Performance evaluation, Optimization and exergy analysis of a high temperature co-electrolysis power to gas process using Aspen Plus®-a model based study

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Abstract
In this paper, a high temperature co-electrolysis power to gas (LTE PtG) setup was developed that was fed a stereotypical feed in CO₂ one could acquire from carbon capture and sequestration (CCS) retrofit. The electrolyzer was fed an equimolar 10 kmol/s feed in water and CO₂ and the electrolyzer product was composed of 38.80 mole% CO₂, 30.96 mole% CO, and 30.24 mole% H₂ for a syngas conversion of 43.8%. The product from the methanation unit was only composed of 21.38 mole% CH₄, with the rest (76.53 mole%) being predominantly CO₂. The methanation unit was composed of only one Sabatier reactor operating at 313°C, which had 90% of its product recycled back to the front end of the unit. The electrolyzer was found to have a LHV efficiency of 31.49%, and the entire HTCE PtG process was found to have an efficiency of 74.31% with methane storage and 76.49% without methane storage. A novel adaptation was developed on previous work on the exergy analysis for flow-sheet simulators which can be used for cyclic and noncyclic processes. The procedure was determined to be accurate, with irreversibilities determined across all the major subunits found to equal the irreversibility around the processes a whole. The electrolyzer was found to be responsible for the majority of the irreversibility within the setup, and this was attributed to the fact that water electrolysis is a very energy intensive process. The exergy efficiency of the electrolyzer was found to be 87.07% and that of the entire LTE PtG processes was found to be 84% with methane storage, and 87% without methane storage. In the end, it was determined that HTCE is unsuitable for the production of methane via retrofit with a methanation unit, and that it would be better suited for the production of liquid hydrocarbon fuels with much higher molecular carbon to hydrogen ratios.

KEYWORDS
Aspen Plus, efficiency, electrolyzer, exergy analysis, high temperature co-electrolysis power to gas, methane storage, power to gas
1 INTRODUCTION

Climate change which comes as a result of global warming is today a critical issue that poses a threat to global food security and the planet's biosphere. Global warming is a phenomenon whereby average global temperatures rise because of an increase in insulating gases (greenhouse gases) in our atmosphere that trap a proportion of sun's heat (this is also known as the greenhouse effect). And of all the anthropogenic pollutants, it has been found that CO₂ emissions contribute the most to the greenhouse effect.

The sectors that contributed to all growth in emissions between the years 2000 and 2010 were the energy and industry sectors which contributed 47% and 30%, respectively. Options available for decarbonization of the energy sector include: power plant efficiency improvements, fossil fuel switching, fugitive emission reduction during fossil fuel extraction, as well as carbon-free energy production (renewables, nuclear energy, carbon capture and sequestration [CCS], and power to gas (PtG)). CCS and PtG can also be used to decarbonize the industrial sector.

Renewable sources of energy such as wind and solar energy are an ideal solution that emits little to no CO₂, they are the cheapest means of providing decentralised power, their cost is declining, and efficiencies are improving rapidly. Though renewable energy sources have seen significant efficiency improvements and growth, especially wind (which grew 5 fold) and solar energy (which grew 25 fold) between the years 2005 and 2012. They are not yet competitive. Most of their growth and improvement came about because of massive support through subsidies, feed in tariffs, and quota obligations. An added disadvantage is their intermittence (this comes about because renewable sources such as solar and wind energy fluctuate in strength wildly across the course of a day) an attribute which further increases their cost significantly.

Fuel switching, specifically switching from coal to natural gas (NG), has the potential to reduce CO₂ emissions from a fossil fuel power plant by as much as a half for every kilowatt-hour of electricity produced. One reason for this is the lower carbon to hydrogen ratio in natural gas. Another reason is the higher efficiency (around 60%) one gets with natural gas power plants (specifically natural gas combined cycle power plants (NGCC)) as opposed to even advanced supercritical coal-fired power plants (around 45%). NGCC power plants are also very flexible, an attribute that results from being gas-fired.

