Modelling and Simulation of Methanation Catalytic Reactor for Renewable Electricity Storage

Hanaâ Er-rbib, Chakib Bouallou*

MINES ParisTech, CES - Centre Efficacité énergétique des Systèmes, 60, Bd Saint-Michel 75006 Paris
chakib.bouallou@mines-paristech.fr

Storing renewable electricity in a natural gas grid is an innovative concept. Renewable energy (wind or solar power) is stored as chemical energy in existing storage capacities, which is an advantage over hydrogen. Storage and power conversion technologies for natural gas are state-of-the-art, commercial technologies unlike hydrogen. A further advantage of storage is the higher energy density of methane. Renewable natural gas substitute (SNG) can be stored, distributed and reconverted on demand in balance power. In this novel approach, renewable energies are converted via reversible solid oxide cells (RSOC) into CO and Hydrogen. Syngas (H₂ and CO) is then converted into methane. Thus, the main conversion step is methanation. Methanation synthesis is a catalytic exothermal process at temperatures of 473-673 K and high pressure from 20 to 70 bar. Syngas enters the methanation reactor with H₂/CO molar ratio of 3. The reactions considered in the proposed model are CO methanation and Water Gas Shift conversion (WGS). Modelling and simulation of the methanation catalytic reactor was developed using the Aspen Plus™ software considering an isothermal fixed bed reactor with steam recovery and CO methanation kinetic on Ni catalyst. The model was validated by comparing the calculated gas concentration profiles (CH₄, CO, CO₂ and H₂) with the recent experimental data obtained on bench-scale and with industrial data. The mean absolute percentage error was 12 %. The mixture leaving methanation reactor contained 47.3 % of CH₄, 1.2 % of H₂, 6.6 % of CO₂, 0.1 % of CO and 44.7 % of H₂O.

1. Introduction

Climate change has been changing as a consequence of anthropogenic activities like excessive combustion of fossil fuels, industrial processes, deforestation and greenhouse gases (GHG) released into the atmosphere (Er-rbib et al., 2012). Potential policies, legislation, and regulation are expected to have an impact on the way, energy is generated, delivered, and used, whether by specific measures or through pricing incentives or disincentives (NREL, 2012). Therefore, it is imperative to develop and promote alternative sources of energy that can lead to sustainability of energy and the environment system. Indeed, renewable electricity contributes to global sustainability through GHG reduction (Van-Dal and Bouallou, 2012).

However, many renewable sources of energy, such as wind power and solar energy provide energy in a fluctuating manner (Čuček et al., 2012). Electrical energy storage (EES) is one solution. EES can potentially smooth the variability in power flow from renewable generation and store renewable energy in order to decrease the cost of integrating renewable power with the electricity grid, increase market penetration of renewable energy, and lead to GHG reductions (Gahleitner, 2013).

A new approach to seasonal storage of renewable energy is based on using excess electricity produced from a renewable source to co-electrolyse steam and a natural pollutant (CO₂) into syngas via RSOC in Solid Oxide Electrolysis Cell (SOEC) mode. The syngas produced (H₂ + CO) enters a methanation reactor where it is converted into CH₄. This gas is then injected into the natural gas network. This methane can be used to produce electricity via RSOC in Solid Oxide Fuel Cell (SOFC) mode when high consumption peaks appear. The global diagram of this process is detailed in the reference Redissi et al. (2013). Besides conversion of SNG to electricity in large power plants, the SNG can also be used in decentralized combined heat and power (CHP) units or as a transportation fuel in the mobility sector. Compared to
hydrogen, methane is a lot easier to handle, requiring less complicated modifications of engines, boilers, power plants and pipelines.

