Self-recuperative high temperature co-electrolysis-based methanol production with vortex search-based exergy efficiency enhancement

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ABSTRACT

The reduction of greenhouse gas emission via the transformation of carbon dioxide into methanol results in several secondary benefits including the production of a valuable by-product that can be used for energy storage and as a fuel source. As such, this is a promising approach for mitigating climate change. Methanol production via the co-electrolysis process using solid oxide electrolyzer cells is an efficacious solution to the issue of excess electricity storage in the context of renewable energy and carbon dioxide utilization. However, this process is an energy-intensive and temperature-sensitive method, mainly due to the requirement of high-temperature electrolysis. In this context, this study investigates and evaluates the potential for overall performance improvement by minimizing energy consumption and increasing methanol production using self-heat recuperation technology. The newly developed vortex search strategy was employed to achieve the maximum potential benefit from retrofitted recuperators. Detailed exergy analysis was performed for the process and the evaluation of its performance. The findings revealed that the electrochemical system for co-electrolysis has the highest exergy destruction rate. By employing the vortex search approach, the exergy loss of the energy process system can be reduced by 61.7% with a total reduction of the exergy loss of 15.9%, while improving methanol production and decreasing distillation reboiler duty. The simple solution of self-recuperation with optimization that was utilized in this study is a flexible approach that can be directly applied to the improvement of co-electrolysis and methanol synthesis.

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1. Introduction

Fossil fuel use has increased atmospheric carbon dioxide (CO2) emission levels in recent years, leading to problems related to the environment and public health including climate change and air pollution. This major issue of CO2 emission has resulted in the global monitoring of this gas (Witze, 2018). Moreover, there has been substantial efforts to limit the carbon footprint of the world’s population by emphasizing the use of renewable energy such as hydropower (Bello et al., 2018), biogas energy (Haider et al., 2019), and solar photovoltaic systems (Parida et al., 2011) as power sources. In addition, other technologies have been exploited to facilitate the improvement of CO2 electroreduction into useful fuels (Gao et al., 2016) and the transition to solar, wind, and geothermal energy (Mekonnen et al., 2016). However, not all renewable energy alternatives results in a reduction of CO2 emissions. In the worst case, a renewable energy fails to offset the emitted CO2, e.g., biofuel production (DeCicco et al., 2016). Renewable energy intermittency is another drawback, e.g., in May 2016, in Germany, electricity supply far exceeded demand and the price of electricity became negative, and consumers were paid for their electricity consumption (Andika et al., 2018). Thus, there is a need for systems that can use excess electrical energy, in anticipation of positive renewable growth towards 2023 (Gielen et al., 2019). In addition, CO2 is an essential material for many industrial processes (Pierantozzi, 2003). To address the aforementioned issues, several promising solutions have been proposed in which CO2 emissions are reduced and converted into useful products, energy storage and fuels, that are both environmentally and economically beneficial.

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Among the various possible products, methanol (MeOH) is of particular interest because it can be utilized as a transport fuel (Verhelst et al., 2019). In addition, it can be further processed to produce an alternative to conventional diesel via MeOH dehydration (Sabour et al., 2014) or can be used as an energy carrier for hydrogen (H2) (Rosen and Scott, 1988), while also serving as a chemical for electricity storage (Kauw et al., 2015). Moreover, MeOH is considered to be a versatile chemical intermediate that is widely used in the manufacture of other chemicals and can be used to produce a wide variety of products used in daily life (Bozzano and Manenti, 2016). MeOH production from CO2 is a favorable, clean technique (Riaz et al., 2013) with the integration process facilitated by accessing excess electricity (Kauw et al., 2015). This avoids the need for CO2 seclusion which is a very expensive process (Olah et al., 2009). To convert CO2 to MeOH that utilizes surplus electrical energy, the power to the MeOH (PtM) concept can effectively use the excess electricity and concurrently incorporate the usage of CO2 as feedstock.

