Sustainable ammonia production from sun, air and water

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Ammonia and fertilizer production

Hydrogen from natural gas

Nitrogen from air separation unit

Haber-Bosch process
> 200 bar
> 400 °C
Fe/Al₂O₃

Ammonia (NH₃)

Intermediates
for instance: nitric acid HNO₃ + additives

Nitrogen Fertilizer

Images: CC BY 3.0 Wikimedia (Drahkrub, Rasbak)
Thermochemical hydrogen production

Techno-economic Study: LCOH: 6.7 – 13.0 €/kg [1]

Thermochemical air separation – Project Düsol
Thermochemical cycles for air separation

N₂ purification cycle

Air

\[ T_{\text{red}} \]

\[ T_{\text{ox}} \]

\[ \text{ABO}_3 \]

Reduction

Oxidation

Oxygen

Nitrogen < 3ppm O₂

Choice of redox material

Perovskites - SrFeOₓ
- Low temperature → low \( p_{O_2} \)
- Rapid kinetics
- Cycleability
- Abundant materials
- Low gravimetric O₂ capacity

 выбранный вариант: ✗
Perovskite Materials Design

Theoretical study of > 240 perovskites

Spectrum of redox enthalpies

- Higher reduction temperatures
- More energy required
- More effective air separation
- Lower oxygen partial pressures achievable

Example: SrFeO$_{3-\delta}$-based perovskites

Exchange some Fe by Mn $\Rightarrow$ Higher redox enthalpy

Exchange some Fe by Co $\Rightarrow$ Lower redox enthalpy

Laboratory scale air separation test

**Experimental details**

- 50 g SrFeO$_x$
  - Heating/cooling in Argon
- Air separation: synthetic air
- Several consecutive cycles

50g material produced:
- 0.6 l purified N$_2$ from air
- 2 l purified N$_2$ from semi-purified stream (purity suitable for the Haber-Bosch process)
Scaling up to 20 kW solar – reactor design

**Reduction:**
\[
\text{ABO}_{3-\delta_{\text{ox}}} \xrightarrow{\text{heat in } \Delta \delta \Delta H_0} \text{ABO}_{3-\delta_{\text{rd}}} + \frac{\Delta \delta}{2} \text{O}_2, \quad T_{\text{rd}}
\]

<table>
<thead>
<tr>
<th>Material</th>
<th>( T_{\text{rd}} )</th>
<th>Atmosphere</th>
<th>( T_{\text{max}} )</th>
<th>( p_{\text{O}_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrFeO(_3)</td>
<td>800 – 1000 °C</td>
<td>Air</td>
<td>1150 °C</td>
<td>0.2 bar</td>
</tr>
</tbody>
</table>

**Oxidation:**
\[
\text{ABO}_{3-\delta_{\text{rd}}} + \text{Air(20\% O}_2) \xrightarrow{\text{heat out } -\Delta \delta \Delta H_0} \text{ABO}_{3-\delta_{\text{ox}}} + \text{N}_2(p_{\text{O}_2} \ll 0.2\text{bar}), \quad T_{\text{ox}}
\]

<table>
<thead>
<tr>
<th>Material</th>
<th>( T_{\text{ox}} )</th>
<th>Atmosphere</th>
<th>( T_{\text{min}} )</th>
<th>( p_{\text{O}_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrFeO(_3)</td>
<td>300 – 500 °C</td>
<td>Air</td>
<td>250 °C</td>
<td>0.2 - ppm</td>
</tr>
</tbody>
</table>
Solar rotary kiln

- Suitable for up to 2 kg redox material
- Stainless steel crucible (1.4828)
  - welded window flange and inlet-outlet pipes
  - 1.4828 because of its low amount of chrome
  - Temperature resistant up to 1000 °C
- Zirconia coating
  - Increase heat and reaction resistance
- Gastight design with a quartz window
- Feedthrough flange for inlet and outlet pipe in the back of the crucible
- Bayonet thermocouples – 5 measurement points
- Mass flow controllers at the inlet and outlet pipe
- Oxygen sensor and filter
Experiments in the solar simulator