The main conversion step in such process is methanation. The principle of catalytic synthetic production of methane from carbon monoxide and hydrogen was discovered in 1902 by Sabatier and Senderens (Sudiro et al., 2010). It can be described by the CO methanation reaction:

\[
\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H = -206.28 \text{ kJ/mol} \quad (1)
\]

Another reaction called Water Gas Shift (WGS) occurs simultaneously whenever active catalysts are used:

\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H = -41.16 \text{ kJ/mol} \quad (2)
\]

However, the commercial deployment of technologies for the production of SNG has technical constraints. Few experimental pilot plants have been constructed and only one commercial plant was built in North Dakota in 1984 which produces 1.53 billion Nm\(^3\)/y (Sudiro and Bertucco, 2010). The main issue of methanation is the strong exothermicity of the methane formation reactions. Methanation is used as the final syngas purification step in the production of ammonia, but methanation for SNG production is more complex because it involves much higher concentrations of CO and CO\(_2\). The high reaction heat results in a large potential adiabatic temperature increase that may cause catalyst sintering and possibly leads to carbon particle formation (Kopyscinski et al., 2011). Monitoring temperature increase can be ensured by recycling of reacted gas or steam dilution, or by special technologies such as isothermal reactors or fluidized beds, each with indirect cooling by evaporating water (Sudiro and Bertucco, 2010).

In this study the Aspen Plus™ software is used to model and simulate the syngas-to-methane process accommodated in an isothermal fixed bed reactor. The model incorporates the catalytic reaction kinetics for the methanation process. Our simulation results will be compared to experimental data reported in the literature for model validation.

2. Modelling of methanation reactor

2.1 Components and thermodynamical model

The simulation model was developed using Aspen Plus™. The used physical properties of the following compounds are provided in the Aspen Plus™: Water (H\(_2\)O), carbon dioxide (CO\(_2\)), methane (CH\(_4\)), hydrogen (H\(_2\)) and carbon monoxide (CO).

For the thermodynamic model, the RKSMHV2 is used. The RKSMHV2 property method is based on the Redlich – Kwong - Soave equation of state with modified Huron-Vidal mixing rules. This model is used for mixtures of non-polar and polar compounds, in combination with light gases. All the binary interaction parameter values needed for these models were provided by Aspen Plus™ library.

2.2 Model implementation

An isothermal fixed bed reactor is modeled on an ideal Plug Flow Reactor (PFR). An isothermal reactor presents many advantages over an adiabatic methanation reactor: Product recycle may be reduced and one pass operation at high concentration is practical, heat exchange duties and cooling costs are lower, avoiding extremely high reactor exit temperatures and hot spots prevents sintering of the catalyst, thereby preserving catalyst life and the need for internal refractory insulation as normally used for high temperatures adiabatic methanation reactors is eliminated (this is also a cost saving).

Assumptions considered in the model are:
- System is in steady state condition;
- The two phases (bubbles and emulsion) are independent;
- The concentration of gas in the dense phase is the same as that in the catalyst particles;
- Axial mass and heat transfer are assumed to be negligible;
- The reactor operates at isothermal conditions. As a result, the hydrodynamic parameters of the bed, physical properties of components and reaction rate constants are considered to be constant throughout the bed;
- Coke formation is neglected.

The methanation reactor model is based on kinetics developed by Kopyscinski (2010) over a commercial catalyst Ni/Al\(_2\)O\(_3\) (50 wt% Ni/Al\(_2\)O\(_3\), BET surface area = 183 m\(^2\)/g) in fixed bed reactor. The kinetic model over Ni-based catalyst is considered for methanation reaction Eq(1) and water gas shift reaction Eq(2). The kinetic rate equations for the methanation and water gas shift reaction are as follow:
For reaction 1 (Eq(1)):

\[ R_1 = \frac{k_1 \cdot K_{\text{OH}} \cdot P_{\text{CO}}^0 \cdot P_{\text{H}_2}^{0.5}}{(1 + K_{\text{OH}} \cdot P_{\text{CO}}^0 \cdot P_{\text{H}_2}^{0.5})} \]  \quad \text{(mol/kg cat.s)}  \tag{3}

For reaction 2 (Eq(2)):

\[ R_2 = \frac{k_2 \cdot (K_{\text{OH}} \cdot P_{\text{CO}}^0 P_{\text{H}_2}^{0.5} P_{\text{CO}_2}^{0.5})}{(1 + K_{\text{OH}} P_{\text{CO}}^0 P_{\text{H}_2}^{0.5} P_{\text{CO}_2}^{0.5})^2} \]  \quad \text{(mol/kg cat.s)}  \tag{4}