To realize the PtM concept, H2 production is required via a process that utilizes excess electricity. Co-electrolysis is an economically competitive process that is capable of achieving various functions including the production of H2 from an abundant source (such as water) and implementation using various renewable electric sources (Fu et al., 2010). Solid oxide electrolyzer cells (SOEC) are electrolysers that can undergo a co-electrolysis process. In comparison with other electrolysis devices (polymer electrolyte membrane (PEM) electrolysis and alkaline water electrolysis), SOEC is much more efficient because of their thermodynamic and kinetic advantages with respect to water splitting (Chen et al., 2014). Another advantage of SOEC in the PtM concept is that it is capable of producing carbon monoxide (CO). MeOH synthesis is conducted mainly with CO; thus, CO production is required in addition to H2 and CO2. Furthermore, the reaction is 100 times faster and catalyst durability is enhanced in the presence of CO2 (Wender, 1996). Due to these advantages, SOECs that can produce CO and H2 and controlling their composition could play a key role in MeOH synthesis from a CO2 source. In addition, the superior energy conversion efficiency of SOEC is still under investigation (Im-orb et al., 2018). Widespread application of this technology will require significant process improvements together with performance analysis to ensure that the demonstrated potential is realized. In addition to these advantages, compared to PEM and alkaline water electrolysis, the SOEC-based co-electrolysis process requires considerably more heating energy but has a lower electricity demand (Bhandari et al., 2014). This is because co-electrolysis process involves high-temperature processes between the energy source and the electrolysis process (Uhm and Kim, 2014). This requires additional processing, which in turn is an issue that affects the realization of the process objectives. Thus, the biggest concerns are the use of appropriate materials including the catalyst (Kim et al., 2018), and the recovery of heat (Götz et al., 2016). Another concern is the amount of energy generated from the MeOH synthesis process during the high-temperature exothermic reaction that creates the need for a heat recovery system.

Techno-economic and off-design analysis of SOEC (Reznicek and Braun, 2018) and dynamic temperature control of SOEC (Wang et al., 2019a) for co-electrolysis are currently under investigation studies. However, these studies only consider standalone co-electrolysis processes and do not specifically target the composition ratio in the co-electrolysis process product that is required for MeOH production in the PtM concept. Incorporating the co-electrolysis of CO2 and H2O into MeOH production is vital to MeOH production from CO2 that involves excess electrical power. This is because attempts at co-electrolysis improvement will benefit MeOH production as a synergistic effect. Another process for MeOH production from CO2 via the co-electrolysis process was evaluated by employing SOEC using a heat exchanger network (HEN) in the integrated process from CO2 capture to MeOH synthesis and utility (Al-Kalbani et al., 2016). However, this approach is difficult to implement in simulation or practice due to the use of numerous heat exchangers. Further, it is difficult to analyze the important variables that affect MeOH production for further process improvement. Thus, a simpler and efficient process configuration is required for progressive improvement of co-electrolysis and MeOH integrated system configuration.

In contrast, the use of a recuperator (either for cooling or heating) represents a simpler design and can retrofit the target process that requires energy recovery to increase process efficiency (Qyyum et al., 2019b). The larger the temperature difference between the cold stream and the hot stream input of a recuperator, the higher is the recuperator’s effectiveness (Cao et al., 2016). However, the following issues must be addressed for the effective use of recuperators in a system that involves co-electrolysis and MeOH synthesis: (i) the recuperator design is affected by the minimum internal temperature approach (MITA). Thus, the target temperature determination using the reasonable specific MITA within the recuperator process is essential. (ii) The product of co-electrolysis consequently influences the MeOH production process; thus, high-temperature recovery via the inclusion of additional processing for efficiency improvement must satisfy the specific composition ratio of the co-electrolysis product. The issue of finding the best solution for process variables can be resolved via the appropriate implementation of optimization (Wang et al., 2019b). Process optimization (either design or operational) is considered as one of the most important and critical steps during the scaling up of or improvement of any process, with the aim of achieving maximum performance at minimal cost.

The objective of this study is to design a simple efficient process via the development and implementation of rigorous optimization for application towards the progressive improvement of co-electrolysis and the MeOH integrated system configuration, including process performance evaluation. In this regard, self-recovery-assisted co-electrolysis and the MeOH synthesis process are introduced. They were simulated and analyzed using Aspen HYSYS V10 and rigorously optimized via a newly developed single-solution, metaheuristic, vortex search (VS) approach by linking the MATLAB 2017b with HYSYS model. The single-solution-based VS algorithm was developed by Dogan and Olmez (Dogan and Olmez, 2015). The dominant characteristic of this algorithm is the adaptive interval (step) size phenomenon that significantly improves the functionality of the search mechanism. The VS algorithm program balances neighborhood weak and strong locality to determine an optimal solution. Various optimization methods have been implemented with respect to renewable energy (Baños et al., 2011). To the best of the authors’ knowledge, the VS algorithm program is the first approach to be implemented in co-electrolysis and MeOH production systems. To evaluate the retrofitted integrated process performance, exergy analysis, which is an appropriate scientific concept for energy studies, can be applied to achieve sustainable development (Bilgen and Sarıkaya, 2015). The analysis provides good insight into the best approach for achieving system sustainability in an efficient manner.

