Validation of a Fuel Reactor Model for
In-situ Gasification Chemical Looping Combustion

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What is intended?

- High CO$_2$ capture rates: necessity of a CARBON STRIPPER
- High combustion efficiency: to minimize unburnt compounds exiting the fuel reactor together CO$_2$ and H$_2$O

Performance of the Fuel Reactor + Carbon Stripper
**Oxygen carriers**
- Ilmenite
- Hematite
- Iron ore
- Bauxite waste: Fe-ESF
- Manganese ore
- CaSO₄

**Solid fuels**
- Petcoke
- Anthracite
- Bituminous coals
- Lignite
- Biomass

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**iG-CLC: Status of the art**

**Oxygen carriers**

- **10 kW<sub>th</sub>**
  - Chalmers UT
  - Sweden

- **100 kW<sub>th</sub>**
  - Darmstadt
  - Germany

- **50 kW<sub>th</sub>** (5atm)
  - Southeast U
  - China

- **25 kW<sub>th</sub>**
  - Hamburg UT
  - Germany

- **10 kW<sub>th</sub>**
  - IFP
  - France

- **10 kW<sub>th</sub>**
  - Southeast U
  - China

- **1 kW<sub>th</sub>**
  - Southeast U
  - China

- **10 kW<sub>th</sub>**
  - Chalmers UT
  - Sweden

- **3 MW<sub>th</sub>**
  - Alstom
  - USA

- **0.5 MW<sub>th</sub>**
  - ICB-CSIC
  - Spain

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**Introduction**

Increasing size
**iG-CLC: Status of the art**

- **CO₂ capture efficiency**
  - High CO₂ capture rate values are reached when a carbon separation system (CSS) is implemented

- **Combustion efficiency**
  - Usually evaluated by the “Oxygen demand” defined by:
    \[ \Omega_i = 1 - \eta_{comb} = \frac{\text{Oxygen for complete combustion of FR gas}}{\text{Oxygen demanded by the coal}} \]
  - Complete combustion is not reached
  - Oxygen demand decreases if:
    - the solids inventory increased
    - the oxygen carrier reactivity increased
Objective

To identify key operating parameters and design options to minimize the oxygen demand in a G-CLC process

- Development of a mathematical model for the coupled fuel reactor and carbon stripper
- Validation of the model against experimental results in a CLC unit analyzing:
  - CO₂ capture efficiency
  - Oxygen demand
- Process simulation of different options
Modelling FR and CS

Fluidized bed
- Fluid dynamics
  - Solid flow
  - Gas flow

Coal conversion
- Volatiles generation
- Char gasification
  - Kinetics of char gasification
    - H₂O, CO₂
  - Kinetics:
    - OC reduction by volatiles and gasification products
    - WGS reaction

Modelling the process

Modelling reactor design improvements

Process simulation and optimisation

Model validated against results in 100 kW CLC unit (Chalmers UT)
FLUID DYNAMICS: high velocity fluidized bed (FR)

- **Dense bed**
  - Two phases: bubble/emulsion
  - Plug flow gas in each region
  - Gas exchange between phases
  - Solids are in perfect mixing

- **Cluster phase in splash**
  - Plug flow gas
  - Solids are in perfect mixing
  - Exponential decay of solids

- **Transport phase**
  - Core-annulus structure
  - Exponential decay of solids

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**DILUTE REGION**
- Cluster phase
- Core in transport phase
- Wall in transport phase

**DENSE BED**
- Emulsion phase
- Bubble phase
### Coal reactions

**Devolatilization**<sup>(1)</sup>

\[
\text{Coal} \rightarrow \text{Char(C)} + \text{Volatile}
\]

**Gasification**<sup>(2)</sup>

\[
\begin{align*}
C + H_2O & \rightarrow CO + H_2 \\
C + CO_2 & \rightarrow 2 CO
\end{align*}
\]

### Reactions involving oxygen carrier<sup>(2)</sup>

\[
\begin{align*}
\text{MeO} + CO & \rightarrow CO_2 + Me \\
\text{MeO} + H_2 & \rightarrow H_2O + Me \\
4 \text{MeO} + CH_4 & \rightarrow CO_2 + 2 H_2O + 4 Me
\end{align*}
\]

### WGS reaction<sup>(3)</sup>

\[
\text{CO} + H_2O \leftrightarrow CO_2 + H_2
\]

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**Notes:**

2. Kinetics determined in ICB-CSIC by TGA.
100 kW$_{th}$ CLC unit at CUT(*)

**Input data**

<table>
<thead>
<tr>
<th>Oxygen carrier</th>
<th>Solid fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norwegian</td>
<td>“El Cerrejón” bituminous coal, Colombia (50µm)</td>
</tr>
<tr>
<td>ILMENITE (170µm)</td>
<td></td>
</tr>
</tbody>
</table>

**Fuel Reactor geometry**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Height (m)</td>
<td>5</td>
</tr>
<tr>
<td>Diameter (m)</td>
<td>0.154</td>
</tr>
</tbody>
</table>

**11 experimental conditions**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (ºC)</td>
<td>950-980</td>
</tr>
<tr>
<td>Pressure drop (kPa)</td>
<td>15-23</td>
</tr>
<tr>
<td>Steam flow (Nm$^3$/h)</td>
<td>6-18</td>
</tr>
<tr>
<td>Solids circulation rate (kg/h)</td>
<td>900-3210</td>
</tr>
</tbody>
</table>