Power to gas (PtG) is an innovative means with which to solve renewable energy intermittence (especially over longer seasonal time frames) and switch from coal to natural gas fired power through methane storage. It involves retrofitting a water electrolyzer to a CO₂ emission source (either a power plant or industrial emission source) and methanating the CO₂ emissions using the hydrogen produced by the cell in a methanation unit composed of several Sabatier reactors. Because the cell is fed renewable energy, this setup provides much needed flexibility to a grid by storing renewable energy during off-peak hours as methane, which can then be converted back to electricity using a NGCC power plant when demand returns.

Since there are no commercial-scale PtG facilities, their costs for the moment can only be estimated using design studies or the few existing pilot projects: This is important when estimating required capital investment and efficiency. Very little research has been conducted assessing the economic feasibility, or attempted to produce detailed process layouts of PtG. Water electrolysis in PtG can be conducted at either high temperature, in what is known as high temperature coelectrolysis (HTCE) (occurring at temperatures between 600°C and 1000°C) or low temperature, in what is known as low temperature electrolysis (LTE) (occurring at 80°C), and there is not much consensus as to which of these two is more efficient as there are not many studies on either, and fewer still comparing them. With this in mind, the research in this paper was undertaken to produce a detailed design on a HTCE PtG setup. In the first part of the paper, the flow sheet for the setup is developed before the first law thermodynamic and exergy efficiency of the setup are determined in the second part of the paper. The efficiencies are then compared with those determined in the work of KIT (2018, pp.1-36): a pilot project developed to demonstrate the proof of concept for high temperature electrolysis (HTE) coupled to PtG within the European Union. The two processes were compared on their efficiencies, as well as their ability to produce a stream of methane at the tail end suitable for transportation and storage in pipeline networks. The software used to model the processes is ASPEN plus (V8.4), the Peng-Robinson thermodynamic property package was used, and the IAPWS-95 free water method was used for the water flows.

2 PROCESS DESCRIPTION

The HTCE electrolyzer model was developed in a similar manner to the model which was developed in the work of Redissi and Bouallou (2013) using the results reported by Luo et al (2014). The methanation unit that follows the electrolyzer was developed in a similar manner to models of Agerborg and Lingehed (2013), Hoekman et al (2010), and Bailera et al (2016).

2.1 Electrolyzer

Figure 1 shows the electrolyzer model. It is composed of an initial heat exchanger (WATER-HX) that heats the incoming
feed (stream EL-1) to the temperature required for electrolysis before it is fed to the RSTOIC block as stream EL-2. The RSTOIC block is meant to simulate the electrolyzer. The overall reaction enthalpy drop is measure of the electrolyzer work requirement11,12; this is reported as the unit operation heat duty in the RSTOIC block results summary. Once the incoming feed has reacted, it then reports to splitter block as electrolyzer product stream EL-3. The less desirable products (stream P-103) then leave as a stream of oxygen and water at the electrolyzer conditions. The more desirable products leave in stream P-102 as a stream of syngas at the electrolyzer conditions. The reason the products are separated cleanly at the electrolyzer conditions is because the gasses evolve from different electrolyzer compartments in reality. And so the work output from the splitter needs to be ignored for it to resemble an electrolyzer closely.

The model developed in this paper is a tubular solid-oxide electrolysis cell, and the electrolyzer characteristics used to develop this model are shown in Table 1.13 In this study, only the main reaction was taken into consideration (Equation 2 [10]); the reversible water gas shift reaction (Equation 1) was ignored. The condition of the feed streams to the HTCE electrolyzer were acquired from an identical setup that converted the CO2 emissions from a natural gas combined cycle (NGCC) power plant to CH4. The setup was initially designed for conversion of CO2 emissions via low temperature electrolysis (LTE). However, due to the higher demand for CO2 in HTCE, an external amount in CO2 had to be added in to supplement that which was provided by the NGCC power plant (stream P-101). This was done until the feed was equimolar in both CO2 and H2O.10,13 The feed streams were then normalized such that the molar flow rate of CO2 and H2O both equalled 10 kmol/s (see Table 1). The electrolyzer in the HTCE model will be fed an equimolar feed in water and CO2 (nCO2/nH2 = 1) as was the case in the research conducted by Luo et al (2014) and Redissi and Bouallou (2013). Equation (3) is used to determine the hydrogen conversion, Equation (4) is used to determine the carbon monoxide conversion and Equation (5) is used to determine the syngas conversion.

