Optimized design and operation strategy of a Ca-Cu chemical looping process for $\text{H}_2$ production

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Outline

1. Introduction

2. Model description and experimental validation

3. Dynamic operation of the Ca-Cu looping process

4. Process design

5. Conclusions
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Sorption Enhanced Reforming (SER)

- Equilibrium is shifted to H₂ production (>90 vol.% H₂ on a dry basis)
- The reforming process in one single stage
- Overall reaction is slightly exothermic
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**Sorption Enhanced Reforming (SER)**

- **$H_2$ rich gas**
  - Carbonation (Reforming + Shift)
    - CaCO$_3$
    - CaO
  - CO$_2$
- **Heat IN**
- **Fuel + Steam**

**High T for calcination required ($T > 850^\circ C$)**

**Unsurmountable challenge?**

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**Graph:**
- Equilibrium CO$_2$ Pressure, bar
- Temperature, °C

**Reactions:**
- CaO(s) + CO$_2$(g) $\rightleftharpoons$ CaCO$_3$(s)
Proposed solutions for sorbent regeneration

- **Oxy-combustion** of additional fuel in a regenerator
- **External heating** through high temperature heat transfer surfaces
- **Direct heating** by contact with hot solids or hot gases obtained from additional fuel combustion
- Use of the waste heat from a fuel cell coupled to the SER process

Low thermal efficiencies and/or
High equipment cost
The Ca/Cu chemical looping process

(Abanades & Murillo, CSIC, EP09382169.2, 16th Sep 2009)

Based on the “Unmixed reforming” concept (Kumar et al., 2000):

Calcium looping + Chemical Looping Combustion

- CaO for CO₂ capture in the reformer (higher H₂ yield)
- The reduction of oxygen carrier (CuO) with fuel gas supplies the heat for CaCO₃ calcination

Endothermic/exothermic reactions coupled in the same bed matrix

- Higher efficiency
- Lower equipment cost
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The Ca/Cu chemical looping process

- Steam Reforming
- CaO Carbonation

Reduction/Calcination

Oxidation

Fuel gas + H₂O

H₂ (CO₂ free flue gas)

CO₂ + H₂O

Air

N₂
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The Ca/Cu chemical looping process

- **CO\(_2\)+H\(_2\)O**
- **H\(_2\) \text{ (CO}_2\text{ free flue gas)**
- **Fuel gas**
- **Fuel gas}H\(_2\)O**
- **Air**
- **N\(_2\)**
- **Reduction/Calcination**
- **SER**
- **Oxidation**

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The Ca/Cu chemical looping process

CuO Reduction + CaCO₃ Carbonation

Fuel gas + H₂O

Air

N₂

H₂ (CO₂ free flue gas)

CO₂ + H₂O
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The Ca/Cu chemical looping process

- CO₂-rich stream suitable for storage

- CuO Reduction + CaCO₃ Carbonation

- Fuel gas

- Redox cycle:
  - Reduction/Calcination
  - Oxidation
  - SER

- CO₂ + H₂O

- H₂ (CO₂ free flue gas)

- Fuel gas + H₂O

- N₂
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MODEL DESCRIPTION

Assumptions

- Pseudo-homogeneous model
- Mass and thermal dispersion in axial direction
- Ideal gas behaviour
- Negligible intraparticle mass and temperature gradients
- Constant bed void fraction ($\varepsilon=0.5$)
- Uniform particle size ($d_p=5$ mm)
- Uniform mixture of the solids in the packed bed
- CuO-based particles: 60% active
- Ca-based particles: 35% active
- Cycle duration: 15 min
MODEL DESCRIPTION

Mass balance:

\[ \varepsilon \frac{\partial C_i}{\partial t} = \frac{\partial (u C_i)}{\partial z} + \eta (1 - \varepsilon) r_i \]