Rate constants \( k_1 \) and \( k_2 \) for the above equations are defined as function of temperature:

\[ k_1 = 3.34 \times 10^6 \exp \left(-\frac{74000}{RT}\right) \]  \quad \text{(mol/kg cat.s)}  \tag{5}

\[ k_2 = 9.62 \times 10^{14} \exp \left(-\frac{161740}{RT}\right) \]  \quad \text{(mol/bar\textsuperscript{1.5}kg cat.s)}  \tag{6}

\( K_{\text{OH}} \), \( K_c \) are the constants which related to surface adsorption in equilibrium that are functions of temperature.

\[ K_{\text{OH}} = 3.97 \times 10^{-7} \exp \left(-\frac{72650}{RT}\right) \]  \quad \text{(bar\textsuperscript{-1/2})}  \tag{7}

\[ K_c = 8.1 \times 10^6 \exp \left(-\frac{61200}{RT}\right) \]  \quad \text{(bar\textsuperscript{-1})}  \tag{8}

\( K_a \) is a combination of the adsorption constants of CO, H\textsubscript{2}, CO\textsubscript{2} and H\textsubscript{2}O or OH

\[ K_a = 9.3 \times 10^7 \exp \left(-\frac{65000}{RT}\right) \]  \tag{9}

\( K_{\text{eq}} \) is the equilibrium constant of water gas shift reaction:

\[ K_{\text{eq}} = \exp \left(\frac{4400}{RT} \cdot 4.063\right) \]  \tag{10}

Pre-exponential factors of the kinetic rate and adsorption coefficients as well as the corresponding activation energies and heats of adsorption described above were taken from Kopyscinski (2010).

This kinetic model operates in a temperature range of [473-673] K and high pressure. Based on the electrolysis output, the molar ratio of H\textsubscript{2} to CO is greater than 3. Under these conditions, coke formation is lower.

The Ergun momentum balance equation is used to give the pressure drop along the PFR reactor:

\[ \frac{dp}{dx} = 150 \left(1 - \varepsilon\right) \mu_\text{g} \frac{u_\text{g}}{d_p^2} + 1.75 \left(1 - \varepsilon\right) \mu_\text{p} \frac{u_\text{p}}{\varepsilon d_p} \]  \tag{11}

In which:

- \( u_\text{g} \): Linear velocity of fluid phase (m/s)
- \( \mu \): Effectiveness factor used for the intra particle transport limitation
- \( d_p \): Particle diameter (m)
- \( \rho \): Density of catalyst bed (kg/m\textsuperscript{3})
- \( \varepsilon \): Void fraction of the catalytic bed

In this work, the methanation reactor not only converts syngas to methane, but it also provides steam needed for electrolysis and heating or for generating electricity by using steam turbine. This method allows increasing global efficiency of the electricity storage process.

In addition, the use of water as coolant helps control the temperature of the process gas within the desired limits. This recognizes the fact that the paramount function of existing methanation systems is to convert syngas to acceptable quality synthetic natural gas rather than to efficiently extract energy from the process.
In order to validate the present simulation model, a comparison of experimental data at a bench-scale (Kopyscinski, 2010) with the simulated results by the present model was made. Then a scale up is validated by an industrial data taken from a technical report (Davis, 1981).

3. Results and discussion

Figure 1 shows the simulation results of gas concentration profiles compared with the experimental one. This latter is provided by Kopyscinski (2010) at bench scale at 593 K, 2 bar and H₂/CO = 5.