$$2\text{CO}_2(g) + \text{H}_2 \leftrightarrow \text{CO}(g) + \text{H}_2\text{O}$$  \hspace{1cm} (1)

$$\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_2 + \text{CO} + \text{O}_2$$  \hspace{1cm} (2)

$$\xi_{\text{H}_2} = \frac{q_{\text{H}_2}^{\text{out}}}{q_{\text{H}_2\text{O}}}$$  \hspace{1cm} (3)

$$\xi_{\text{CO}} = \frac{q_{\text{CO}}^{\text{out}}}{q_{\text{CO}_2}^m}$$  \hspace{1cm} (4)

$$\xi_{\text{tot}} = \frac{q_{\text{H}_2}^{\text{out}} + q_{\text{CO}}^{\text{out}}}{q_{\text{H}_2\text{O}}^m + q_{\text{CO}_2}^m}$$  \hspace{1cm} (5)

### 2.2 Methanation unit

Figure 2 is a generic diagram of the electrolyzer and the methanation unit. The methanation unit model is generic because the actual process layout still needs to be determined through design and optimization. So while the methanation unit in Figure 2 has 3 Sabatier reactors; in reality this still needs to be decided which is what will be done in this paper. The methanation unit receives renewable hydrogen (stream P-102) from the electrolyzer and CO2 (stream P-101) from an industrial emission source to produce methane via Sabatier reactors. The methanation unit operates at 1 atmosphere to take advantage of the fact that the products are favored at lower pressures.14 The feed to each reactor first gets heated to 468.15K in heater blocks (PU-01, PU-04, PU-07 etc) before it is fed to the Sabatier reactors (These have been modeled on RGibbs reactors: unit operations PU-02, PU-05, PU-08 etc). The products from each Sabatier reactor then get flashed to ambient conditions in flash blocks before getting recycled.
back into the reactor for temperature control (the temperature must be between 450°C and 200°C\textsuperscript{15}) and improved conversion. Once the methane stream reaches a quality suitable for pipeline transportation (95 mole%\textsuperscript{3}), it then reports to the PtG compressor PTG-COMP where it is then compressed by a five-stage compressor with intercooling (each stage is cooled to 298.15 K). The efficiencies of the process were determined for two scenarios: a scenario in which there would be methane storage in metallic organic frameworks (MOFs\textsuperscript{16}), and a scenario in which the methane is prepared for pipeline transport. Storage in MOFs requires a final product methane pressure of 65 bar, and preparing the methane for pipeline transport requires the methane be compressed to a pressure of 5 bar.\textsuperscript{14,16}

The reactions that can take place across the Sabatier reactor are methanation of CO\textsubscript{2} (Equation 6), the reverse water gas shift reaction (Equation 7), methanation of CO (Equation 8), and the Boudouard reaction (Equation 9).\textsuperscript{14,17} It is assumed the CO\textsubscript{2} feed to the methanation unit (stream P-101) is derived from a power utility emission source: Specifically, a natural gas combined cycle power plant retrofitted with sorption enhanced water gas shift (SEWGS) precombustion capture.\textsuperscript{18}

$$\text{CO}_2(g) + 4\text{H}_2 \leftrightarrow \text{CH}_4(g) + \text{H}_2\text{O} \quad \Delta H^\circ_{\text{reaction}} = -165 \text{ kJ/mol} \quad (6)$$

$$\text{CO}_2(g) + \text{H}_2(g) \leftrightarrow \text{CO}(g) + \text{H}_2\text{O}(g) \quad \Delta H^\circ_{\text{reaction}} = +41.2 \text{ kJ/mol} \quad (7)$$

$$\text{CO}(g) + 3\text{H}_2 \leftrightarrow \text{CH}_4(g) + \text{H}_2\text{O} \quad \Delta H^\circ_{\text{reaction}} = -206.4 \text{ kJ/mol} \quad (8)$$

$$2\text{CO}(g) \rightarrow \text{C(s)} + \text{CO}_2(g) \quad \Delta H^\circ_{\text{reaction}} = -172.5 \text{ kJ/mol} \quad (9)$$

