Sorption-enhanced CO₂ methanation to SNG: optimizing conditions in a Ni-Fe/Al₂O₃ fixed bed reactor

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INTRODUCTION

There is a great concern about finding feasible low CO₂ emission energy sources. While renewable sources, like wind and solar power, are increasing their capacity and share in electricity generation [1] [2], most of them depend on weather conditions and cannot provide a reliable supply of energy. Thus, the Power to Gas strategy (PTG or P2G) uses temporary energy surpluses to split water by electrolysis and generate hydrogen, which later reacts with CO₂ to obtain methane (CH₄).

The resulting Synthetic Natural Gas (SNG) can be used as an energy source when other alternatives are not available.

It is possible to modify the equilibrium through use of zeolites as an adsorbent solid, removing water from the reaction atmosphere as soon as it is generated [3]. Hence, a very important matter is in which conditions the Sorption Enhanced Sabatier Reaction (SESaR) is carried out.

EXPERIMENTAL

Catalyst: Ni-Fe (7.5 wt% Ni-2.5 wt% Fe) with γ-Al₂O₃ as support material
AdSORBent solid: LTA zeolite, 5Å
Reactor: fixed bed. 5 thermocouples, located at 1, 3, 6, 9 and 12 cm.
Atmospheric pressure.

Analysis parameters:
- Catalyst weight (W)
- Reactants flowrate (Q)
- Reaction temperature (T)
- Feeding gas (biogas, H₂/CO₂ mixtures)
- H₂/CO₂ proportion

Reaction conditions
W = 0.125, 0.25, 0.5, 0.75 and 1 g.
q = 250 mL(STP)/min.
T = 250, 300, 350 and 400 °C.
CH₄/CO₂ = 7:3 (when feeding biogas).

Stages: 3 methanation stages (M₁, M₂, and M₃) lasting 1 hour, with 2 desorption process (D₁ and D₂) lasting 30 and 10 minutes, respectively. D₁ takes place at the same temperature as M₁, M₂ and M₃, while D₂ is carried out at 500 °C.
There is a previous activation, lasting 2 hours, at 500 °C, with 50 % H₂ and 50 % inert.
5 % N₂ and 5 % Ar were always introduced as an internal standard and as a diluant, respectively.

RESULTS

Table 1. Intensification for the methanation process (ratio H₂/CO₂ = 4:1) quantified as relative amount of water adsorbed (mol H₂O/g zeolite) as a function of temperature. H₂/CO₂ = 4:1. Dashed lines: theoretical equilibrium values

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>M₁</th>
<th>M₂</th>
<th>M₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>2.18E-07</td>
<td>1.29E-04</td>
<td>2.20E-04</td>
</tr>
<tr>
<td>350</td>
<td>4.50E-05</td>
<td>2.16E-04</td>
<td>9.57E-05</td>
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<tr>
<td>300</td>
<td>1.97E-05</td>
<td>1.91E-04</td>
<td>1.36E-04</td>
</tr>
<tr>
<td>250</td>
<td>3.02E-05</td>
<td>3.04E-05</td>
<td>3.05E-05</td>
</tr>
</tbody>
</table>

Table 2. Intensification for the methanation process when using biogas (ratio CH₄/CO₂ = 7:3) as mol H₂O/g zeolite

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>M₁</th>
<th>M₂</th>
<th>M₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>-4.49E-05</td>
<td>-5.18E-05</td>
<td>7.19E-05</td>
</tr>
<tr>
<td>350</td>
<td>-3.02E-05</td>
<td>2.89E-05</td>
<td>1.48E-04</td>
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<tr>
<td>300</td>
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<td>1.96E-04</td>
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<tr>
<td>250</td>
<td>3.02E-05</td>
<td>3.04E-05</td>
<td>3.05E-05</td>
</tr>
</tbody>
</table>

CONCLUSIONS

- With a W/q = 4*10⁻³ g catalyst*min*mL(STP)⁻³, the greatest yields of methanol are achieved.
- When using this W/q ratio, the maximal intensifications are met at 250 °C in the M₁ stage when using biogas and at 300 °C in the M₂ and M₃ stages. When no methane is fed, 300 °C is the optimal temperature for any methanation stage (M₁, M₂ and M₃).
- Similar results are achieved while supplying biogas and when using mixtures of only H₂ and CO₂, except when working at 400 °C (due to reaching equilibrium). At this temperature, yields reduce considerably if methane is part of the feeding mixture.
- Finally, deactivation was proven to exist. Its causes are coke formation and, in a lesser degree, sintering.

REFERENCES

[3] RINCÓN, M. Metanación de CO₂ en reactor de lecho fijo con catalizador basado en Ni-Fe mejorado por adsorción selectiva de agua con zeolitas LTA (Sorption Enhanced Sabatier Reaction – SESaR). (Degree’s Thesis). Universidad de Zaragoza.

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