Energy balance:

\[ \left( (1 - \varepsilon) \rho_s C_{ps} + \varepsilon \rho_g C_{pg} \right) \frac{\partial T}{\partial t} = -u_g \rho_g C_{pg} \frac{\partial T}{\partial Z} + \frac{\partial}{\partial Z} \left( \lambda_{eff} \frac{\partial T}{\partial Z} \right) - \Sigma n_i (1 - \varepsilon) H_{r i} r_i - U(4/d)(T - T_w) \]

Axial pressure distribution (Ergun equation):

\[ \frac{dP}{dz} = -[K_D u - K_V u^2] 10^{-6} \quad / \quad K_D = \frac{150 \mu_g (1 - \varepsilon)^2}{d_p^2 \varepsilon^3} \quad ; \quad K_V = \frac{1.75 (1 - \varepsilon)}{d_p \varepsilon^3} \frac{M_g P}{0.082 T} \]
MODEL DESCRIPTION

Axial mass dispersion coefficient

\[ D_{\text{eff}} = \left[ \frac{0.73}{ReSc} + \frac{0.5}{\varepsilon + 0.7\varepsilon^2} \right] \frac{u_g}{d_p} \quad (Edwards \ and \ Richardson, \ 1968) \]

Effective axial heat dispersion

\[ \lambda_{\text{eff}} = \lambda_{0\text{bed}} + \frac{RePr_k}{Pe_{\text{ax}}} + \frac{Re^2Pr^2_k}{6(1-\varepsilon)Nu} \quad (Vortmeyer \ and \ Berninger, \ 1982) \]

\[ \lambda_{0\text{bed}} = \left( \frac{k_s}{k_g} \right)^{0.28 - 0.757\log(\varepsilon) - 0.057\log\left( \frac{k_s}{k_g} \right)} \quad (Krupiczka, \ 1967) \]

\[ Pe_{\text{az}} = \frac{2p}{1-p} \quad p = 0.17 + 0.29e^{-\frac{24}{Re}} \quad (Gunn \ and \ Misbah, \ 1993) \]

Gas-to-particle heat transfer coefficient

\[ Nu = 2 + 1.8Re^{0.5}Pr^{0.33} \quad (Gunn, \ 1987) \]
MODEL DESCRIPTION

Kinetics of SMR and WGS

\[
R_1 = \frac{1}{(DEN)^2} \frac{k_1}{p_{H_2}^{3.5}} \left( \frac{p_{\text{CH}_4}p_{\text{H}_2} - p_{\text{H}_2}p_{\text{CO}}}{K_1} \right) \\
R_2 = \frac{1}{(DEN)^2} \frac{k_2}{p_{H_2}^{3.5}} \left( \frac{p_{\text{CH}_4}^2p_{\text{H}_2} - p_{\text{H}_2}^4p_{\text{CO}_2}}{K_2} \right) \\
R_3 = \frac{1}{(DEN)^2} \frac{k_3}{p_{H_2}} \left( \frac{p_{\text{CO}p_{\text{H}_2} - p_{\text{H}_2}p_{\text{CO}_2}}}{K_3} \right) \\
DEN = 1 + K_{\text{CO}}p_{\text{CO}} + K_{\text{H}_2}p_{\text{H}_2} + K_{\text{CH}_4}p_{\text{CH}_4} + K_{\text{H}_2O} \frac{p_{\text{H}_2O}}{p_{\text{H}_2}}
\]

(Xu and Froment, 1989)

Kinetics of CuO reduction/Cu oxidation

\[
\frac{t}{\tau} = 1 - (1 - X_{\text{red}})^{1/2} \quad / \quad \tau = \frac{\rho_{m,CuO}L_{CuO}}{k_{\text{red}}C_g^n}
\]

(Abad et al., 2007)

Kinetics of CaCO$_3$ calcination

\[
\frac{dX_{\text{calc}}}{dt} = k_{\text{calc}} (1 - X_{\text{calc}})^{2/3} (c_{\text{CO}_2,eq} - c_{\text{CO}_2})
\]

