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POWER-TO-GAS PROCESS WITH HIGH TEMPERATURE ELECTROLYSIS AND CO₂ METHANATION

IRES 2013 – Session E1
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NOVEMBER 19th 2013
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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
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      • Modelling
   3. CO$_2$ methanation
      • Presentation
      • Modelling
   4. Full power-to-SNG process
3. Results and conclusion
   1. Parametric study results
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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
A LINK BETWEEN TWO NETWORKS

Electric network
- Use of existing natural gas network
- Mid or long term storage
- Transportation
- Production of electricity
- Connection of the 2 networks

Power-to-SNG

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

Irregular production
- Unstorable
- Irregular production
- Network congestion

Final user

Avantages PtSNG and GtP

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POWER-TO-SNG PROCESS
WITH HIGH TEMPERATURE STEAM ELECTROLYSIS AND CO$_2$ METHANATION
STUDIED POWER-TO-SNG PROCESS ARCHITECTURE

STORING

Methanation

Recycling CO₂, H₂O and H₂

Thermal integration

HTSE

Power-to-SNG : HSTE + CO₂ methanation

Specification setting

Wobbe index

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

NG type H  NG type L

HHV (kWh/Nm³)
10,7 – 12,8
9,5 – 10,5

W (kWh/Nm³)
13,4 – 15,7
11,8 – 13

Composition (%vol)

CO < 2, CO₂ < 3, H₂ < 6

H₂O < 55

Steam reforming

Purification

Thermal integration

HT Fuel Cell

Power-to-SNG  : HSTE + CO₂ methanation

RECOVERY

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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

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To determine $P_{elec}$ and $N_{cell}$ for an incoming flow:

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

Experimental and phenomenological laws:

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

\[ R_{eq} = \frac{(U_{op} - U_{Nernst})}{j} \quad \text{Ω.cm}^2 \]

**Pressure effect and stack effect**

\[ R_{eq} = R_{eq, P} P^{-0.09} \quad \text{for } P [1;10 \text{ bar}] \]
\[ R_{eq, Stack} = (R_{eq, cell} + 0.034) N_{cell} \]

**Experimental data**

\[ n_{cath, cell} (\text{NmL/min.cm}^2) \]

- $O_2$ reg
- Air reg
- C 941 air
- C 944 air
- E 15 O2
- E 18 O2
- D 261 O2

Experimental data and interpolated law linking $\dot{n}_{cath, cell}$ and SC for $T = 1073 K$, $P = 1 \text{ bar}$, $U_{op} = U_{tn}$, $H_2 / H_2O = 10 / 90$, on cells referenced C 941, C 944, D 261, E 15 et E 16.

**HTSE modelling**

Modelling: Calculation of $j$ and $N_{cell}$ 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 craking**  \[ \text{CO}_2 + 2 \text{H}_2 \rightleftharpoons \text{C}(s) + 2 \text{H}_2\text{O} \]

- Catalysed reaction
- Favorable operating conditions for \( \text{CH}_4 \) production: \( P \uparrow \) et \( T \downarrow \)

**Avantages of CO₂ methanation**
- No CO at moderate T
- High \( \text{CH}_4 \) 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 \( P = 15 \) bar for \( \text{H}_2/\text{CO}_2 = 4 \)
SIMULATION : METHANATION MODELLING

![Diagram of a plug-flow reactor with fixed-bed catalyst and boundary conditions.](image)

**Methanation modelling**

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

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

\[
\begin{align*}
    r \left[ \text{mol.s}^{-1}.\text{m}^{-3} \right] &= 2691.7 \times 10^3 e^{-\frac{64121}{RT}} \left( \frac{P_n^{\text{CO}_2} P_4^{\text{H}_2}}{K_{eq}(T)^n} - \frac{P_2^{\text{H}_2\text{O}} P_1^{\text{CH}_4}}{K_{eq}(T)^n} \right) \\
    K_{eq}(T) &= \exp \left( \frac{28183}{T^2} + \frac{17430}{T} - 8.254 \ln T + 2.87 \times 10^{-3} T + 33.17 \right)
\end{align*}
\]

<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>

Kinetic law from literature (Cat Ru) [Lunde 1974, Ohya 1997]

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

Higher P, lower gap between simulation and experimentation, \( \forall n \) used
**SIMULATION : PERIMETER AND HYPOTHESES**

AC Electricity:
- HTSE, mechanical work, cold unit, electric heaters

<table>
<thead>
<tr>
<th>Material</th>
<th>Pressure</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>1 bar, 293 K</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>100 bar, 293 K</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>1 bar, 303 K</td>
<td></td>
</tr>
<tr>
<td>Natural gas</td>
<td>4 bar, 293 K</td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>18 bar, 293 K</td>
<td></td>
</tr>
<tr>
<td>Natural gas</td>
<td>4 bar, 293 K</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>1 bar, 293 K</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>40 bar, 293 K</td>
<td></td>
</tr>
</tbody>
</table>

**Pinch analysis module**
**Process thermal integration**

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

- Hot Utility
  - Electric heaters
  - η = 0.90

- η_{AC/DC} = 0.92
- ΔP_{hexch} = 0.2 bar
- ΔT_{hexch} = 100-150 K

- H₂/H₂O_{HTSE} = 1/9
- H₂/CO₂_{meth} = 1/4
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\[ \eta = \frac{\dot{\eta}_{SNG \text{ HHV}_{SNG}}}{P_{\text{elec, HTSE}}} + \frac{P_{\text{elec, mech}}}{P_{\text{elec, hot}}} + \frac{P_{\text{elec, hot}}}{P_{\text{elec, cold}}} \]

\[ \eta_{\text{SNG HHV}_{SNG}} = 0.89 \]
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

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**Electricity consumption**

**Electricity consumption except HTSE**

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$U_{op} = U_{tn}$, $SC = 75\%$, $H_2/CO_2 = 4$, $P_{meth} = 16$ bar, $T_{HTSE} = 1073$ K

**Reference case**: $P_{CO_2} = 100$ bar $P_{SNG} = 4$ bar $P_{HTSE} = 17$ bar $H$ gas

**Sensitivity**: $P_{CO_2} = 5$ bar $P_{SNG} = 16$ and 80 bar $P_{HTSE} = 2.5$ bar $B$ gas

**Ref**

$P_{CO_2} = 5$ bar $P_{SNG} = 16$ and 80 bar $P_{HTSE} = 2.5$ bar $B$ gas

**Results and conclusion**

**Parametric study results**

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

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Thank you for your attention

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