New Technologies for gas cleaning and CO\(_2\) capture – Summary results of the Polish National Strategic Research Programme

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Polish National Strategic Research Programme, „Coal gasification”

Polish National Strategic Programme
Advanced Technologies for Energy Generation

Planned co-financing from NCRD in 2010-2015 about PLN ~300 000 000
(€ ~72 100 000)

Multidisciplinary programme concerning
high Energy Efficiency,
Clean Coal Technologies,
reduction of pollutants emission to the atmosphere,
biomass and waste utilization
Project No. 3:

Development of coal gasification technology for highly efficient production of fuels and energy generation

Participants:

- AGH University of Science and Technology (Leader),
- Institute for Chemical Processing of Coal (IChPW),
- Central Mining Institute (GIG),
- Silesian University of Technology,
- KGHM Polska Miedź S.A., (copper and silver production),
- Katowicki Holding Węglowy S.A., (coal production),
- TAURON Polska Energia S.A., (management of Tauron group),
- TAURON Wytwarzanie S.A., (power generation company),
- TAURON Wydobycie S.A., (coal production),
- Grupa Azoty S.A. (fertilizer company).

Total budget: PLN 96 mil. (22.9 M€)
NCRD financing: PLN 80 mil. (19 M€)
The objectives of coal gasification R&D project

The primary goal of the Project (the Research Task No. 3) is to develop the optimal configuration, process guidelines and design of coal gasification systems constituting the basis for the construction of national demonstration plant, particularly:

- development and validation of a pilot-scale pressure coal gasification process,
- development and testing of underground hard coal gasification process,
- optimization and testing of the bench-scale processes for the purification and conversion of gas in conjunction with a CO$_2$ capture system.
Work Packages oriented on gas cleaning and CO$_2$ capture

- Raw syngas cleaning
- CO$_2$ capture
  - Absorption
  - Calcium looping
- Gas conversion
  - Adsorption
  - High-temperature H$_2$S removal
  - Hydrogen separation (via CLC)
  - Tars conversion

...beyond standards!
Calcium Looping

Calciner (850 - 950°C) → CaO

CaCO₃ → CaO + CO₂ \( \Delta H_{298}^0 = -178.3 \text{ kJ/mol} \)

\[ C + O_2 \rightarrow CO_2 \quad \Delta H_{298}^0 = -393.5 \text{ kJ/mol} \]

Carbonator (650 - 750°C) → CaCO₃

CO + H₂O → CO₂ + H₂ \( \Delta H_{298}^0 = -41.2 \text{ kJ/mol} \)

\[ CaO + CO_2 \rightarrow CaCO_3 \quad \Delta H_{298}^0 = -178.3 \text{ kJ/mol} \]

Coal

O₂

CO₂

Syngas with lower content of CO₂ and increased content of H₂

Hot syngas

Calciner:
- C + O₂ → CO₂ \( \Delta H_{298}^0 = -393.5 \text{ kJ/mol} \)
- CaCO₃ → CaO + CO₂ \( \Delta H_{298}^0 = 178.3 \text{ kJ/mol} \)

Carbonator:
- CaO + CO₂ → CaCO₃ \( \Delta H_{298}^0 = -178.3 \text{ kJ/mol} \)
- CO + H₂O → CO₂ + H₂ \( \Delta H_{298}^0 = -41.2 \text{ kJ/mol} \)
Calcium Looping

Scheme of calcium looping bench scale installation at IChPW
Calcium Looping

Calcination of the limestone

Carbonation of the limestone

Example of experiment: limestone flux: 30 kg/h, steam to carbonator: 1 Nm³/h

<table>
<thead>
<tr>
<th></th>
<th><strong>Inlet gas to carbonator</strong></th>
<th><strong>Outlet gas from carbonator</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gas flow Nm³/h</td>
<td>Gas concentration without N₂</td>
</tr>
<tr>
<td>CH₄</td>
<td>0,050</td>
<td>5,19%</td>
</tr>
<tr>
<td>H₂</td>
<td>0,250</td>
<td>25,85%</td>
</tr>
<tr>
<td>CO</td>
<td>0,467</td>
<td>48,28%</td>
</tr>
<tr>
<td>N₂</td>
<td>0,304</td>
<td>-</td>
</tr>
<tr>
<td>CO₂</td>
<td>0,200</td>
<td>20,68%</td>
</tr>
<tr>
<td>O₂</td>
<td>0,000</td>
<td>0,00%</td>
</tr>
<tr>
<td>sum</td>
<td>1,271</td>
<td>100,00%</td>
</tr>
</tbody>
</table>

...beyond standards!
H₂S removal from hot syngas

- Two parallel columns with bed of monolithic sorbent which are working in the two modes: adsorption mode and regeneration mode.

- Sorption of H₂S is occurring at 500 - 550°C on the sorbent according to the reaction:
  \[ \text{H}_2\text{S} + \text{ZnO} \rightarrow \text{ZnS} + \text{H}_2\text{O} \]

- Untill the breakthrough of the bed the stream of hot syngas is switched to the second column with regenerated sorbent.

