Chemical Looping Reforming with Packed Bed Technology: Experimental Study and Modelling

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OUTLINE

- Motivation of the study
- Description of the concept
- Experimental study
- Conclusions
- Future works
• **Chemical Looping Reforming** has been studied only using interconnected Circulating Fluidized Beds but H₂ production (as well as CH₃OH) is more convenient (techno-economic) at high pressure
  → **Packed Bed Reactor**

• **Fuel-to-chemicals conversion** is less demanding in terms of heat management than fuel-to-heat: the overall heat of reaction is lower when compared to fuel combustion
  → **CLR vs CLC**

• O₂ (from ASU) and H₂O (from steam turbine extraction) are not for free
  → **auto-thermal reforming using oxygen carrier**

• **CCUS** applied to chemical industry
  → **CO₂ capture convenient without subsides (e.g. carbon tax)**

• Exploiting **chemical looping technology** in other industrially relevant processes
  → **chemical looping convenient without CO₂ capture policies**
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The main concept:

- Oxidation
  - Me (i.e. Ni)
  - MeO (i.e. NiO)
  - Air

- Reduction
  - CO₂ + H₂O
  - PSA offgas

- Reforming
  - CH₄ (+H₂O)

Reformed syngas
The concept for $\text{H}_2$ production

\[ \eta_{\text{ref}} = 75.4\% \]

\[ \text{HR} = 3.04 - 3.14 \text{ Gcal/kNm}^3_{\text{H}_2} \]

\[ \text{EE} = 30 - 40 \text{ kWh/kg}_{\text{H}_2} \]

$\text{CO}_2 + \text{H}_2\text{O}$

Reformate (39.4\%$\text{H}_2$, 29\%$\text{H}_2\text{O}$, 19.2\%$\text{CO}$, 11\%$\text{CO}_2$, 1.1\%$\text{CH}_4$)

$\text{H}_2\text{O}$

PSA offgas (CH$_4$ 2.5\%, CO 13.7\%, $\text{H}_2$ 28.3\%, $\text{CO}_2$ 55.5\%)

Gas turbine

Air

N$_2$

$\text{CO}_2 + \text{H}_2\text{O}$

Steam

HT-WGS

PSA

$\text{H}_2$

Export steam (180°C, 6 bar)

Import steam at (500°C, 100 bar)

Natural gas

$\text{H}_2\text{O}$

PSA

Steam

Reformate (39.4\%$\text{H}_2$, 29\%$\text{H}_2\text{O}$, 19.2\%$\text{CO}$, 11\%$\text{CO}_2$, 1.1\%$\text{CH}_4$)

$\text{CO}_2 + \text{H}_2\text{O}$

Steam
## Advantages:

- The system is convenient also when CO₂ capture is considered
- Compared to FTR-SMR there are less conversion/separation steps
- Steam to process is significantly lower: S/C for FTR is 3.4; in this process is 1.9 (comb. ATR/FTR)
- Conventional turbomachines are considered
- The technology is flexible to different applications (i.e. Methanol, Fischer-Tropsch, etc.)

### Table

<table>
<thead>
<tr>
<th></th>
<th>units</th>
<th>FTR-SMR</th>
<th>FTR-SMR</th>
<th>CLR-PBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ capture</td>
<td></td>
<td>NO</td>
<td>MDEA</td>
<td>H₂O cond</td>
</tr>
<tr>
<td>reforming efficiency (LHV basis)</td>
<td>%</td>
<td>74</td>
<td>69</td>
<td>75.4</td>
</tr>
<tr>
<td>Heat Rate (no steam export)</td>
<td>Gcal₁₅₂/kNm³₃_H₂</td>
<td>3.45</td>
<td>3.71</td>
<td>3.43-3.55</td>
</tr>
<tr>
<td>Heat Rate (with steam)</td>
<td>Gcal/kNm³₃_H₂</td>
<td>3.21</td>
<td>3.69</td>
<td>3.04-3.14</td>
</tr>
<tr>
<td>Electricity (prod/cons)</td>
<td>GWh/kg_H₂</td>
<td>0.3</td>
<td>-10</td>
<td>30-41.8</td>
</tr>
</tbody>
</table>

- The reactor model has been validated for CLC using Cu, Ni, Fe and Mn oxygen carriers
- The model has been used for design and optimization of dynamically operated PBR
- Pseudo-homogeneous model
- Radial temperature or concentration gradients are neglected
- Heat losses through the reactor wall are neglected (not true for lab-scale experimental validation)
- Kinetics of Ni/CaAl$_2$O$_4$ G-S reactions and heterogeneous reactions are based on Medrano(2015)