### 3 | HTCE ELECTROLYZER RESULTS

The electrolyzer was fed an equimolar 10 kmol/s feed in water and CO\textsubscript{2}. The CO\textsubscript{2} enters through two streams EX-CO\textsubscript{2} and stream P-101. Figure 3 is a graph charting syngas conversion (across the horizontal axis) against the H\textsubscript{2}, CO and CO\textsubscript{2} mole fractions in the product stream from the electrolyzer for an equimolar feed in H\textsubscript{2}O and CO\textsubscript{2} to the unit. Table 2 shows the stream results across all streams in the HTCE electrolyzer, among the results is the composition of the stream reporting to the methanation unit from the electrolyzer at the reported conversion in syngas of 43.8% (stream P-102 in Figure 4). Looking at Figure 3, it is clear that initially the CO\textsubscript{2} molar composition is very high, before it slowly begins fall at a decreasing rate until its slightly higher than the CO and H\textsubscript{2} mole fractions in the product stream. The reason the CO\textsubscript{2} mole fraction starts at 1 is because initially nothing reacts in the electrolyzer. The reason the CO\textsubscript{2} mole fraction then reduces is because as the syngas conversion begins to rise the CO\textsubscript{2} gets

![Diagram](image-url)

**TABLE 1** Electrolyzer characteristics for HTCE\textsuperscript{13}

| Electrolyzer characteristics | Value |
|-----------------------------|-------|
| Temperature [°C]            | 700   |
| Hydrogen conversion %       | 52.60 |
| CO conversion %             | 39.32 |
| Syngas conversion %         | 48.30 |
| Efficiency %                | 58.80 |
| Water feed [kmol/h]         | 10    |
| CO\textsubscript{2} feed [kmol/h] | 10    |

**FIGURE 2** Generic diagram of the methanation unit
used up and the H₂ and CO mole fractions begin to increase. The H₂ and CO mole fractions are identical for all syngas conversions because their produced in an equimolar ratio according to Equation (2). The mole percentages of CO₂, CO, and H₂ in the more desirable product stream (stream P-102) are 38.80%, 30.96%, and 30.24%, respectively. Although the RWGS reaction was ignored, the final product possesses a molar H₂/CO ratio of 0.9767 which lies very close to that which was reported by Redissi and Bouallou (2013) of 1.19.

4 | PTG FLOW-SHEET RESULTS

Figure 5 is a graph charting the recycle fraction (in the horizontal axis) against methane composition in the stream leaving the first Sabatier reactor and the temperature of the unit (in the vertical axis). The feed to the methanation unit is that which was predicted for the HTCE electrolyzer hydrogen product (stream P-102 in Table 2). As expected, the temperature drops as the recycle fraction increases until one gets to a point where the methane composition begins to asymptote at around 21 mole % and a unit operation temperature of around 313°C. One of the reasons the CH₄ composition rises as the recycle fraction increases is that a portion of the product gets removed (water is condensed out) before recycling which gives the unreacted feed multiple passes which increases conversion. Another reason for it, is that the temperature drop upon recycling promotes methanation as the reaction is exothermic. The final CH₄ composition of 21.38 mole% occurs at the maximum recycle fraction of 0.9. The reason that the final CH₄ composition cannot exceed 21 mole% is that all the hydrogen that entered the Sabatier reactor completely reacted. Evidence of this can be found in Table 3, which contains the molar composition of the stream leaving the first Sabatier reactor. The final ASPEN flow sheet and process layout for the methanation unit and the entire HTCE PtG process is shown in Figure 5: It has a single Sabatier reactor with a recycle fraction of 90 mole% and a methanation unit temperature of 313°C. With a methane composition of only 21.38 mole%, the process fails to meet the specifications for methane product composition required for pipeline transport of around 95 mole %. This makes HTE PtG superior for the production of methane, as it was found to be able to produce a methane stream with composition greater than 95 mole% in the pilot plant developed by KIT (2018, pp.1-36). To remedy this, the HTCE electrolyzer could be designed to operate with lower feed molar compositions in CO₂. There have also been suggestions made that HTCE is more advantageous in situations in which the setup produces syngas 19-21 for the production of liquid hydrocarbon fuels. This is because liquid fuels will have a much higher molecular carbon to hydrogen

