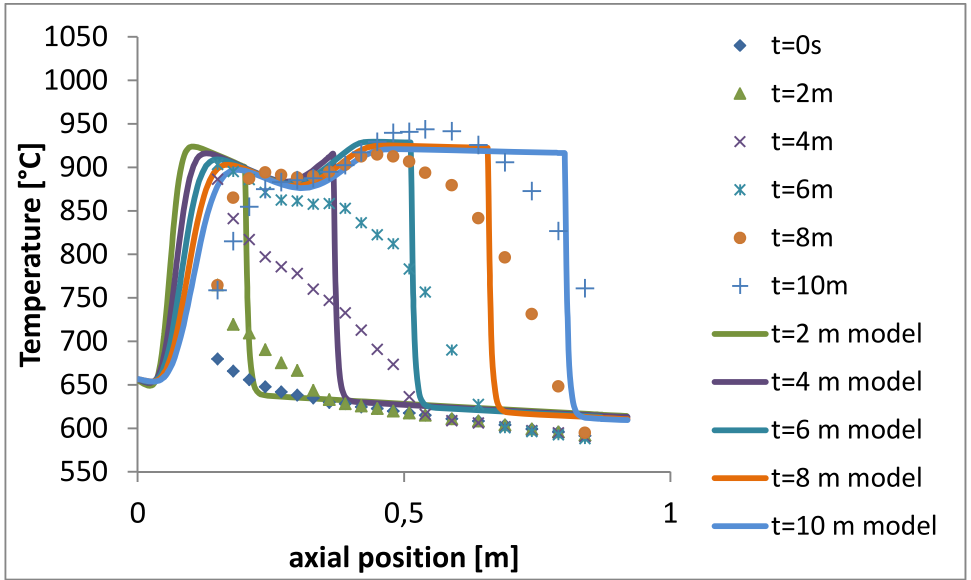
Pressure 4 bar

- **Description of O_2 breakthrough curve not totally good**
- **Good description of temperature profile**

Gas concentration



Temperature profile



Conclusions

- For the first time CLC with ilmenite in a packed bed reactor has been demonstrated on this scale
- The influence of pressure on the CLC process:
  - increased degree of reduction
  - increased reaction rate
- Numerical 1D model:
  - describes temperature increase during oxidation
  - includes the influence of the Inconel reactor parts
    predicts breakthrough times well

Thank you for your attention

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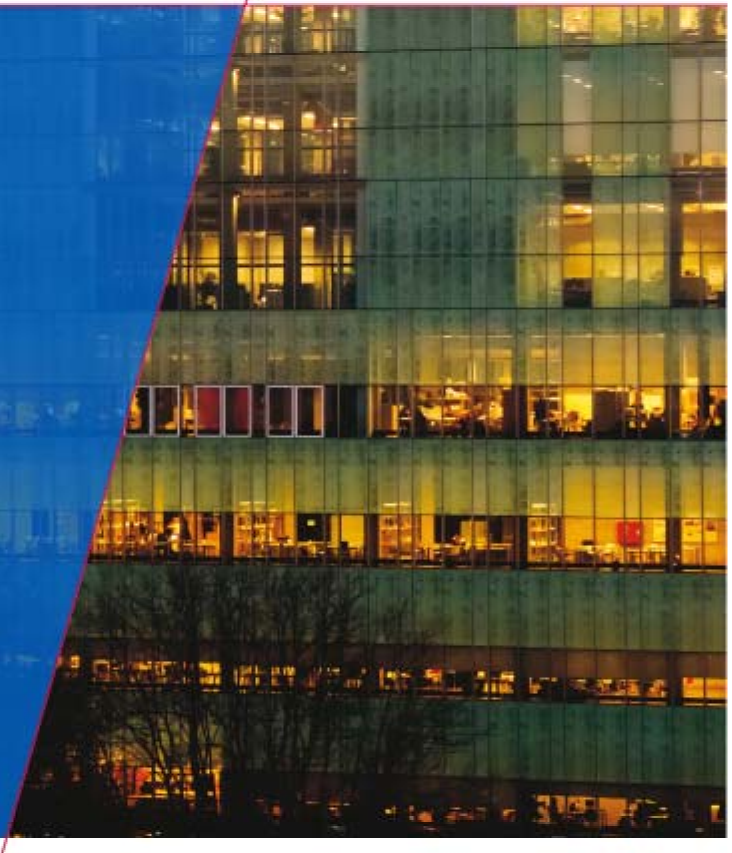

