Experimental investigation and numerical simulation of CO-to-CO2 shift conversion for enrichment in hydrogen of syngas from air-blown updraft coal gasifiers

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Outlook

✔ Introduction

✔ Experimental method
  ✗ Experimental apparatus
  ✗ Catalyst and reactant flow rates
  ✗ Numerical prediction of catalyst performance

✔ Results
  ✗ High temperature reactor
  ✗ Low temperature reactor
  ✗ Whole WGSR

✔ Conclusion
Introduction

In WGSR, carbon monoxide reacts with steam to produce hydrogen, carbon dioxide and trace components which are separated for final use or captured for sequestration in the case of CO₂, using CCS technologies.

The purpose of the present study is to investigate the performance of the WGSR by varying the main process parameters:

- Catalyst type (Fe/Cr or Pt/Al for high temperature and Cu/Zn or Pt/Al for low temperature);
- Residence time of reactants in the catalyst bed;
- Reaction temperature;
- H₂O/CO ratio.

The experimental results are compared with numerical analyses based on equilibrium and kinetic models for the WGSR simulations.
Outlook

✔ Introduction

✔ Experimental Apparatus

✔ Experimental method

✔ Conclusion
Experimental Method

✓ Experimental Apparatus

✓ Water-gas mixture preparation unit
✓ Water gas shift reaction unit
✓ Gas analysis unit

<table>
<thead>
<tr>
<th></th>
<th>Reactor</th>
<th>Max bed length [mm]</th>
<th>Diameter [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>High temperature</td>
<td>453</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Low temperature</td>
<td>226.5</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

Department of Mechanical Engineering, University of Cagliari (DIMECA)
## Experimental Method

### Catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Temperature range [°C]</th>
<th>Geometry and Size [mm]</th>
<th>Nominal Content [wt. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sud-Chemie ShiftMax 120</td>
<td>300÷380</td>
<td>Cylindrical 6 × 3</td>
<td>Fe$_2$O$_3$ 80</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cr$_2$O$_3$ 8.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CuO 2</td>
</tr>
<tr>
<td>Sud-Chemie ShiftMax 200-C18</td>
<td>180÷250</td>
<td>Cylindrical 5 × 3</td>
<td>CuO 58</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ZnO 31</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al$_2$O$_3$ 11</td>
</tr>
<tr>
<td>PRAXAIR</td>
<td>200÷800</td>
<td>Spherical 3 Ø</td>
<td>Pt 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al$_2$O$_3$ 99</td>
</tr>
</tbody>
</table>

*High temperature reactor*
Experimental Method

✔ Length of Catalyst bed
  ✗ HTR bed length: 1/2 and 1 of max allowed BL (453 mm)
  ✗ The full bed length is used in LTR: 226,5 mm

✔ Mixture composition in HTR
  ✗ The mass flow rate of the dry feeding gas: 0.5 kg/h;
  ✗ Sets of H₂O/CO ratios: 2, 3, 4, 6 and 8;
  ✗ Water flow rate: 0.223, 0.334, 0.445, 0.667 and 0.890 kg/h.

✔ Mixture composition in LTR
  ✗ The feeding mixture is composed of H₂, CO, CO₂, N₂ and steam

✔ Experimental study is supported by a computational model based on:
  ✗ Continous Stirred Tank Reactor equilibrium model (CSTR-EQ)
  ✗ Ideal Continuous Plug Flow Tubular Reactor model (PFR)

<table>
<thead>
<tr>
<th>Species</th>
<th>Molar weight [kg/kmol]</th>
<th>Mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>2.016</td>
<td>0.180</td>
</tr>
<tr>
<td>CO</td>
<td>28.010</td>
<td>0.300</td>
</tr>
<tr>
<td>CO₂</td>
<td>44.010</td>
<td>0.060</td>
</tr>
<tr>
<td>N₂</td>
<td>28.014</td>
<td>0.460</td>
</tr>
<tr>
<td>Mixture</td>
<td>24.293</td>
<td>1.000</td>
</tr>
</tbody>
</table>
Outlook

✔ Introduction

✔ Experimental method
   ✓ Experimental apparatus
   X Catalyst and reactant flow rates
   X Numerical prediction of catalyst performance

✔ Results
   X High temperature reactor
   X Low temperature reactor
   X Whole WGSR

✔ Conclusion
Results

✔ High temperature reactor: Pt/Al Catalyst

✗ Operating temperature: 300, 330, 360 °C

To identify the influence of increasing bed length on the performance of the WGSR, the distribution of the relatively improving efficiency (RIE) is used:

![Graph showing RIE % Pt/Al, BL=1/2->1 vs. H2O/CO ratio]

**RIE (relatively improving efficiency)**:

\[
RIE(\%) = \frac{CO_{\text{conversion}_e} - CO_{\text{conversion}_o}}{CO_{\text{conversion}_o}} \cdot 100\%
\]

Where the subscripts \(o\) and \(e\) denote the original and extended bed lengths, respectively.


Half Bed length-Pt/Al catalyst  Full Bed length-Pt/Al catalyst
Results

✔ High temperature reactor: Fe/Cr catalyst
✗ Operating temperature: 300, 330, 360 °C

RIE (relatively improving efficiency) [%]:

\[
RIE \% = \frac{CO_{\text{conversion}} - e - CO_{\text{conversion}} - o}{CO_{\text{conversion}} - o} \times 100 \%
\]

Where the subscripts o and e denote the original and extended bed lengths, respectively.


Half Bed length-Fe/Cr catalyst
Full Bed length-Fe/Cr catalyst
Results

✔ Low temperature reactor

✗ Operating temperature: 200 °C

Full Bed length

Conversion Gap
Testing the whole HT and LT WGSR in the same reactor

When the Pt/Al catalyst is used, the whole WGSR carries out a strong reduction in CO concentration, up to equilibrium values.
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✔ Conclusion
Conclusion (1)

The experimental and numerical studies described above provide significant deepening of the mechanisms that regulate the WGSR using different commercial catalyst and an operating mixture similar to syngas.

- **Residence time determines the cost and performance of the WGSR, mainly for HTR.**
- **Pt/Al catalyst can operate in a very short residence time condition and reach a high-performance CO conversion.**
✓ A WGSR operated with Fe/Cr in HTR can be enhanced by an increase in reaction temperature.

✓ In LTR the Cu/Zn and Pt/Al catalysts perform the reaction practically in a chemical equilibrium condition.

✓ With Pt/Al catalyst both high and low temp. reactions can be performed in a single stage reactor. This solution makes it possible to avoid cooling between the two reaction stages.
THANKS FOR YOUR ATTENTION!

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