This study is limited to energy recovery in pre- and post-high temperature co-electrolysis and MeOH synthesis processes to achieve energy efficiency and MeOH production improvement in a PtM process that utilizes electricity from a cleaner source. Thus, a detailed model for MeOH synthesis is required to present the
optimization effect. However, establishing a complex SOEC model is not the aim of this study because during intensification in a large-scale process, transforming a model from complex to simple has significant benefits in terms of its simulation (O’Brien et al., 2007).

2. Base case and proposed optimal retrofitting scheme

Given that the continuous process of the co-electrolysis and MeOH production system is still under development, there are numerous unresolved challenges, which presents an opportunity for the improvement and refinement of this approach. This work uses the configuration process (Al-Kalbani et al., 2016) in which the CO2 absorber is excluded by rearranging the recycle stream before entering the SOEC unit as a base case. Further, the base case is retrofitted with a recuperator on a pre and post SOEC and a MeOH reactor, followed by optimization in to achieve the maximum potential benefit. The performance comparison between the base and optimal retrofitted cases was analyzed via exergy analysis. There are three main stages in the process of MeOH production from captured CO2: CO and H2 production via co-electrolysis process that utilizes SOEC (CO and H2 unit), MeOH synthesis, and MeOH purification.

The base case is presented in Fig. 1. There are three key aspects of the process: CO and H2 unit — from stream 1 and 2 to stream 16; MeOH synthesis — from stream 17 until stream 30, including recycling at stream 34; MeOH purification — from F-5 until C-1. In this process, the CO2 feed stream or stream 2 was assumed to be 95 mol% with water as the remainder at 1000 kmole/h, and was introduced to compressor K-1 to increase the desired operating pressure. The H2O stream was introduced to pump (P) with the same pressure as K-1, to obtain saturated steam or vapor fraction = 1. These two feeds were combined in the mixer and then heated using heater E-2 to obtain an appropriate temperature was achieved to maintain the water gas shift (WGS) reaction at approximately 800 °C, before entering the co-electrolysis process. In a simulator flowsheet, the co-electrolysis process that utilized SOEC is represented as Co-E. The base case of the Co-E duty without a recuperator (HX) was 206,175.79 kW. The ratio of H2, CO, and CO2 (or S(H2/CO) = H2/CO2 = 2), which has been characterized in several studies, was implemented in this study. The initial split ratio, T-1, for the return stream to the co-electrolysis process was 0.2. We recycled H2O from stream to M-1 and the H2O feed at stream 1 was automatically adjusted to be 2191 kmole/h to maintain the S(H2/CO) ratio at stream 16. The SOEC

Fig. 1. Base case process without a recuperation unit.
product from stream 16 was then introduced to the MeOH reactor (R-1), via a series of compressors until a pressure of 70.93 bar was achieved, with each compressor pressure ratio below 3. H₂O is then consecutively removed using flash drums F-2, F3, and F4. Stream 26 was combined with recycled stream 34 in a stream 34/stream 26 ratio of 3.643. The Inlet stream 27 was fed at 265 °C (Al-Kalbani et al., 2016) and the gases associated with stream 29 were cooled to 40 °C using cooler E-8. The purge gas from the reactor was set as 1.00% mole/mole. The final process was MeOH purification. Preliminary purification of MeOH was achieved using two simple flash drums, F-5 and F-6, until the pressure was reduced to 2 bar. Subsequently, a distillation column (C-1) was used to purify MeOH in the liquid phase of the top product at a reasonable MeOH stream product temperature.

SOEC implementation for co-electrolysis with the electrochemical reduction reaction is energy-intensive and MeOH synthesis is performed at a high temperature. This requires additional work to realize efficiency improvement. To address these issues, two recuperators were installed, before Co-E and R-1, as shown in Fig. 2. The H₂O feed was pre-heated by E-1 before being vaporized by recuperator-1 (HX-1). This is because the enthalpy associated with the Co-E output stream is insufficient to directly transform H₂O to steam. The E-1 output vapor fraction composition variable, which represents E-1 enthalpy consumption, is affected by the temperature variation in HX-1. Another issue is the determination of the appropriate temperatures for the hot and cold stream outputs from HX-1, within the optimal process constraints of MITA. After heating in HX-1, steam and CO₂ were introduced to an exothermic reactor or WGS to maintain the desired temperature before entering Co-E. For MeOH synthesis, before entering R-1, the stream was introduced to recuperator-2 (HX-2) to utilize the heat output from R-1 due to the moderately high temperature of the highly exothermic reaction. Direct temperature adjustment in HX-2 with specific MITA may be unfavorable to the conversion in R-1; thus, to maintain or improve the performance and efficiency of R-1, heater E-6 and cooler E-7 were used before and after R-1, respectively. The final step was MeOH purification using flash drums and a distillation column.