![Figure 1: Simulation results compared to experimental data at 593 K and 2 bar](image)

Table 1: Reactor dimensions and operating conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (m)</td>
<td>10.57</td>
</tr>
<tr>
<td>Inner diameter (m)</td>
<td>2.44</td>
</tr>
<tr>
<td>Outside diameter (m)</td>
<td>2.64</td>
</tr>
<tr>
<td>Number of tube</td>
<td>336</td>
</tr>
<tr>
<td>Tube diameter (m)</td>
<td>ID = 0.092, OD = 0.102</td>
</tr>
<tr>
<td>Tube length (m)</td>
<td>6.86</td>
</tr>
<tr>
<td>Catalyst mass (kg)</td>
<td>1,500</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>560.77</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>62</td>
</tr>
<tr>
<td>Mass flow (kg/h)</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>33,021.16</td>
</tr>
<tr>
<td>H₂</td>
<td>5,120.60</td>
</tr>
<tr>
<td>CO</td>
<td>17,362.70</td>
</tr>
<tr>
<td>CO₂</td>
<td>8,989.02</td>
</tr>
<tr>
<td>H₂O</td>
<td>24,841.53</td>
</tr>
</tbody>
</table>

The predicted model results are in excellent agreement with the experimental data. At higher temperatures, the rate of disappearance of CO an H₂ and the rate of formation of H₂O and CH₄ increase. At 593 K, CO is completely converted at the end of the reactor. The concentrations of CH₄ and H₂O at the outlet reach almost the equilibrium concentration of 12.5 mol% for CH₄ and H₂O. The concentration profiles show at first a slight increase of CO₂, which pass through a maximum and then decreases again. The increase of CO₂ is caused by the water gas shift reaction accompanied by water consumption. It can be seen that the H₂O concentration is smaller than the CH₄ concentration when CO₂ reaches values of 1 mol%. As soon as the CO concentration is below 1 mol%, the CO₂ concentration decreases as well. This is explained by the fact that the conversion of CO is almost exclusively by hydrogenation to CH₄ and H₂O. As the concentration of H₂O increase, the water gas shift reaction becomes important and leads to the
formation of small amounts of CO$_2$. The dominant route for CO disappearance is still the methanation. When the concentration of CO reaches a level below equilibrium value of the water gas shift reaction, the reverse water gas shift occurs because there is still a high concentration of H$_2$ present (Kopyscinski, 2010). This lead to a decrease of the CO$_2$ concentration and to an increase of the H$_2$O concentration to a value again equal to the CH$_4$ concentration at the end of the reactor.

For scale-up, reactor dimensions, catalyst specification, operating conditions and the concentration of the reactor input components (Table 1) are adopted from the only reference in the open literature (Davis, 1981). Simulation results and output data of the industrial reactor have been compared in Table 2.

Table 2: Simulation results compared to industrial data

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Industrial process (Davis, 1981)</th>
<th>Simulation results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass fraction (%)</td>
<td>Mass fraction (%)</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>46.9</td>
<td>47.3</td>
</tr>
<tr>
<td>H$_2$</td>
<td>1.4</td>
<td>1.2</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>7.4</td>
<td>6.6</td>
</tr>
<tr>
<td>CO</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>43.9</td>
<td>44.7</td>
</tr>
</tbody>
</table>

Good agreements are observed between the industrial data and those obtained by the present model. The mean absolute percentage error is 12 %. We also investigated the effect of CO$_2$ addition. Indeed, at the output of the co-electrolysis, there is an amount of CO$_2$ that has not reacted, so this gas can impact the methanation reaction. Figure 2 illustrates the effect of CO$_2$ addition and temperature on CO conversion.

Figure 2: CO$_2$ and temperature effect on CO conversion

At lower temperature CO conversion is slightly affected by CO$_2$ addition. But at higher temperature, CO$_2$ does not retard the CO conversion; it rather has a positive effect due to the reverse water gas shift producing additional CO. It can be concluded that at 585 K, CO is completely converted and CO$_2$ has no effect.
4. Conclusions

In the renewable natural gas substitute process, syngas produced by co-electrolysing steam and CO\textsubscript{2} is converted to methane in an isothermal fixed bed reactor. In this study, a methanation catalytic reactor is modelled using the Aspen Plus™ software. The comparison between the model results and the experimental data indicates that the proposed model can predict methanation reactor performance with a good accuracy. This reactor allows also producing steam required for electrolysis and heating. The mean absolute percentage error of the proposed model is 12%.

Acknowledgment

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