4. Medrano JA, Hamers HP, Williams G, van Sint Annaland M, Gallucci F, NiO/CaAl$_2$O$_4$ as active oxygen carrier for low temperature chemical looping applications, accepted for publication (Applied Energy)
- Reduction with PSA off-gas leads to full gas conversion and the gas is delivered at high temperature.
- The reforming step is providing H\textsubscript{2}-rich gas at the equilibrium conditions. Due to the lower temperature, the CH\textsubscript{4} conversion decreases at the end of reforming.
- During Oxidation the Gas temperature is in the range of 770-800°C.
The OXIDATION step heats up the bed (850-900°C)

The REDUCTION with PSA-offgas moves the heat front to the reactor outlet (cooling less than 30% of the bed)

The REFORMING acts as heat removal:
- the heat front cools down the reactor ‘from left to right’
- the reaction front cools down the reactor ‘from top to down’
the experiments

small size PBR (heated)
(about 500 g of OC/catalyst)
10-20 L/min flow rate (1 bar up to 1100°C)

medium size PBR (semi-adiabatic)
(about 5 kg of OC/catalyst)
50-160 L/min flow rate (7 bar up to 1100°C)
the experiments

REATIONS:

RED:  
\[
\begin{align*}
H_2 + NiO & \rightarrow H_2O + Ni \\
CO + NiO & \rightarrow CO_2 + Ni \\
CH_4 + 4NiO & \rightarrow 2H_2O + CO_2 + 4Ni \\
\end{align*}
\]
\[\Delta H_R = -15 \text{ kJ/mol}_i \]
\[\Delta H_R = -47 \text{ kJ/mol}_i \]
\[\Delta H_R = 134 \text{ kJ/mol}_i \]

REF:  
\[
\begin{align*}
CH_4 + H_2O & \leftrightarrow CO + 3H_2 \\
CH_4 + CO_2 & \leftrightarrow 2CO + 3H_2 \\
CO + H_2O & \leftrightarrow CO_2 + H_2 \\
\end{align*}
\]
\[\Delta H_R = 206 \text{ kJ/mol}_i \]
\[\Delta H_R = 247 \text{ kJ/mol}_i \]
\[\Delta H_R = -41 \text{ kJ/mol}_i \]

OX:  
\[
\frac{1}{2} O_2 + Ni \rightarrow NiO \\
\]
\[\Delta H_R = -468 \text{ kJ/mol}_i \]

small size PBR (heated)
10 L/min flow rate (1 bar up to 1100 °C)

Reactor Length 0.5 m
Ni-CaAl$_2$O$_4$ as catalyst/oxygen carrier
The stability of the OC has been tested for more than 200h of operation by checking the breakthrough of the H$_2$ using 10 l/min (20 H$_2$ / 20 H$_2$O / 60 N$_2$)

- Different breakthroughs occur in presence of syngas (H$_2$/CO$_2$/H$_2$O 20/20/10)
- Reverse WGS after the OC reduction has been completed
REFORMING

- Different industrially relevant compositions (combination of CH₄/H₂O/CO₂) diluted with N₂ have been tested.
- The experiments have been done at 900°C, the same tests will be carried at 800°C.
- The CH₄ full conversion has been achieved in both cases (working with high H₂O or CO₂ dilution).
- The methane reforming (both steam and dry) reduces the temperature → carbon deposition control has to be taken into account.

The experiments

Reformate composition 10 L/min CH₄/H₂O/N₂ 10/50/40

Steam Reforming

Dry Reforming

Bed Temperature profile (Reforming)
the kinetic model is predicting the breakthrough of the oxygen with high accuracy → results confirms the previous experiments by Kooiman et al. (2015) using the same OC and reactor

the temperature rise is almost 600°C) very close to the adiabatic value (≈700°C)

The thermal model is not able to catch the temperature rise at the beginning of the reactor (heat losses model need to be refined and adjusted)
Chemical Looping Reforming is a very promising way to combine \( \text{H}_2 \) production and \( \text{CO}_2 \) capture

A preliminary assessment shows already the gain (+1.5 percentage points compared to benchmark technologies)

Several industrial relevant processes can benefit from chemical looping

Commercial Ni-based OC has been (is being) successfully tested in a lab-scale reactor (more than 200 h)

The first lab tests confirm the proof-of-principle (at 900°C and 1 bar for 10 L/min of syngas using different composition)

Carbon deposition play an important role due to the temperature variation (high syngas dilution)

Reformate composition is different than conventional plant (is that a problem in case of plant retrofitting?)

...but the way is long →
### Experiments
- Mapping the operating conditions of the reactors: composition, temperature, dilution (i.e. S/C), flow rate
- Oxygen carrier characterization and stability test (under multiple cycles)
- Scale-up from 10 L/min (small PBR) to 100 L/min and 5 bar @TU/e

### Modelling
- Design of the reactor
- Investigation with different reactor concepts
- Heat transfer modelling (i.e. heat losses, etc...)
- Heat management strategies
- Techno-economic assessment of full scale plant and comparison with conventional technologies for H₂ production
- Techno-economic assessment of the system for different process (CH₃OH, Fischer-Tropsch, etc..)
THANK YOU FOR YOUR ATTENTION!

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