Power-to-gas process with high temperature electrolysis and CO2 methanation
Myriam De Saint Jean, Pierre Baurens, Chakib Bouallou

To cite this version:
POWER-TO-GAS PROCESS WITH HIGH TEMPERATURE ELECTROLYSIS AND CO$_2$ METHANATION

IRES 2013 – Session E1

Myriam De Saint Jean$^{1,2}$
Pierre Baurens$^1$
Chakib Bouallou$^2$

$^1$LTH LITEN CEA & $^2$MINES ParisTech

Contact: myriam.desaintjean@cea.fr

NOVEMBER 19$^{th}$ 2013
1. Energy background
2. Power-to-Substitute Natural Gas process with high temperature steam electrolysis and CO$_2$ methanation
   1. Power-to-SNG : architecture studied
   2. High temperature steam electrolysis
      • Presentation
      • Modelling
   3. CO$_2$ methanation
      • Presentation
      • Modelling
   4. Full power-to-SNG process
3. Results and conclusion
   1. Parametric study results
   2. Conclusion
ENERGY BACKGROUND
Renewable resource development: 3 issues for transportation and distribution electrical networks

- High consumption periods
- Excess electric production
- Transportation of energy from production areas to consumption areas

Source: Spetch et al. 2011

SNG
Substitute Natural Gas (methane)
A LINK BETWEEN TWO NETWORKS

Electric ressource
- Unstorable
- Irregular production
- Network congestion

Excess
Production = Consumption

Power-to-SNG

Gas-to-heat
Gas-to-mobility
Gas-to-chemistry
Gas-to-power

Excess Production = Consumption

Distribution and storing
Natural gas network

Final user

Avantages PtSNG and GtP
- Use of existing natural gas network
- Mid or long term storage
- Transportation
- Production of electricity
- Connection of the 2 networks
POWER-TO-SNG PROCESS
WITH HIGH TEMPERATURE STEAM ELECTROLYSIS AND CO$_2$ METHANATION
STUDIED POWER-TO-SNG PROCESS ARCHITECTURE

- Thermal integration
- Methanation
- Recycling CO\(_2\), H\(_2\)O and H\(_2\)

\[ W = \frac{HHV}{\sqrt{\rho}} \]

<table>
<thead>
<tr>
<th></th>
<th>NG type H</th>
<th>NG type L</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHV (kWh/Nm(^3))</td>
<td>10,7 – 12,8</td>
<td>9,5 – 10,5</td>
</tr>
<tr>
<td>W (kWh/Nm(^3))</td>
<td>13,4 – 15,7</td>
<td>11,8 – 13</td>
</tr>
<tr>
<td>Composition (% vol)</td>
<td>CO &lt; 2, CO(_2) &lt; 3, H(_2) &lt; 6</td>
<td></td>
</tr>
<tr>
<td>(mg/Nm(^3))</td>
<td>H(_2)O &lt; 55</td>
<td></td>
</tr>
</tbody>
</table>

- Steam reforming
- Purification

Myriam De Saint Jean
IRES 2013
Power-to-SNG process with HTSE and methanation
HIGH TEMPERATURE STEAM ELECTROLYSIS

**HTSE avantages**
- High temperature : $\Delta H$ decrease
- Irreversibility decrease
- High efficiency
- Reversible (SOEC / SOFC techno)
- Thermal behaviours:
  - Exo, auto et endothermal
- Reactants : $H_2O$ and / or $CO_2$ : co-electrolysis

**HTSE current limitations**
- R&D
- Cost
- Long-term degradation of performances

\[ \text{H}_2\text{O}_{(g)} \leftrightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \]

\[ T = 1073 \text{ K} \]

Source: Graves et al. 2011

Source: Graves et al. 2011

Power-to-SNG : HSTE + CO$_2$ methanation
HTSE Modelling: To determine $P_{\text{elec}}$ and $N_{\text{cell}}$ for an incoming flow

- SOEC technology
- $U_{\text{op}} = U_{\text{tn}}$ and SC: fixed values
- Molar and energy balances: $P_{\text{elec}}$
- Electrochemical modelling: exp. law
- Determination of $N_{\text{cell}}$ (and $j$)
- Correction with pressure and stack effects

**Experimental and phenomenological laws**

\[
\begin{align*}
\dot{n}_{\text{cath, cell}} & = -0.829 \ SC + 83.2 \quad \text{with air sweep} \\
\dot{n}_{\text{cath, cell}} & = -0.727 \ SC + 81.8 \quad \text{with O}_2 \text{ sweep}
\end{align*}
\]

\[
R_{\text{eq}} = \left( U_{\text{op}} - U_{\text{Nernst}} \right) / j \quad \Omega \cdot \text{cm}^2
\]