- Used sorbent is regenerated up to 700°C with O₂/N₂ stream to produce SO₂ according to the reaction:
  \[ \text{ZnS} + \text{O}_2 \rightarrow \text{ZnO} + \text{SO}_2 \]
H₂S removal from hot syngas

Experiments:
- one reactor (column) with bed of Zn-Co-Ti monolithic sorbent
- the gases were switched after breakthrough of the bed
- load of sorbent: 510 g (566 cm³).
- sulfidation temperature: 540°C,
- syngas composition: 50% vol. CO, 24.4% vol. H₂, 20% vol. CO₂, 0.6% vol. H₂S, 5% vol. CH₄,
- sulfidation GHSV: 446 and 892h⁻¹,
- regeneration temperature: 540 – 650°C,
- regeneration gas composition: 5% vol. O₂ in nitrogen,
- regeneration GHSV: 446 and 892h⁻¹

Reactor scheme: A – layer of Al₂O₃ grains; B - bed of monoliths; T1, T2, T3 – thermocouple 3; P1 - port to sampling.
H$_2$S removal from hot syngas

**Sulfidation of the sorbent**

**Regeneration of the sorbent**

Monolithic sorbent: fresh (A) and used (B).
Separation of gas from coal gasification to hydrogen and carbon dioxide streams using chemical looping

**Goal:**
Elaborating of concept of enriching synthesis gas with hydrogen using chemical looping.

New concept of synthesis gas separation from coal gasification was proposed. Pure hydrogen is obtained together with carbon dioxide separation. Main advantage of the process is low temperature of reaction conducted in reactors working in chemical loop, which is the result of using appropriate catalyst (oxygen carrier). Syngas is used as fuel and strong reducing agent. Steam is used as oxidizing agent, which enables producing of pure hydrogen and catalyst regeneration.

Basic concept of pure hydrogen production connected with coal gasification.
Separation of gas from coal gasification to hydrogen and carbon dioxide streams using chemical looping

Scheme of experimental set up for research on hydrogen separation in chemical looping.

Oxygen carrier requirements:

- Sufficient oxygen transport ability
- Favorable thermodynamics towards conversion to CO₂ and H₂O in chemical loop
- High reactivity in redox reactions after multiple cycles
- Low abrasity
- Low susceptibility towards carbon deposits formation
- Good fluidization properties (no agglomeration)
- Low cost
- Environmentally friendly
Separation of gas from coal gasification to hydrogen and carbon dioxide streams using chemical looping

Catalyst oxidation in H$_2$O/Ar in programmed temperature after reduction at 400°C.

SEM images of catalyst after reduction in CO at 600 °C.

Hydrogen concentration during reduction cycles at 400°C.

Hydrogen concentration during oxidation cycles using H$_2$O at 400°C.

Process parameters of hydrogen separation from synthesis gas using chemical looping were chosen. Guidelines for upscaling of the process were elaborated.

...beyond standards!
Research on thermocatalytical conversion of tars in raw gas from coal gasification

Goal:
Elaborating of effective thermocatalytic process of tars conversion in raw gas from coal gasification in reactor with porous barrier.

Nickel catalyst (10 % weigh) set on mixed cerium and zirconium oxide (Ce$_{0.62}$Zr$_{0.38}$O$_2$)

Scheme of experimental set up for research on thermocatalytic process of tars conversion in raw gas from coal gasification

...beyond standards!
Research on thermocatalytical conversion of tars in raw gas from coal gasification

Tar compounds are important components of the raw gas that is obtained from the gasification of solid fuels. Tars are unnecessary wastes that must be removed. Modern methods utilize thermal cracking in the absence of oxygen or an oxidizing atmosphere, as well as catalytic steam or the autothermal reforming of tar compounds contained in the raw synthesis gas.

Conducting high-temperature conversion without a catalyst requires an energy supply to effectuate the desired reactions. Typically, this process requires a heat supply to facilitate the endothermic cracking and reforming reactions through the diaphragm. The partial oxidation (POX) of tar products and raw gas can also supply the energy for endothermic reactions.

One of modern solution to supply heat to the reaction system is using a reactor with a porous barrier. These porous barriers consist of a ceramic filter, which functions as a distributor of the oxidant inside the reactor. Oxidation only occurs close to the surface of the porous barrier. This approach is safer than traditional methods because it decreases the partial pressure of oxygen. Partial oxidation is preferable to total oxidation because the temperature gradient in the reactor is minimized, which also minimizes local gas overheating.
Research on thermocatalytical conversion of tars in raw gas from coal gasification

Comparison of thermal and thermocatalytic tars conversion in raw gas.

Ni-Ce-Zr catalyst activity in conversion of 1-methylnaphtalene

...beyond standards!
The research results presented herein were obtained during the course of the project "Development of coal gasification technology for high-efficiency production of fuels and energy generation", Task No. 3 of the Strategic Program for Research and Development: "Advanced energy generation technologies" funded by the Polish National Center for Research and Development.

Thank you for your kind attention