(Martínez et al., 2012)
EXPERIMENTAL VALIDATION

TEST RIG AT INCAR-CSIC

- Material: Inconel
- Internal diameter: 0.038 m
- External diameter: 0.042 m
- Height: 1 m
- Solids mass: around 1 kg
- Multipoint type K thermocouple (15 points)
- Insulating material: quartz wool
- IR and Paramagnetic Gas Analizers

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**EXPERIMENTAL VALIDATION**

Reduction/calcination tests

The dynamic model gives a good description of the experimental results

- Evolution of the temperature along the fixed bed
- Dynamic profiles at the reactor exit (gas temperature and gas composition)
- Prediction of the breakthrough period
EXPERIMENTAL VALIDATION

Cu oxidation tests

The dynamic model gives a good description of the experimental results

- Evolution of the temperature along the fixed bed
- Dynamic profiles at the reactor exit (gas temperature and gas composition)
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STAGE A: SORPTION ENHANCED REFORMING

Reference case:
30000 Nm$^3$H$_2$/h (after PSA)

Inlet flow: 130 mol CH$_4$/s
(around 100 MW$^{th}$)

Operating Conditions

$T_{gin} = 700^\circ$C
P = 10 bar
S/C ratio = 3

To avoid CaO hydration

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STAGE A: SORPTION ENHANCED REFORMING

Axial profiles

Heat plateau at $T_{\text{max}} = 730^\circ \text{C}$

$T_{\text{min}}$ downstream around 600°C (no CaO hydration)

Initial T profile resulting from a previous stage C'

Sharp carbonation front (enhanced Reforming and WSG)

Partial carbonation downstream the heat plateau

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STAGE A: SORPTION ENHANCED REFORMING

Profiles at the reactor exit

Product gas composition (dry basis):
- ≈ 90% H₂
- ≈ 8% CH₄
- up to 4% CO (heat plateau)
- <1% CO₂

Tₘᵢₙ at 590°C
Heat plateau at Tₘₐₓ=730°C
STAGE B: Cu OXIDATION

Operating Conditions

- $T_{\text{gin}} = 300^\circ\text{C}$
- $P = 20$ bar

Recycle ratio=0.9

Inlet flow=4300 mol/s
- $O_{2,\text{in}} = 2.6\%\text{.vol}$
- $CO_{2,\text{in}} = 1\%\text{.vol}$

$T_{\text{max}} = 860^\circ\text{C}$

To minimize $CO_2$ loss by sorbent calcination
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STAGE B: Cu OXIDATION

Initial conditions:
- Reaction Front (RF) advances slower than Heat Exchange Front (HF), $O_2$ dilution
- Initial solids bed temperature at $520^\circ C$
- $T$ sufficiently high to allow a rapid Cu oxidation

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STAGE B: Cu OXIDATION

Reaction Front (RF) advances slower than Heat Exchange Front (HF): O₂ dilution

T sufficiently high to allow a rapid Cu oxidation

Narrow oxidation fronts

Part of the bed at reactor exit is left calcined
**STAGE B: Cu OXIDATION**

Profiles at the reactor exit

Product gas composition:

- \( t < 11 \text{ min} \): no \( O_2 \) (prebreakthrough)
- \( 8 < t < 13 \text{ min} \): increase of \( CO_2 \) in the flue gas (heat plateau at \( T_{\text{max}} \)) up to 2% vol. \( CO_2 \)

\[ u_{RF} < u_{HF} \]

\( T_{\text{Gout}} \) low during the first part of stage B

Heat plateau at \( T_{\text{max}} = 860^\circ C \) \( (t>10\text{min}) \)
At the end of stage B most of the bed is left at around 300 °C