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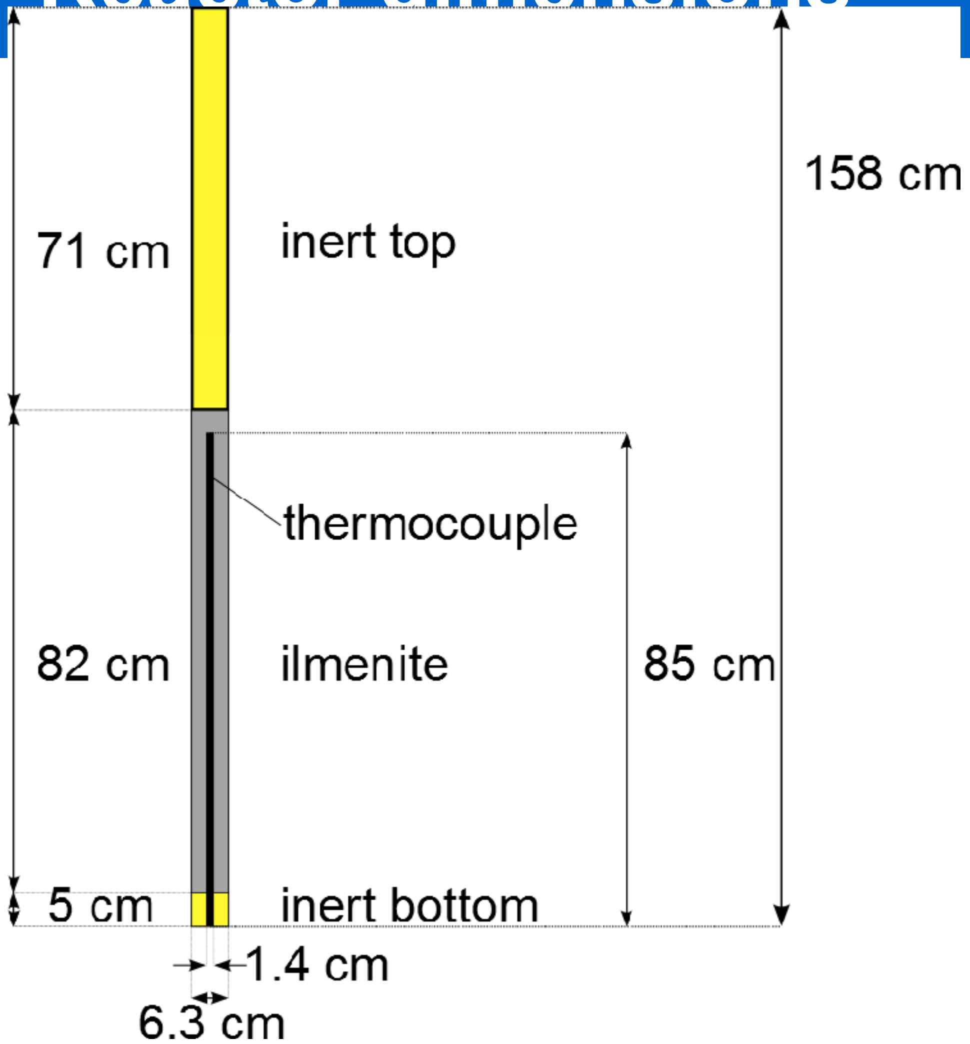
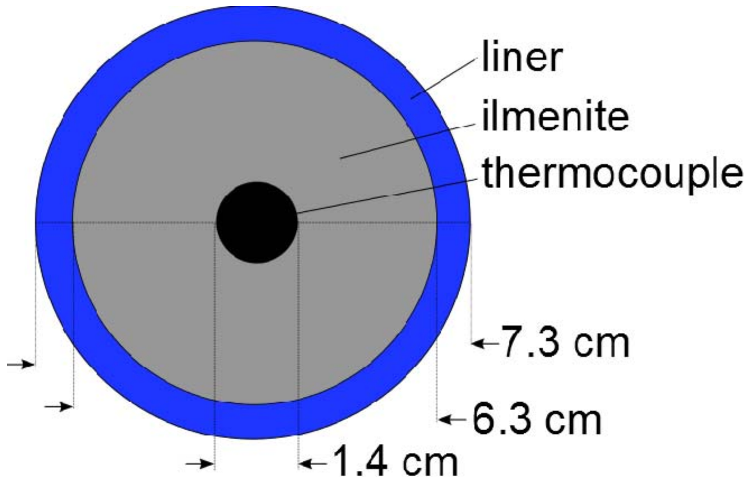
Results
Reactor dimensions





Results
Experiments

Experiment	H_2	CO	CO_2	H_2O (steam)	Pressure
1	15 %	15 %	15 %		4 bar
2	20 %	10 %	15 %		4 bar
3	10 %	20 %	15 %		4 bar
4		30 %	15 %		4 bar
5	30 %			15 %	4 bar
6	15 %	15 %		15 %	4 bar
7	30 %		15 %		2 bar
8	30 %		15 %		4 bar
9	30 %		15 %		6 bar
10 (syngas)	18.2 %	50.2 %	2.2 %	17.4 %	2 bar
11 (syngas)	18.2 %	50.2 %	2.2 %	17.4 %	4 bar
12 (syngas)	18.2 %	50.2 %	2.2 %	17.4 %	6 bar
13		30 %	40 %		2 bar
14		30 %	40 %		4 bar
15		30 %	40 %		6 bar

Results
Pressure influence

- **Effects of increasing the pressure:**
  - **Positive effect on the reaction rate due to increased partial pressures**
  - **Negative effect on the reaction rate due to decreased diffusivities**

