ASCENT - Advanced Solids Cycles with Efficient Novel Technologies

Matesa Day
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Project Overview

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www.ascentproject.eu
ASCENT project and its consortium

FP7- THEME: ENERGY.2013.5.1.2 – topic: New generation high-efficiency capture processes

16 European Partners:

7 Countries:

5 Member States: Netherlands, UK, Italy, France, Spain

2 Associate Countries: Norway, Swiss

+ 1 Twinned country: Australia

4 years duration: Starting date: on March 1st, 2014

Budget size: 9.2M €:

7.0M € EC grant

2.2M € own Partners funding
Overall goal of ASCENT project

Provide a proof of concept of three thematically-related and sustainable technologies using industrially relevant materials under industrially relevant conditions for power and H₂ production.

**Material**
- Industrially relevant materials can be manufactured at the scale needed for real implementation.

**Process**
- Industrially relevant conditions are those to be expected in an actually operational environment.

**Proof of concept**
- The Proof-of-concepts will help to increase the Technology Readiness Level of the investigated technologies.
Expertise of the ASCENT consortium

Each process is backed by an SME seeking to take their technological knowledge to a robust proof of concept.

Each process is championed by a EERA affiliated research institute translating the needs of industry into relevant questions to be solved at the research level.

Each process is examined by academic research labs, combining their abilities in chemistry and chemical engineering to address the technological challenges in a robust manner.

Each process is sponsored by an European material supplier looking to expand their product portfolios related to sustainable processes.
ASCENT: an experimental framework of solid-based technologies for \( \text{H}_2 \) and power production

\[
\begin{align*}
\text{CaO} & \rightarrow \text{CaCO}_3 \\
\text{CuO} & \rightarrow \text{Cu} \\
\text{CaCO}_3 & \rightarrow \text{CaO} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2 \text{ (CO}_2 \text{ free)} & \rightarrow \text{Fuel Gas} + \text{H}_2\text{O} \\
\text{CO}_2 + \text{H}_2\text{O} & \rightarrow \text{CaO} \rightarrow \text{CaCO}_3 \quad \text{(Cu)} \\
\text{Cu} & \rightarrow \text{CuO} \quad \text{(CaCO}_3) \\
\text{CuO} & \rightarrow \text{Cu} \\
\text{CaCO}_3 & \rightarrow \text{CaO} \\
\text{Fuel Gas} & \rightarrow \text{Air} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ca-Cu} & \\
\end{align*}
\]

\[
\begin{align*}
\text{Endex Recycle} \quad \text{CO}_2 + \text{H}_2\text{O} & \rightarrow \text{2KAl(CO}_3\text{(OH)}_2 \rightarrow \text{Al}_2\text{O}_3,2\text{KOH} \\
\text{Hot Endex Heat} & \rightarrow \text{2KAl(CO}_3\text{(OH)}_2 \rightarrow \text{Al}_2\text{O}_3,2\text{KOH} \\
\end{align*}
\]

\[
\begin{align*}
\text{C-Shift} & \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2 \text{ (CO}_2 \text{ free)} & \rightarrow \text{H}_2 \text{ (CO}_2 \text{ free)} \\
\text{H}_2 \text{ (CO}_2 \text{ free)} & \rightarrow \text{CaO} \rightarrow \text{CaCO}_3 \quad \text{(Ni-activated reforming)} \\
\text{CaCO}_3 & \rightarrow \text{CaO} \quad \text{(heat exchange)} \\
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Hot Exhaust} \\
\text{H}_2\text{O} & \rightarrow \text{Cold Exhaust} \\
\end{align*}
\]

\[
\begin{align*}
\text{SER} & \\
\end{align*}
\]

\[
\begin{align*}
\text{CO}_2 \text{ acceptor} \\
\text{Reactor engineering} \\
\text{Reaction models} \\
\end{align*}
\]
### Three Technologies, Many Synergies

<table>
<thead>
<tr>
<th>Feature</th>
<th>Ca-Cu</th>
<th>CSHIFT</th>
<th>SER</th>
<th>Advantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simultaneous Reaction &amp; Sorption</td>
<td>✗</td>
<td>✗</td>
<td>✗</td>
<td>Higher conversions and process intensification, reduction in number of pieces of equipment</td>
</tr>
<tr>
<td>High temperature CO$_2$ capture</td>
<td>✗</td>
<td>✗</td>
<td>✗</td>
<td>Increased efficiency, reduced steam knock-out</td>
</tr>
<tr>
<td>Highly engineered CO$_2$ capture materials</td>
<td>✗</td>
<td>✗</td>
<td>✗</td>
<td>Economics, through cheap production methods, increased capacity and lifetime</td>
</tr>
<tr>
<td>Integrated CaO-CaCO$_3$ looping cycle</td>
<td>✗</td>
<td></td>
<td>✗</td>
<td>In situ heat production through matched chemical reactivity</td>
</tr>
<tr>
<td>Pressure Swing driven regeneration</td>
<td>✗</td>
<td>✗</td>
<td></td>
<td>Decreased demand for regeneration energy</td>
</tr>
<tr>
<td>Capture of CO$_2$ at high pressure</td>
<td>✗</td>
<td>✗</td>
<td></td>
<td>Increased fuel utility due to pressurized hydrogen, facilitated integration with CC</td>
</tr>
<tr>
<td>Integrated heat exchange within reactor concept</td>
<td>✗</td>
<td>✗</td>
<td>✗</td>
<td>Process intensification</td>
</tr>
<tr>
<td>Fluidized bed technology</td>
<td></td>
<td>✗</td>
<td>✗</td>
<td>Allows active control in solid handling, efficient heat transfer, continuous operations</td>
</tr>
<tr>
<td>Hot Hydrogen Production</td>
<td>✗</td>
<td>✗</td>
<td>✗</td>
<td>Highly aligned to power generating technology</td>
</tr>
<tr>
<td>Common Framework for techno-economic assessment</td>
<td>✗</td>
<td>✗</td>
<td>✗</td>
<td>Direct Comparison Available</td>
</tr>
</tbody>
</table>
Synergies between the ASCEmt technologies