| Electrolyzer stream results | Feed | Products |
|-----------------------------|------|----------|
| Molar flow [kmol/s] | 2.55 | 10 | 7.45 | 10 | 14.40 |
| Mass flow [kg/s] | 110.52 | 180.15 | 332.52 | 241.40 | 381.80 |
| Temperature (K) | 301.15 | 298.15 | 298.15 | 973.15 | 973.15 |
| Pressure (Pa) | 8 000 000 | 101 325 | 1500 000 | 101 325 | 101 325 |
| Vapor fraction (V) | 1 | 0 | 0 | 1 | 1 |
| Liquid fraction (L) | 0 | 1 | 1 | 0 | 0 |
| Mole percentages | | | | | |
| Carbon dioxide | 95.87% | 0.00% | 100.00% | 0.00% | 38.80% |
| Carbon monoxide | 4.13% | 0.00% | 0.00% | 0.00% | 30.96% |
| Water | 0.00% | 100.00% | 0.00% | 56.20% | 0.00% |
| Oxygen | 0.00% | 0.00% | 0.00% | 43.80% | 0.00% |
| Hydrogen | 0.00% | 0.00% | 0.00% | 0.00% | 30.24% |

**TABLE 2** Stream results across HTCE electrolyzer. Stream P102 (Figure 3) is the stream that reports to the methanation unit from the electrolyzer.
ratio than CH₄, which will enable more of the CO and CO₂ to get converted as the molecular hydrocarbon chain of the final product is lengthened.

5 | EXERGY ANALYSIS

5.1 | Exergy analysis methodology

Consider Exergy analysis is a means of determining the potential a process and its subprocesses have for improvement through the application of the second law of thermodynamics. This requires that you determine the useful work content (also known as the exergy content \( \dot{E} \)) of all streams entering and leaving a process, before subtracting the total exergy in from the total exergy leaving to determine the irreversibility of the processes. The irreversibility is a measure of how far a process lies from being reversible and therefore how much potential it has for improvement (see Equation 10).

\[
\dot{I} = \dot{E}_{\text{in}} - \dot{E}_{\text{out}} \tag{10}
\]

Here, \( \dot{I} \) represents the irreversibility of the process, \( \dot{E}_{\text{in}} \) represents the total amount in exergy flowing into the process or control region and \( \dot{E}_{\text{out}} \) represents the total amount in exergy flowing out of the process or control region. The exergy content of a heat flow \( Q \) can be determined using Equation 11. Here, \( T_H \) is the temperature at which the heat is delivered in kelvin, \( T_0 \) is the prevailing ambient temperature in kelvin and \( Q \) is the flow in heat delivered.

\[
\dot{E}^Q = Q \frac{T_H - T_0}{T_H} \tag{11}
\]

The exergy content of a stream of matter is the maximum amount of work attainable from it as it moves from its process conditions \((T, P)\) to the dead state \((T_0, P_0)\). The dead state is defined by thermal, mechanical, and chemical
equilibrium with the environment where each component is in its ambient chemical state, ambient partial pressure, and ambient temperature.\textsuperscript{23} Kotas (1985, pp.1-296) provides a more conventional mean of determining the exergy content of material, heat, and work streams, and the method employed in this study is an adaptation or extension on that of Hinderink, et al (1996) which conveniently splits the exergy employed in this study is an adaptation or extension on that of

\[ E_{\text{tot}} = E_{\text{ch}} + E_{\text{ph}} + E_{\text{mix}} \]  \hspace{1em} (12) 

Here, \( E_{\text{tot}} \) represents the total stream exergy, \( E_{\text{ph}} \) represents the stream physical exergy, \( E_{\text{ch}} \) represents the stream chemical exergy and \( E_{\text{mix}} \) represents the exergy of mixing. The method proposed in this paper includes the flow sheet one could employ to acquire the requisite information for the assessment of cyclic and noncyclic processes using ASPEN plus. The best way to determine the exergy content of multi-phase material streams is by initially separating the said phases out (ie, for gas-liquid phases, this can be done using a flash block) then conducting the exergy analysis on both phases separately before adding them back together again.\textsuperscript{22}

When one does this, one can then determine the exergy of mixing, physical exergy, and chemical exergy using Equations (13)-(15).