- **What effect is most dominant?**

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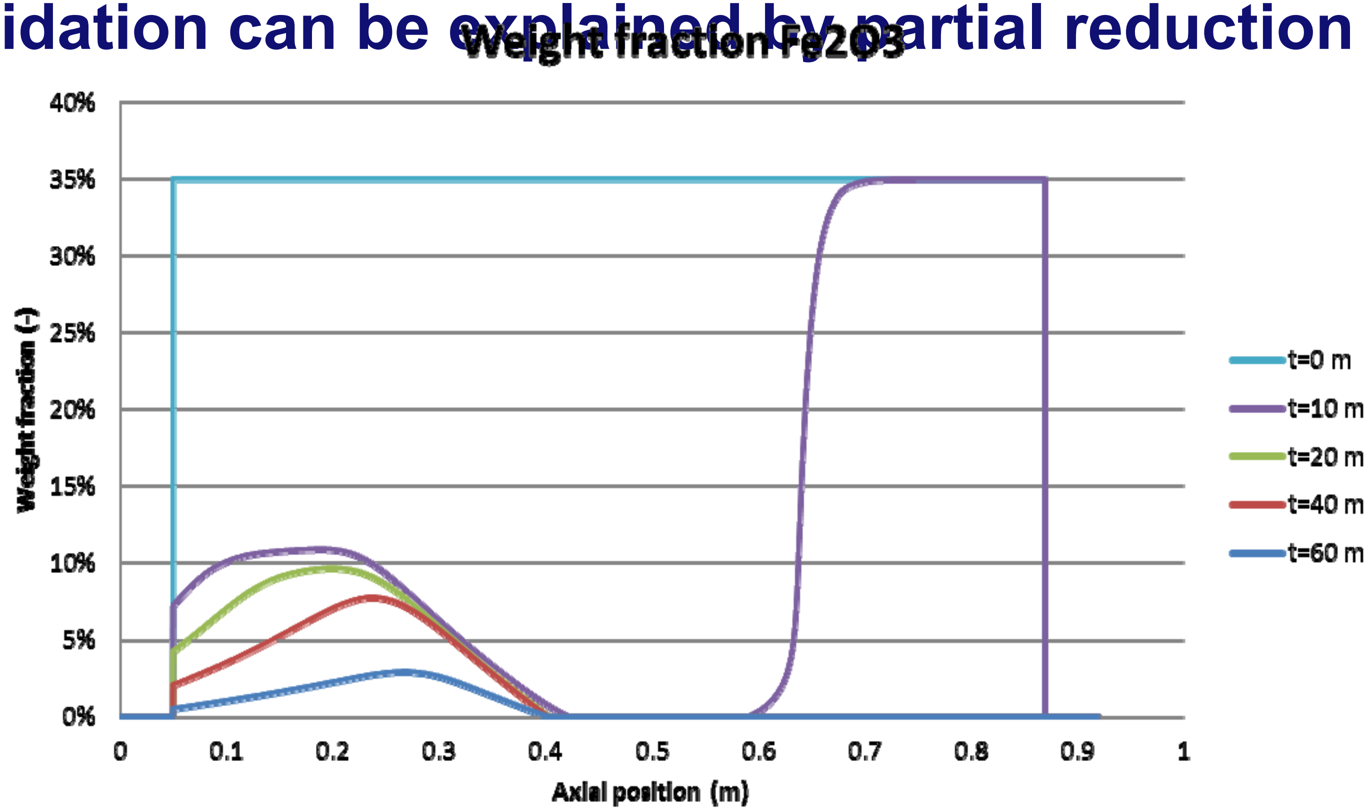
Results
Model results

- **Temperature 'bump' at the begin of the bed during oxidation can be explained by partial reduction**



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Model
Input parameters

Model parameter	Value
Length (m)	0.92 (0.05m TiO_2, 0.82m ilmenite, 0.05m TiO_2)
Diameter (m)	0.063
Oxygen carrier	35wt% Fe_2O_3 on TiO_2
Particle diameter (mm)	3
Solids bulk density in oxidized state, $\varepsilon_s \rho_s$ (kg/m^3)	(1-0.592)*(1-0.180)*4386 = 1469
Gas porosity ($m^3_{gas}/m^3_{reactor}$)	0.180
Mass flow (kg/(m^{2}s))	0.1786
Inlet gas composition	30 % H_2, 15 % H_2O, 55 % N_2
$T_{gas,in}$ (°C)	660
$p_{gas,in}$ (bar)	4
$T_{environment}$ (°C)	300
$\varepsilon_{liner}/\varepsilon_{reactor}\, \rho_{liner} C_{p,liner}$ (J/kg)	0.49*7870*599 = $2.3 \cdot 10^6$
Superficial velocity (40 L_n/min 1100 K and 4 bar) (m^3/m^2 1/s)	0.28
Velocity (40 L_n/min 1100 K and 4 bar, porosity) (m/s)	1.5

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