Task 1. Selection of performance criteria of material and process conditions
Task 2. Synthesis of the functional materials for solids looping processes
Task 3. Detailed experimental investigation at particle scale
Task 4. Development of multi-scale modelling: particle and reactor models
Task 5. Proof of concept and validation of the material performances and of the developed models
During the first reporting period, the development of the conceptual design of the Cu-Ca process was carried out and delivered (D2.1). Several synthesis routes were explored for the CO₂ sorbents, for the Cu-based materials and for the combined CaO-CuO materials, and the solids produced have been extensively tested in the TGA apparatus available by the partners from the WP.
WP2: synthesis procedures

**SPRAY DRYING**
- Boehmite slurried in water
- Cu nitrate dissolved in water and added to boehmite slurry
- Spray Drying parameters set
- Slurry fed to spray dryer
- Spray Dried product collected
- Calcination
- Analysis of samples

**CO-PRECIPITATION**
- Cu nitrate & Al Nitrate solutions mixed
- Na₂CO₃ slowly fed to water, controlling pH
- Aging of solution
- Filtration and Washing
- Drying
- Calcination
- Analysis of samples

**DEPOSITION-PRECIPITATION**
- Cu nitrate solution heated
- Alumina is slurried in water and heated adjusting pH with Na₂CO₃
- Hot nitrate solution fed to the pH and T controlled alumina slurry to precipitate
- Filtration and Washing
- Drying
- Calcination
- Analysis of samples

**MECHANICAL MIXING**
- Copper oxide
- Alumina
- Mixing of solids
- Calcination
- Analysis of samples
WP2 Characterisation and testing of materials

• CHEMICAL AND MECHANICAL STABILITY
  TESTS IN THERMO GRAVIMETRIC ANALYZER (TGA)
  ▷ Powder: TGA tests via 100 red/ox cycles at 870°C.
  ▷ Pellets: TGA tests via 200 red/ox cycles at 870°C.

TESTS:
  Reduction: 20% H\textsubscript{2} in N\textsubscript{2} at 870°C
  Oxidation: 20% O\textsubscript{2} in N\textsubscript{2} at 870 °C
  1 min purge in N2 between stages

• CHARACTERIZATION
  - X-Ray Diffractometry Analysis (XRD) \(\rightarrow\) to identify crystalline species
  - Temperature-programmed reduction test (TPR) \(\rightarrow\) to determine reducible species
  - He picnometry \(\rightarrow\) to calculate solid density
  - Physisorption (BET method) \(\rightarrow\) to calculate specific surface area
Work has been performed on pelletisation for pressurized fluidized bed reactors. In-situ DRIFTS and XRD studies have been performed on as received and CO$_2$/steam loaded samples in order to obtain insight into bonding modes of CO$_2$ and structure. Fixed bed tests to assess CO$_2$ capacity at elevated pressure, and also in the presence of H$_2$S, have been initiated. Initial modelling developments have been carried out.
WP3: Materials optimisation studies

Sorbent characteristics:
- Effect of Steam/CO₂
- Effect of T
- Effect of pressure
- WGS reactivity
- H₂S tolerance
- Cyclic stability

Hydrotalcites are layered solid inorganic materials with the general formula \( \text{Mg}_{1-x}\text{Al}_x(\text{OH})_2(\text{CO}_3^2-) \frac{x}{2}\cdot n\text{H}_2\text{O}. \)
WP3: Water Gas Shift reactivity

WGS reactivity

Status:
- $\text{H}_2\text{S}$ tolerance: ok

Other sorbents: Dawsonite derived sorbents (alkali aluminium carbonate hydroxide)
- by product aluminium industry
The work performed has been focused on the four following topics:
1. Determination of material performance criteria and operating process conditions
2. Development of CaO-based sorbent, reforming catalysts and combined materials (CSCM)
3. Measurement of attrition index of selected materials
4. Modelling of the SER looping process
WP4: SER looping cycle (Sorption Enhanced Reforming)

- Higher $H_2$-yields (95 vol% +) than in conventional SMR, in one single step, and at lower temperature (600-650°C)
- No need for shift reactors and catalysts
- Production of relatively pure $CO_2$
- Simplified process layout and **process intensification**
- Potential for ~20% energy savings and lower costs
WP4: TGA tests on Combined Sorbent Catalyst Materials (CSCMs)

- 2-particle system and CSCM stable in dry regeneration condition
- CSCM not stable in wet regeneration condition
WP4: modelling of CSCM

- The particle model has been derived from a previously developed sorbent grain model [1] by implementing the SMR and WGS reactions together with the carbonation heterogeneous reaction.

Cooperation with the twinned Australian projects

Selection of performance criteria and synthesis and characterisation of the material

Thermodynamic optimisation: Australian National University

Economic optimisation: CO2CRC
The research leading to these results has received funding from the European Union’s Seventh Framework Programme under grant agreement nº 608512.

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