Design and Evaluation of a High-Density Energy Storage Route with CO₂ Re-Use, Water Electrolysis and Methanol Synthesis

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Abstract

The energy transition corresponding to more electricity generation from variable and decentralized renewable energy sources requires the development of electricity storage technologies ranging from seconds to seasons. The power-to-fuel process provides a way to store electricity as a liquid energy vector, leading to high energy density and cheap long-term storage at ambient conditions. In the present work, we study the power-to-methanol process combining CO₂ capture, water/CO₂ co-electrolysis and methanol synthesis. An Aspen Plus model focusing on the electrolysis and methanol synthesis sub-processes is presented. The energy conversion efficiency is improved from 40.1 to 53.0 % thanks to heat integration using the pinch method. Further works include the experimental demonstration of this technology as well as the development of control strategies for its regulation.

Keywords: Power-to-fuel, energy storage, process modelling, heat integration.

1. Introduction

In the context of climate change, the European Commission has set goals to cut CO₂ emissions by 80-95 % in 2050 compared to 1990 levels and up to 96-99 % in the electricity sector (European Commission, 2012). In consequence, challenges appear due to the higher share of variable renewables in the electricity grid which conflicts with the low flexibility of most conventional generators. Besides demand-response and better grid interconnections, a third solution to match demand and supply at any time consists in developing efficient means to store and release electrical energy. In a previous work (Léonard et al., 2015a), we showed that seasonal patterns appear in the storage level when electricity is produced from variable renewables only. Thus, storage technologies playing on time-scales varying from seconds to seasons are required. In the present paper, we study a power-to-fuel process in which electricity (presumably from renewable sources) is co-electrolysing water and CO₂ (presumably from flue gas capture) to produce syngas that is then reacted into methanol as liquid energy vector. Liquid fuels like methanol have a high energy density, both gravimetric and volumetric (22.4 MJ/kg for methanol vs. less than 1 MJ/kg for batteries or pumped hydro storage; 17.8 MJ/L vs. 0.01 and 0.03 MJ/L for H₂ or CH₄ respectively). This high energy density and the stability of methanol at ambient conditions make its long-term storage and transport easy and very cheap. Moreover, methanol can be converted back to electricity...
(via fuel cell or combustion) or used as a fuel substitute for transportation thanks to its interesting properties compared to gasoline. Finally, if produced with renewable energies and captured CO$_2$, methanol may also be considered as a decarbonized energy carrier, opening the way to the “Methanol Economy” discussed by Olah (2005).

Although all sub-processes of the power-to-methanol technology have been extensively studied, very few modelling works of the whole process were found. A preliminary evaluation of the combined process (Sayah et al., 2010) evidenced the price of water electrolysis as limiting factor for the technology economic viability. However, no simulation was performed in this theoretical study and no interaction between the three sub-processes was considered. Galindo Cifre and Badr (2007) performed a cost evaluation of different methanol synthesis routes, stating that using syngas from biomass gasification leads to lower methanol cost than using syngas from electrolysis and CO$_2$ capture. Again, no process modelling was performed in this study. More recently, a study has investigated the flexibility of methanol synthesis at varying hydrogen flow rates resulting from intermittent energy sources (Fournel and Wagner, 2013). This study was performed in the framework of the French project ViTESSE², and it led to an optimized design of the methanol synthesis reactor. However, the CO$_2$ capture and water electrolysis were not modelled in details, so that there is still a knowledge gap about the process integration that may be achievable. Moreover, the main drawback of the power-to-fuel process is the low conversion efficiency, reaching about 50 % (LHV) in industrial conditions (Lübbehusen and Becker, 2014). Thus, the present work proposes a model of the power-to-methanol process with focus on improving the integration of the water/CO$_2$ co-electrolysis and methanol synthesis sub-processes. The main modelling assumptions are discussed and the results of a heat integration using the pinch method are presented in the next sections.

2. Model description

The modelling study is performed using Aspen Plus. Three sub-processes are described in the followings: CO$_2$ capture, water/CO$_2$ co-electrolysis and methanol synthesis. The model has been designed to produce 1.12 tonnes of methanol per hour.

2.1. CO$_2$ capture

The CO$_2$ capture model for the present study was previously presented (Léonard et al., 2014 and 2015b). Process improvements and optimized flowsheet configurations led to a heat requirement of 2.92 GJ/tCO$_2$ (electricity consumption of the process utilities can be neglected in first approach). However, the CO$_2$ capture sub-process is not included in the heat integration described in the present work, but the value mentioned above is used for the calculation of the global power-to-fuel efficiency.