Operating Conditions

- $P = 20$ bar
- Not all gas recycle to $B'$, only the fraction at the highest temperature ($\approx 860^\circ$C)
- Inlet flow=1300 mol/s
A large part of the bed is left at favourable T for the reduction/calcination stage (around 50% at T>800ºC)

Most of previously calcined Ca-sorbent is carbonated (1.5% CO₂ in gas feed)
STAGE C: REDUCTION/CALCINATION

Operating Conditions

- \( P = 1 \text{ bar} \)
- Fuel gas: PSA off-gas and syngas from SMR stage C’
- \( T_{\text{gin}} = 700^\circ\text{C} \)
- Composition inlet fuel gas: \( 40\%\text{H}_2, 30\%\text{CH}_4, 15\%\text{CO}, 5\%\text{CO}_2 \)
- \( \text{Cu/Ca molar ratio}=2 \)

**CO\(_2\)** stream suitable for storage
STAGE C: REDUCTION/CALCINATION

- Rapid increase of temperature due to the reduction of CuO
- Heat plateau at $T_{\text{max}}$ around 900°C
- $u_{RF} \gg u_{HF}$ (most of the bed is left at 900°C)

- For $t=0$ min, part of the solids are already converted. But this does not cause hot spots during the operation because both Ca- and Cu-converted solids are at reactor inlet.
- Both reduction and calcination fronts advance together leaving behind the solids totally converted
STAGE C: REDUCTION/CALCINATION

- Cycle duration

Mole percent out, %

Time, min

- H2
- CH4
- CO
- H2O
- CO2

- Cycle duration

Temperature, ºC

Time, min

- t<4 min: <2% CO₂ (low T of product gas)
- t>5 min: maximum CO₂ content (55%)
- Complete fuel conversion during pre-breakthrough

T_{gout} low during the first part of stage C
Heat plateau at 900ºC (t>8min)
STAGE C’: STEAM METHANE REFORMING

Operating Conditions

- P = 1 bar
- T{\text{gin}} = 700\,^{\circ}\text{C}
- S/C = 1.5

- High content of CO+H{\text{2}}
- Low CO{\text{2}} formation (minimum Ca-solids carbonation)

- **Cooling solid bed** for Stage A (SER)
- Readily available **source of CO and H{\text{2}}** for Stage C (reduce the Cu/Ca ratio required)
STAGE C’: STEAM METHANE REFORMING

- **Drop in temperature** at reactor inlet because of the *steam methane reforming*
- **Almost complete conversion of CH₄** when it reaches the solids at 900ºC
- **Only carbonation at the reactor inlet** where the low temperature favours carbonation reaction
- **Most of the bed is left at a temperature around 600ºC** (suitable for the subsequent SER stage)
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Shorter cycle times lead to smaller areas, but also to higher pressure drops.

Larger L/D ratios reduce the total area required, but at the expense of higher ΔP.

Limiting stage: Stage B (with the highest inlet gas flow)

Assumptions:
- Minimum L/D=2
- Maximum pressure drop (ΔP/P)=10%
- Minimum duration of single stage=15 min

H₂ efficiency (LHV basis)=76%
CO₂ capture efficiency=96%

5 reactors, L=6 m, D=2.9 m
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CONCLUSIONS

- Each stage of the Ca-Cu looping process has been simulated using a pseudo-homogeneous model and dealing with solids temperature and solids conversion profiles left in previous stages.

- SER stage has been designed at a relatively low pressure (10 bar) and low S/C ratio (3) to avoid CaO hydration.

- The use of a PSA unit downstream SER reactor allows H₂ efficiency and CO₂ capture efficiency to be improved.

- A process design for a reference H₂ plant (30000 m³NH₂/h) shows that 5 reactors (6 m long with an inner diameter of 2,9 m) operating in cycles of 15 min are required.

- Future work: this reactor model will be incorporated into a comprehensive process model for the complete integration of the Ca-Cu looping process.
THANKS FOR YOUR ATTENTION!

Any questions…..?