Validation of the Model

Output results

- Axial profiles
  - Axial profile of solids concentration is properly predicted by the fluid dynamic model
  - Char fraction increases with height
  - CO and H₂ flows increase with height

- Oxygen carrier conversion
- Char conversion
- Concentration of gases at exit
- Oxygen demand
- CO₂ capture efficiency
Validation of the Model

Model predictions vs. Experimental results

- Good fitting of experimental results
- Tendency is predicted
- There are always unburnt compounds exiting from the Fuel Reactor

• $\eta_{cs}$ is calculated to fit the reported $\eta_{cc}$ value in every experimental condition

- The value for the efficiency of the carbon stripper is 99.3%!!
Options to decrease the oxygen demand:

To optimize operating conditions

- Temperature, solids inventory, solids circulation rate

To modify design of the CLC unit

- D-1: To improve the gas-solid contact by disposing internals in the dilute region of the fuel reactor
- D-2: To include a second fuel reactor fed by the exhaust gases
- D-3: To recycle exhaust gas to the fuel reactor or carbon stripper
- D-4: To separate unburnt compounds in connection with the purification of CO₂ and to send these gases to the fuel reactor
Effect of operating conditions

- It is preferable to operate at higher temperature and solids inventory as possible
- The solids circulation flow must be chosen by a tradeoff between $\eta_{CC}$ and $\Omega_T$

Reference conditions

- Temperature: 1000°C
- Solids inventory in FR: 1000 kg/MW$_{th}$
- Solids circulation flow: 4 kg/s per MW$_{th}$
- Efficiency of carbon separation system: 99%
  - Oxygen demand: 11.4%
  - CO$_2$ capture efficiency: 96.4%
D-1: to insert internals in the dilute region

Factors affecting the solids distribution

- Distance between internals: $\Delta h$
- Incremental in solids concentration: $f_S$

For $\Delta h = 0.75 \text{ m}$ and $f_S = 2$

- Oxygen demand: 7.5%
- $CO_2$ capture efficiency: 95.1%

Reference conditions:
- Oxygen demand: 11.4%
- $CO_2$ capture efficiency: 96.4%
D-2: to include a secondary fuel reactor

Modeling the secondary fuel reactor
- High-velocity fluidized bed
- Similar model to the fuel reactor:
  - no char
  - fuel gas fed through the distributor plate

For $m_{FR-2} = 500 \text{ kg/MW}_{th}$
- Oxygen demand: 1.5%
- $CO_2$ capture efficiency: 96.4%

Reference conditions:
- Oxygen demand: 11.4%
- $CO_2$ capture efficiency: 96.4%
D-3A: to recycle exhaust gas to fuel reactor

Recycle conditions

- Steam in FR is replaced by recirculated gases
- Recirculation of dry gases
- The recirculation ratio is varied:
  \[ \phi_{g,\text{dry}} = \frac{F_{\text{rec,dry}}}{F_{\text{outFR,dry}}} \]

For \( \phi_{g,\text{dry}} = 0.85 \)
- Oxygen demand: 3.7%
- \( CO_2 \) capture efficiency: 97.0%

Reference conditions:
- Oxygen demand: 11.4%
- \( CO_2 \) capture efficiency: 96.4%
D-3B: to recycle exhaust gas to carbon stripper

Recycle conditions

- The steam flow is replaced by recirculated flow
- Recirculated flow is equal to steam flow to CS

Reference conditions:
- Oxygen demand: 11.4%
- CO₂ capture efficiency: 96.4%
D-4: to recycle unburnt compounds to the fuel reactor

Recycle conditions

- Ideal $CO_2$ separation is assumed during purification step
- Dry and $CO_2$ free recirculated flow
- Purge stream is required to avoid accumulation of $N_2$ coming from coal

- Oxygen demand: 6.6%
- $CO_2$ capture efficiency: 96.4%

Reference conditions:
- Oxygen demand: 11.4%
- $CO_2$ capture efficiency: 96.4%
Comparing results

Comparison of the results by using the Coefficient of Variation (CV) of oxygen demand or CO$_2$ capture efficiency

\[
CV(\%) = 100 \frac{X_{\text{new}} - X_{\text{ref}}}{X_{\text{ref}}}
\]

Including a second fuel reactor shows the higher decrease in the oxygen demand
But... there is a second reactor in the iG-CLC unit:
The Carbon Stripper!

- The carbon stripper is used as a secondary FR
- There is not recirculation of gases

**System improvements**

- Oxygen demand: 0.9%
- CO$_2$ capture efficiency: 98.8%

Reference conditions:
- Oxygen demand: 11.4%
- CO$_2$ capture efficiency: 96.4%

- The largest drop in oxygen demand
A theoretical model for the couple fuel reactor and carbon stripper model has been validated against experimental results obtained in the 100 kW\textsubscript{th} CLC unit.

A temperature in the fuel reactor of 1000°C and a solids inventory of 1000 kg/MW\textsubscript{th} was considered optimal and factible conditions to decrease the oxygen demand, but unburnt compounds are still in gases from the fuel reactor.

Different design options were evaluated to improve the combustion efficiency of the process: using the carbon stripper as a secondary fuel reactor is proposed as an option to maximize the combustion efficiency.
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Thanks

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