2.2. Water/CO$_2$ co-electrolysis

The water/CO$_2$ co-electrolysis is performed in a solid oxide electrolysis cell operating at 850°C and atmospheric pressure. The thermodynamic model is RK-Aspen, based on the Redlich-Kwong-Soave equation of state. Besides CO$_2$ and water, some hydrogen is also present at the system inlet as reducing agent to avoid coke formation on the electrodes. The cell operates at thermoneutral point, meaning that no heat needs to be supplied or removed and that the energy necessary for the reactions is supplied as electrical energy.
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The electrolysis sub-process is modelled in three stages (Redissi and Bouallou, 2013). The first and third stages consist in reactors bringing all components to equilibrium according to the reverse water-gas shift reaction before and after the cell respectively. The second stage performs the actual water and CO₂ splitting reactions. Between the second and third steps, a separator block separates the produced syngas from the pure oxygen stream that is released at the anode. The electrolysis reactions are modelled assuming fixed conversion rates of 70% for CO₂ and H₂O, similarly to experimental results from the literature (Sun et al., 2012). This model was validated under similar conditions (H₂O/CO₂/H₂ ratio of 45/45/10) to those described by Sun et al. (2012), leading to similar results as presented in Table 1. Then, the composition of the feed was adapted to the current system (H₂O/CO₂/H₂ ratio of 100/45/10) to obtain a higher H/C ratio at the inlet of the methanol synthesis reactor, necessary for methanol synthesis.

Table 1. Comparison of the present electrolysis model with literature results.

<table>
<thead>
<tr>
<th>Component mol-% in electrolysis outlet gas</th>
<th>This work</th>
<th>Sun et al. (2012)</th>
<th>Relative error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>15.2</td>
<td>15.0</td>
<td>1.33</td>
</tr>
<tr>
<td>H₂</td>
<td>39.7</td>
<td>40.0</td>
<td>0.75</td>
</tr>
<tr>
<td>CO</td>
<td>33.2</td>
<td>32.0</td>
<td>3.75</td>
</tr>
<tr>
<td>CO₂</td>
<td>11.7</td>
<td>12.0</td>
<td>2.50</td>
</tr>
</tbody>
</table>

2.3. Methanol synthesis

Regarding the methanol synthesis, the process we modelled is based on the experimental work of Bos and Brilman (2014) that described a small-scale methanol reactor with internal condensation. Indeed, setting a temperature gradient within the reactor allows to condensate the produced methanol and thus to shift the equilibrium in the gas phase towards very high conversion rates. As a result, the conversion of the reactants into methanol reaches very high values in the range of 99.5 % at 250 °C and 50 bar. The experimentally observed methanol selectivity is also higher than 99.5%, so the methanol reactor is modelled as an equilibrium reactor with no side reactions, the only reactions taking place being the synthesis of methanol from CO₂ and the reverse water-gas shift reaction. The internal condensation reactor’s model includes a recycling loop from which methanol is condensed out at 25 °C and 50 bar. A purge stream of 2% of the recycling loop is set to avoid the accumulation of inert compounds, although these have not been modelled in first approach. As a consequence of the high selectivity of the methanol synthesis, the only required purification step is the removal of the water by-product from the final methanol product, which is done by distillation (11 theoretical stages, atmospheric pressure). The same thermodynamic model as for the electrolysis is used at the exception of the methanol distillation column that employs the NRTL model due to the presence of a polar mixture in liquid phase. Similarly to the results presented by Bos and Brilman (2014), the model results in conversion rates larger than 99.5 %.

2.4. Global flowsheet

The flowsheet of the resulting process including water/CO₂ co-electrolysis, syngas 2-stage compression, methanol synthesis and purification is presented in Figure 1.
3. Results

We first briefly describe the main results of the pinch analysis, and then we compare the conversion efficiencies obtained before and after heat integration.

3.1. Heat integration

A systematic heat integration was performed using the pinch method as described by Douglas (1988). We assume a minimum temperature difference of 20 K in the heat exchangers. As shown in Figure 2 (left) by the composite curves (relative heat duties versus temperatures levels), the pinch point is identified at 245.2 °C. The overlap between the hot and cold composite curves represents the maximum heat recovery possible within the process, i.e. 3362 kW heat exchange between hot and cold streams. The maximal heat recovery can be reached if an optimal heat exchangers network is implemented, composed of 12 heat exchangers represented by the matches between hot (black) and cold (light grey) streams in Figure 2 (right). The main contributions to the heat recovery are (1) 1116 kW heat flowing from the hot syngas (at the electrolyser outlet) to the water feed heating (before the electrolyser), (2) 962 kW heat as a part of the heat generated by the methanol synthesis recovered in the reboiler of the methanol distillation column and (3) 506 kW recovered inside the internal condensation reactor, this last contribution coupling the heat recovered when cooling the product gas for methanol to condensate with the heat provided to the unreacted syngas after methanol condensation to bring it up back to the reaction temperature. These three heat exchangers alone already represent 77 % of the maximum heat recovery achievable in a perfect heat exchanger network with 12 heat exchangers.