2.1. Base case high-temperature co-electrolysis process

A typical SOEC consists of a cathode, an anode, and an electrolyte, as shown in Fig. 3. The electrolyte is an ion-conductive, dense ceramic layer, sandwiched between a porous cathode and anode. The principles of SOEC used for electrolysis and co-electrolysis are presented in Fig. 3(a) and b, respectively. As a co-electrolyzer, SOEC converts CO₂ and H₂O into CO, H₂, and O₂, according to the following reactions at the cathode or fuel electrode (Kim et al., 2015)

\[
H_2O(g) + 2e^- \rightarrow H_2(g) + O^2- \quad \Delta H_{800°C} = 151.8 \text{ kJ/mol} \quad (1)
\]

\[
CO_2(g) + 2e^- \rightarrow CO(g) + O^2- \quad \Delta H_{800°C} = 185.9 \text{ kJ/mol} \quad (2)
\]

![Fig. 2. Proposed self-heat recuperation process for retrofitting scheme.](image-url)
The $O^{2-}$ ions are selectively transferred through the solid electrolyte and combined to form $O_2$ molecules at the anode triple-phase boundary (Zheng et al., 2017). An electrochemical reaction occurs at both electrodes, and both the reverse water gas shift (RWGS) and WGS thermochemical reactions take place on the surface of the electrode (Kim et al., 2015). Co-electrolysis is more complicated than the electrolysis $H_2O\rightarrow CO_2$ due to the WGS and RWGS reaction (Zheng et al., 2017). The thermochemical reactions of RWGS and WGS can be expressed as shown in Equation (3), and the visualization of co-electrolysis on SOEC is shown in Fig. 4.

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g) \quad \Delta H_{800°C} = 36.82 \text{ kJ/mol}$$

Compared to PEM and alkaline water electrolysis, high-temperature SOEC has a lower cell voltage of 0.95–1.3 V and its thermodynamic and kinetic advantages lead to higher efficiency compared to that of other devices at 82% LHV, or equal to 3.7 kWh/Nm$^3$ (Andika et al., 2018).

This study does not focus on the complex rigorous SOEC model. Currently, reported SOEC models are complicated, especially when integrated with other process models. (Im-orb et al., 2018). To model Co-E into a simulation, a simple electrolyzer can be represented by a one-dimensional model in HYSYS (KOH et al., 2010) and Aspen Plus (Im-orb et al., 2018), which is performed by using a conversion or stoichiometry reactor. This reactor is represented by reactor model C in the HYSYS model. However, the thermochemical RWGS and WGS reactions occur in parallel on the electrode catalyst (Ni) or cathode (Ni, 2012). Therefore, additional reaction modeling is necessary. This reaction can be validly modeled using a simple equilibrium reactor on the cathode side (O’Brien et al., 2007). To obtain the desired inlet temperature before entering the co-electrolysis process, an equilibrium reactor or reactor model E that supports the structure of the shift reaction is applied (McKellar et al., 2010). The scheme of the HYSYS models for Co-E with reactions that occur in the SOEC is presented in Fig. 5. In the simulation, the Peng-Robinson thermodynamic model is used for the co-electrolysis process.

The temperature range also played a significant role. The advantage of a higher temperature is a trade-off with material stability, and the favorable temperature range for co-electrolysis on SOEC has been reported to be 600–1000 °C (Zheng et al., 2017). In this study, the SOEC temperature was maintained at ~800 °C. In the
SOEC, the sweep gas was used to remove O₂ from the anode; as more sweep gas is blown through the SOEC, the SOEC efficiency is reduced (Barelli et al., 2017). The amount of sweep gas was calculated using the ratio between the SOEC feed and the sweep gas flow that resulted in a CO₂ and H₂O conversion of 100% and 80%, respectively (McKellar et al., 2010). The ratio between the SOEC feed and the sweep gas flow was approximately 1.03/C^2.10^9. In the base case process, the cathode product or stream 10 was cooled by E-3 to 40°C to transform H₂O to the liquid phase. The separation of H₂O from the other gases took place in flash drum F-1, where the composition ratio of H₂, CO, and CO₂ controls the MeOH synthesis process.