- Demonstration of thermal resistance
- Validation of design
Solar air separation

Experimental details

- Test in the solar furnace DLR Köln-Porz
- 250 g redox particle (SrFeO\(_x\))
- Particle size 3-4.5 mm
- Rotation speed 1-6 rpm
- 1-4 l/min synthetic air flow
Solar air separation - results

Temperature distribution

With 250 g redox material:
Reduction: 4 l released oxygen
Oxidation: 3.6 l captured oxygen
Solar air separation – multiple cycles

Temperature distribution

Solar reduction
Energy demand of thermochemical air separation

**Model** (based on equilibrium thermodynamics):

\[ Q_{AS} = (Q_{chem} + Q_{sensible}) \cdot (1 - \eta_{solid-solid}) + Q_{pump} \]

\[ Q_{chem} = \int_{\delta_{ox}}^{\delta_{red}} \Delta H(\delta, T) \, d\delta \]

\[ Q_{sensible} = \int_{T_{ox}}^{T_{red}} C_p(T, \delta_{ox}, \delta_{red}) \, dT \]

\[ Q_{pump}: \quad \text{mechanical pump envelope function, Brendelberger et al.} \]


\[ \eta_{solid-solid} = 0.6 \]

**Data:**

https://portal.mpcontribs.org/redox_thermo_csp/

State of the art: cryogenic air separation!
How can thermochemical air separation be more efficient?

- Improve heat recuperation?
  - Solid-solid heat recovery rates of > 97 % would be required for competitiveness!
    (virtually impossible, realistic maximum values are < 80 %, see Felinks et al.)

- Combine with other technology?
  - Pressure swing adsorption (PSA) is a very efficient technology for air separation,
    as long as the required gas purity is not very high

- Combine PSA and thermochemical air separation!

Only a small fraction of the $O_2$ needs to be transported thermochemically

Felinks, J.; Brendelberger, S.; Roeb, M.; Sattler, C.; Pitz-Paal, R.  
*Applied Thermal Engineering* **2014**, *73* (1), 1006-1013

Vieten, J; Gubán, D.; Lachmann, B.; Bulfin, B.; Kaunzner, D., patent application pending (file no DE 10 2019 126 114.7)
Energy balance of combined PSA and thermochemistry vs. state of the art

Per mol of nitrogen

**PSA:**  \[ w_{\text{sep}} = \ln \left( \frac{p_{O_2,\text{in}}}{p_{O_2,\text{out}}} \right)^2 \cdot 1000 \text{ Jmol}^{-1} \]


**Combined PSA + thermochemistry:**

\[ q_{\text{sep}} = \ln \left( \frac{p_{O_2,\text{in}}}{p_{O_2,\text{trans}}} \right)^2 \cdot \eta_{\text{elec}}^{-1} \cdot 1000 \text{ Jmol}^{-1} \]

\[ + q_{\text{thermochem}} \cdot p_{O_2,\text{trans}} \cdot \eta_{\text{solid\textendash}solid} \cdot \text{mol bar}^{-1} \]

with heat → electricity conversion efficiency \( \eta_{\text{elec}} = 0.3 \)
\( p_{O_2,\text{in}} = 0.21 \text{ bar} \)
\( q_{\text{thermochem}} \) for \( \text{Sr}_{0.875}\text{Ba}_{0.125}\text{Fe}_{0.875}\text{Co}_{0.125}\text{O}_{3-\delta} \),
reduction at 600 °C, \( p_{O_2} = 10^{-3} \text{ bar} \)
oxidation at 400 °C, \( p_{O_2} = 10^{-6} \text{ bar} \)

**Cryogenic AS:**  \[ w_{\text{cryo}} = 12 \text{ kJmol}^{-1} \]

Combined system is more efficient than cryogenic AS

Follow-up project - outlook

Investigation of the entire value chain from hydrogen, nitrogen and oxygen to the fertilizer product.
Thank you for your attention!