**Pressure effect and stack effect**

\[
R_{\text{eq}} = R_{\text{eq, P}} \cdot P^{-0.09}
\]

\[
R_{\text{eq, Stack}} = (R_{\text{eq, cell}} + 0.034) N_{\text{cell}}
\]

**Experimental data**

- SC, $X_{\text{O}_2 \text{ anode}}$

**Modelling**

Calculation of $j$ and $N_{\text{cell}}$ with errors up to 40% → cell dispersion effect
CO₂ METHANATION

**Sabatier reaction**  
\[ \text{CO}_2 + 4 \text{H}_2 \rightleftharpoons \text{CH}_4 + 2 \text{H}_2\text{O} \]

**RWGS reaction**  
\[ \text{CO}_2 + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO} \]

**CO methanation**  
\[ \text{CO} + 3 \text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \]

**Carbon cracking**  
\[ \text{CO}_2 + 2 \text{H}_2 \rightleftharpoons \text{C}_{(s)} + 2 \text{H}_2\text{O} \]

- Catalysed reaction
- Favorable operating conditions for CH₄ production: \( P \uparrow \text{ et } T \downarrow \)

**Avantages of CO₂ methanation**
- No CO at moderate T
- High CH₄ selectivity
- Exothermal reaction
- High conversion yield
- Existing catalysts

**Current limitations of CO₂ methanation**
- Poor literature on kinetic laws
- Not a lot of experimental data published, preference given to syngas (CO + H₂) methanation

Equilibrium at \( P = 15 \text{ bar} \) for \( \text{H}_2/\text{CO}_2 = 4 \)
Methaneation modelling

\[ \text{CO}_2 + 4 \text{H}_2 \leftrightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \]

- 1D plug-flow reactor modelling
- Kinetic law (cat Ru)
- Pressure \(\approx 16\) bar
- Adiabatic behaviour
- Inlet temperature = 573 K
- Outlet temperature < 973 K

\[
r = 2691.7 \times 10^3 \exp\left(-\frac{64121}{RT}\right) \left(\frac{P_{n}^{n}P_{H_2}^{4n}}{P_{CH_4}^{n}} - \frac{P_{H_2O}^{2n}}{K_{eq}(T)^{n}}\right)
\]

\[
K_{eq}(T) = \exp\left(\frac{28183}{T^2} + \frac{17430}{T}\right) - 8.254 \ln T + 2.87 \times 10^{-3} T + 33.17
\]

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>1</th>
<th>2</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n)</td>
<td>0.225</td>
<td>0.5</td>
<td>1</td>
</tr>
</tbody>
</table>

Simulation and experimentation agreement for \(n = 0.5\) (\(P = 2\) bar) for \(P_{exp} \in [3.4; 7]\)

Higher \(P\), lower gap between simulation and experimentation, \(\forall n\) used.
Pinch analysis module
Process thermal integration

Cold Utility
Cold unit (273 K)
$EER_{elec} = 1.73$

Hot Utility
Electric heaters
$\eta = 0.90$

$\eta_{AC/DC} = 0.92$

$\Delta P_{hexch} = 0.2 \text{ bar}$

$H_2/H_2O_{HTSE} = 1/9$

$\Delta T_{hexch} = 100-150 \text{ K}$

$H_2/CO_2_{meth} = 1/4$
Energy Efficiency

\[ \eta = \frac{\dot{\eta}_{\text{SNG}} \text{HHV}_{\text{SNG}}}{P_{\text{elec, HTSE}} + P_{\text{elec, mech}} + P_{\text{elec, hot}} + P_{\text{elec, cold}}} \]

Theoretical Energy Efficiency

\[ \eta = \frac{\dot{\eta}_{\text{SNG}} \text{HHV}_{\text{SNG}}}{P_{\text{elec, HTSE}}} = 0.89 \]
SIMULATION RESULTS & CONCLUSION
Injection on H or L gas network: no influence on energy efficiency $\eta$

Kind of network (transportation or distribution): high influence on $\eta$

$CO_2$ origine (separation or storage): high influence on $\eta$

$P_{HTSE}$: very high influence on $\eta$: loss of 7.4 pts (9.6%) regarding ref. case
CONCLUSION

- HTSE modelling for sizing with experimental law
- Adequation between modelling results and experimental data
- Kinetic law and modelling of methanation
- Adequation between simulation results and observed performances
- Scale-up of methanation stage
- Purification of produced SNG

Modelling

- Production of SNG matching with the specifications
- Two gas qualities (H and L) are achievable
- Higher efficiency if
- The process is operated at high pressure
- CO₂ from industrial storage is used

Process simulation

Results and conclusion
Thank you for your attention

POWER-TO-GAS PROCESS WITH HIGH TEMPERATURE ELECTROLYSIS AND METHANATION

IRES 2013  |  myriam.desaintjean@cea.fr