\[ E_{\text{mix}} = F \left\{ L \left( \left[ h - \left( \sum x_i h_i^l \right) \right] - T_0 \left( S - \left( \sum x_i S_i^l \right) \right) \right) + V \left( \left[ h - \left( \sum y_i h_i^v \right) \right] - T_0 \left( S - \left( \sum y_i S_i^v \right) \right) \right) \right\}_{T,P} \]  \hspace{1em} (13) 

\[ E_{\text{ph}} = F \left[ L \left( \left( \sum x_i h_i^l \right) - T_0 \left( \sum x_i S_i^l \right) \right) + V \left( \left( \sum y_i h_i^v \right) - T_0 \left( \sum y_i S_i^v \right) \right) \right]_{T,P} - F \left[ L \left( \left( \sum x_i h_i^l \right) - T_0 \left( \sum x_i S_i^l \right) \right) + V \left( \left( \sum y_i h_i^v \right) - T_0 \left( \sum y_i S_i^v \right) \right) \right]_{T_0,P_0} \]  \hspace{1em} (14) 

\[ E_{\text{ch}} = F \left[ L \left( \sum x_i E x_{\text{ch},i} \right) + V \left( \sum y_i E x_{\text{ch},i} \right) \right]_{T_0,P_0} \]  \hspace{1em} (15) 

Here: \( F \) represents the total stream molar flow, \( T_0 \) represents the stream temperature in kelvin, \( L \) represents the stream liquid fraction, \( V \) represents the stream vapor fraction, \( x_i \) represents the component mole fraction in the liquid phase, \( y_i \) represents the component mole fraction in the vapor phase, \( h_i^l \) represents the combined stream enthalpy in the liquid phase, \( h_i^v \) represents the component stream enthalpy in the liquid phase, \( h_i^l \) represents the combined stream enthalpy in the vapor phase, \( S_i^l \) represents the component stream entropy in the liquid phase, \( S_i^v \) represents the combined stream entropy in the liquid phase, \( S_i^v \) represents the component stream entropy in the vapor phase, \( \text{Ex}_{\text{ch},i}^l \) is the chemical exergy of component “i” in the liquid phase and \( \text{Ex}_{\text{ch},i}^v \) is the chemical exergy of component “i” in the vapor phase (chemical exergies for all species were acquired from, or determined using the text\textsuperscript{23}). All variables should be in SI units.

To determine stream exergy using Equations (13-15), the stream of interest would need to be flashed once at stream conditions \((T, P)\), before being mixed and returned to ambient conditions and then flashed again at ambient conditions. Additionally, since the evaluation may be conducted on a cycle, you need to ensure that the process of collecting the data does not interfere with the very cycle results the evaluation is dependent on. So if you alter the flow sheet by adding a flash block for the sake of collecting data, you need to return the stream to its initial conditions if both the simulation results, and by extension, the data collected are not to be affected. This can be achieved using a heater block which you can use to return the stream to its initial conditions before feeding it back to the external process. If one ignores the network or heating required to alter the stream within each of the said units (the flash blocks and the heater blocks), you can then use the setup to collect data from the said stream with confidence since each of the properties that we are evaluating are state variables whose values are not dependent on the path taken by a process. This can be achieved through ASPEN plus using the flow sheet shown in Figure 6. The flow sheet is comprised of 6 process units: 2 flash blocks, 2 mixers, and 2 heater blocks. Unit operation [FLASH-1]

\[ \text{is meant to flash the stream at the process conditions } (T, P) \text{ before both phases are mixed using unit operation [EX-01]. The stream emanating from mixer [EX-01] is called [EX-02]. [EX-02] is then heated or cooled to reach the environmental state } (T_0, P_0) \text{ using the heater block [T0,P0], and the resulting stream is called [T0, P0-M]. [T0, P0-M] is then flashed at the environmental state before being mixed by unit operation [EX-03] to make stream [EX-04]. Stream [EX-04] is then returned to the initial stream process conditions } (T, P) \text{ by heater block [T', P] before reporting back to the external process as stream [RETURN]. This is done in order to make sure that the evaluation does not alter the overall process results with each successive run as mentioned before.}