In addition to the 12 heat exchangers, 6 cold and 9 hot utilities are required in the process to remove/supply the minimum amount of external cooling/heating. The overshoot at the bottom of the hot composite curve represents the minimum amount of external cooling required in the optimised process (1563 kW vs. 4925 kW cold utility needed in case of no heat integration), while the overshoot at the top of the cold curve represents the minimum amount of external heating (936 kW vs. 4298 kW in case of no heat integration). This optimal network thus reduces the energy requirement (both cold and hot) by 73%, from 9223 kW down to 2499 kW.
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3.2. Efficiency calculation

The efficiency of the power-to-methanol process can be calculated following Eq. (1).

\[ \varepsilon = \frac{M_{\text{Met, out}} \times \text{LHV}_{\text{Met}} - M_{\text{H₂, in}} \times \text{LHV}_{\text{H₂}}}{P_{\text{in}} + Q_{\text{in}}} \]  

\( \varepsilon \) is the conversion efficiency of power-to-methanol (\(-\)), LHV_{Met} and LHV_{H₂} are the lower heating values of the methanol product and hydrogen feed (to prevent coking on the electrodes), respectively 19.93 and 119.96 MJ/kg. Their flowrates \( M_{\text{Met, out}} \) and \( M_{\text{H₂, in}} \) respectively equal 1118.5 and 20.16 kg/h in the present model. \( P_{\text{in}} \) and \( Q_{\text{in}} \) are the power and heat inputs (cold utilities are neglected in first approximation), represented in Table 2 with and without heat exchanger network. \( Q_{\text{in}} \) includes 1.606 MW heat necessary for the capture of 1980 kg/h CO₂, although this part was not considered in the pinch analysis. Table 2 shows that the heat integration improves the conversion efficiency by 32 %, from 40.1 to 53.0 %. The final conversion is similar to the value of 50 % claimed by Lübbehüsen and Becker (2014) for their power-to-liquid process, although the relevance of the comparison is limited: they consider Fischer-Tropsch fuels instead of methanol, and they do not account for heat in the efficiency calculation, but only power. The present work thus provides for the first time, to the best of our knowledge, a conversion efficiency for the power-to-methanol process that is based on detailed modelling and that also includes heat integration of the electrolysis and fuel synthesis.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>M_{\text{Met, out}}</th>
<th>M_{\text{H₂, in}}</th>
<th>P_{\text{in}}</th>
<th>Q_{\text{in}}</th>
<th>\varepsilon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MW</td>
<td>MW</td>
<td>MW</td>
<td>MW</td>
<td>%</td>
</tr>
<tr>
<td>No heat integration</td>
<td>6.192</td>
<td>0.672</td>
<td>7.873</td>
<td>5.904</td>
<td>40.1</td>
</tr>
<tr>
<td>With heat integration</td>
<td>6.192</td>
<td>0.672</td>
<td>7.873</td>
<td>2.542</td>
<td>53.0</td>
</tr>
</tbody>
</table>

4. Conclusions and perspectives

The power-to-methanol process is a promising technology for storing electricity from variable renewable sources under the form of a high-density liquid energy carrier, stable at ambient conditions and offering cheap long-term storage. However, although CO₂ capture, water/CO₂ co-electrolysis and methanol synthesis sub-processes have already
been largely studied, the efficiency of the whole process is still very low and only a few studies so far have considered the power-to-fuel process as a whole.

In the present work, we propose a process model including water-CO\textsubscript{2} co-electrolysis and methanol synthesis. We then perform a heat integration following the pinch method to improve the process performances, leading to a 32\%-improvement of the process efficiency, from 40.1 to 53.0\% (LHV basis). As far as we know, the present work thus provides for the first time a conversion efficiency of the power-to-fuel technology that is based on detailed process modelling and that includes at least partial heat integration of the different sub-processes. Further improvements may be reached if the CO\textsubscript{2} capture part is included in the heat integration. Moreover, the effect of pressure on the process performances should be studied as experimental results show some interest for that (Sun et al., 2012). In the future, further work may also include experimental demonstration of the process and study of control strategies to adapt the process to the variable availability of renewable electricity sources.

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