This method can also by extension be used to determine the pressure and thermal exergy components of a stream. The pressure exergy component of a stream \( (E_p) \) is by definition the maximum amount of work one can harness from a reversible isothermal process in which the stream moves from its process conditions of \((T, P)\) to the environmental state pressure of 1 atmosphere at the original stream temperature.
(T, P₀)²: So heater block [T₀,P₀] and flash unit [FLASH-2] in this case would operate at conditions (T, P₀). The thermal exergy component of a stream (Eᵀ) is the maximum amount of work one can harness from a stream undergoing an isobaric process in which it moves from its initial process conditions (T, P) to the ambient environmental temperature at the original stream pressure (T₀, P₀)

\[
Eᵀ = E_{mix} + F \left[ L \left( \sum x_i h^i - T₀ \left( \sum x_i s^i \right) \right) + V \left( \sum y_i h^i - T₀ \left( \sum y_i s^i \right) \right) \right]_{T,P} - F \left[ L \left( \sum x_i h^i - T₀ \left( \sum x_i s^i \right) \right) + V \left( \sum y_i h^i - T₀ \left( \sum y_i s^i \right) \right) \right]_{T₀,P}
\]

(16)

\[
Eᵀ = E_{mix} + F \left[ L \left( \sum x_i h^i - T₀ \left( \sum x_i s^i \right) \right) + V \left( \sum y_i h^i - T₀ \left( \sum y_i s^i \right) \right) \right]_{T,P} - F \left[ L \left( \sum x_i h^i - T₀ \left( \sum x_i s^i \right) \right) + V \left( \sum y_i h^i - T₀ \left( \sum y_i s^i \right) \right) \right]_{T₀,P}
\]

(17)

5.2 | Exergy analysis results

Table 4 is a table displaying the first law thermodynamic efficiency of the PtG, HTCE retrofit. Please note that the evaluation only takes the H₂ and CH₄ components of the product streams into account and does not consider other products from the process like CO that have calorific value. What is meant by “LHV of product” or “HHV of product” is that the assessment is based on the LHV or HHV of the product gases. It was assumed that heat was supplied to the heat sinks at a temperature of 586.3 K (the temperature of Sabatier reactor PU-02). The product gas LHV efficiency of the electrolyzer is 31.49%, which lies very far from the efficiency reported for the high temperature water electrolysis unit in the work of Luo, et al (2014) of 58.8%. The LHV efficiency of the entire PtG process is 42.21% with methane storage and 43.45% without methane storage (heat released included). When one considers the heat released, the value of the LHV efficiency of the entire PtG process becomes 74.31% with methane storage and 76.49% without methane storage (heat released included). The HHV efficiency of the entire processes is 78.86% when one takes into consideration the heat released from the methanation unit. This lies very close to the HHV efficiency for the entire high temperature electrolysis process reported in the work of KIT.
Table 4: First law thermodynamic efficiency of the PtG HTCE

| Electrolyzer efficiency (first law) |  |
|------------------------------------|--|
| Electrolyzer net duty [MW]          | 842.27  |
| Q (WATER-HX) [MW]                  | 379.78  |
| Hydrogen flow [kg/s]               | 3.20    |
| Efficiency [LHV] (Only H₂ as product) | 31.49%  |
| Efficiency [HHV] (Only H₂ as product) | 37.24%  |
| Electrical efficiency [HHV] (only H₂ as product) | 54%     |

| PtG efficiency (first law) |  |
|---------------------------|--|
| Electrolyzer net duty [MW] | 842.27  |
| Q (WATER-HX) [MW]          | 379.78  |
| Q (PU-01) [MW]             | 127.83  |
| Q (PU-03) [MW]             | -452.18 |
| PtG-COMP (Net work with methane storage) [MW] | 58.85 |
| PtG-COMP (Net work without methane storage) [MW] | 18.79 |
| CH₄ flow [kg/s]            | 12.61   |
| Efficiency with methane storage [LHV of product] % (Heat released not included) | 42.21% |
| Efficiency with methane storage [LHV of product] (Heat released included) | 74.31% |
| Efficiency without methane storage [LHV of product] % (Heat released not included) | 43.45% |
| Efficiency without methane storage [LHV of product] (Heat released included) | 76.49% |
| Efficiency [HHV of product] (Heat released not included) | 46.76% |
| Efficiency [HHV of product] (Heat released included) | 78.86% |

The value of the HHV electrical efficiency of the HTCE electrolyzer stack is 54%, which lies far from that which was reported in the work of KIT (2018, pp.1-36) of 110% for their HTE electrolyzer. This very large discrepancy can be attributed to the fact that the HHV efficiency reported by KIT (2018, pp.1-36) was based on the thermoneutral voltage.

Table 5 is a table containing the exergy efficiency of the PtG, HTCE retrofit. The figures in megawatts associated with each stream represent the exergy of the said streams and the streams labeled $Q_{EX}$ followed by the name of a unit operation represent the flow in exergy of the heat fed to or from a unit operation. The exergy efficiency of the electrolyzer is 87.07%, and that of the entire HTCE PtG process is 84% with methane storage and 87% without methane storage. The reason the electrolyzer is more efficient is that there are no heat streams that leave its system boundary (PtG-H02); all thermal exergy (thermal exergy component of physical exergy) leaves as sensible heat within the electrolyzer product which is accounted for in the exergy analysis. Additionally, the exergy contained in the flue gases also gets destroyed on route to generating the renewable methane within the methanation unit. For the same process product specification and electrolyzer conversion, it is recommended that the electrolyzer temperature be lowered to improve efficiency. The electrolyzer exergy efficiency is larger than the first law LHV efficiency of the electrolyzer is determined, it is not customary to account for sensible heat. The lower heating value of the product is used instead.

Table 6 shows the irreversibilities around the system boundaries in the PtG, HTCE retrofit and Figure 7 shows the proportion the irreversibilities around each system boundary contribute to the overall process irreversibility. Table 6 shows that the irreversibilities around system boundaries PtG-H01, PtG-H02, PtG-H03 sum up to equal the irreversibility around the entire process. The greatest amount of irreversibility is around the electrolyzer (system boundary PtG-H01), and this can be attributed to the fact that it has to accomplish the energy intensive task of having to convert water and CO₂ to syngas at an elevated temperature of 700°C. As a recommendation, it is suggested that the process be conducted at lower temperatures for the same product specifications and electrolyzer conversion to reduce irreversibility.

The setup fails to produce a product with a high enough mole% in methane for pipeline transport partly due to poor conversion in the HTCE electrolyzer. It is also very inefficient considering its low conversion. The large proportion of CO₂ in the product gas needs to be separated out even if it were to be used as a fuel. Additionally, there is not enough hydrogen to completely react with the CO in the methanation unit even if the reaction were to go to completion in the electrolyzer. But HTCE might perhaps be useful as a means of producing a syngas feed for other processes.
In this paper, a HTCE PtG process was designed in ASPEN plus, before the first law thermodynamic and exergy efficiency of the processes was determined. This was done with the intention of determining how effectively the processes convert renewable electricity, H$_2$O, and CO$_2$ into a stream of CH$_4$ ready for transport and storage in pipeline networks for scenarios with and without methane storage. It was found that as the reaction progressed, the CO$_2$, H$_2$, and CO mole percentages began to converge with increasing syngas conversion across the electrolyzer. The final CO$_2$, H$_2$, and CO mole percentages exiting the electrolyzer were 38.80%, 30.24%, and 30.96%, respectively. Though the RWGS reaction was ignored, the final product had a molar H$_2$/CO ratio of 0.9767, which did not lie very far from findings within the literature that took the reaction into account. It is recommended that further research be conducted into the effect that the RWGS reaction would have on the overall processes.

The feed from the HTCE electrolyzer was then fed to a methanation unit composed of adiabatic Sabatier reactors. The methanation unit was composed of a single Sabatier reactor which recycled 90% of its product back to the front end.
of the unit for temperature control and improved conversion. The temperature of this Sabatier reactor was 313°C, and final product had a methane composition of 21.38%, which makes the setup unsuitable to produce methane streams suitable for transportation and storage in pipeline networks. It was concluded that HTCE would be more suitable to produce syngas which could then be used in the synthesis of liquid hydrocarbon fuels which have a much higher molecular carbon to hydrogen content than methane.

The LHV efficiency of the electrolyzer was found to be 31.49%, and the LHV efficiency of the entire PtG processes was found to be 74.31% with methane storage, and 76.49% without methane storage. The HHV efficiency of the entire process was found to be 54%. The exergy efficiency of the electrolyzer was found to be 87.07%, and that of the entire HTCE PtG processes was found to be 84% with methane storage and 87% without methane storage. The exergy analysis determined the electrolyzer to be responsible for most of the irreversibility within the process.

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