The electricity consumption of the SOECs is represented by the power usage of the reactor, which can be calculated using Equation (4). In this case, the total power supplied to the conversion reactor represents electricity consumption. The electrical power required by the SOEC unit is expressed in (4), where \( W \) is the electrical power supplied to the electrolyzer (W), \( V_{op} \) is the average cell voltage during operation (V), \( I \) is the total current (A), \( i \) is the current density (A/m²), and \( A_{cell} \) is the total active area of the co-electrolysis cells in the SOEC stack (m²) (Fu et al., 2010).

\[
W = V_{op} \cdot I = V_{op} \cdot i \cdot A_{cell} \tag{4}
\]

\( V_{op} \) is written as a function of the current density ((5)), where \( V_N \) is the mean Nernst potential of the operating cell (V) and \( ASR \) is the mean area-specific resistance of the co-electrolyzer stack (Ω m²), which can be experimentally obtained (Fu et al., 2010). \( V_N \) accounts for the variation in the gas composition and the temperature across the operating cell, and can be obtained from an integral form of the steam-hydrogen-based (or the CO₂–CO–based) Nernst equation (Equation (6)).

\[
V_{op} = V_N + \frac{RT}{Y_{H_2} Y_{O_2}} \tag{5}
\]

In (6), \( R \) is the molar gas constant (8.314 J mol⁻¹ K⁻¹), \( T_P \) is the product temperature at the co-electrolyzer outlet (K), and \( T_R \) is the reactant temperature at the co-electrolyzer inlet (K). The mole-fraction subscripts 0, 1, and 2 refer to the cold inlet, hot co-electrolyzer inlet, and hot co-electrolyzer outlet states, respectively (O’Brien et al., 2007).

\[ V_N = -0.5 \left( \frac{RT}{4F} \ln p_{O_2,R} + \frac{RT}{4F} \ln p_{O_2,P} \right) \tag{7} \]

2.2. Base case MeOH production process

MeOH can be synthesized via different reactions routes (Senatore et al., 2018). The overall MeOH production reactions can be categorized as exothermic synthesis, and occur in parallel with the endothermic RWGS reaction (Equations (8), (9), and (10)).
The MeOH synthesis reactor is among the most important aspects of MeOH production. The target of the present work is to minimize energy consumption in this system and to improve MeOH synthesis. Therefore, a detailed model of MeOH synthesis is required for optimization. There are numerous MeOH synthesis kinetic rate equations in the literature (Bozzano and Manenti, 1996). The kinetic equation based on the leading industry catalyst used by Bussche and Froment, for which the reactor dimensions have been proven to be applicable (Chen et al., 2011). This equation was chosen for two reasons. Firstly, the reactor dimensions are not a concern in this study. By using the same catalyst as Bussche and Froment, the same kinetics can be used and can be optimized for the MeOH process in this study. The model is based on the Langmuir-Hinshelwood-Hougen-Watson (LHHW) model (Equation (11) and (12)). Parameters for the kinetic model are provided in Table 1.

The equilibrium constants for $K_1$ and $K_3$ are as follows (Graaf et al., 1990):

$$log_{10} K_1 = \frac{3066}{T} - 10.592$$  \hspace{1cm} (13)

$$log_{10} 1 / K_3^* = \frac{-2073}{T} + 2.029$$  \hspace{1cm} (14)

The reactor dimensions, catalyst data, and pressure drop (approximately 3 bar) were as established from the Lurgi reactor (Chen et al., 2011), with detailed equations, pressures, and reaction rates, as from the previous study on process simulation (Van-Dal and Bouallou, 2013) and (Ghosh et al., 2019). In this study, the MeOH reactor (R-1) in Figs. 1 and 2 was modeled using a plug flow reactor (PFR) in the HYSYS simulator.

To make the original form of Bussche’s equation equivalent to the heterogeneous catalytic reaction expression used in HYSYS, equations (11) and (12) were modified, taking into account the reaction rate unit in HYSYS, kgmol/m³s. Thus, the reactor void fraction significantly affects the kinetics of MeOH synthesis because HYSYS uses a solid density definition on the interface for the PFR and Langmuir kinetics. The MeOH reactor void fraction was assumed to be 0.285, which is similar to that used for a Lurgi reactor. Modified equations for MeOH synthesis and the RWGS reaction were then established (Equation (15) and (16)). A detailed model derivation and validation are presented in the supporting information. To calculate the pressure and temperature of the gas in relation to the kinetic rate and gas fugacity of the MeOH synthesis, the Soave-Redlich-Kwong equation of state (Soave, 1972) is suitable (Graaf et al., 1986). This equation was utilized in the simulation.

### Table 1

<table>
<thead>
<tr>
<th>Parameter (unit)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sqrt{K_{H_0}}$ (bar$^{-1}$)</td>
<td>0.499</td>
</tr>
<tr>
<td>$K_{H_0}$ (bar$^{-1}$)</td>
<td>6.62 x 10$^{-11}$</td>
</tr>
<tr>
<td>$k_{RWGS}$ (mol s$^{-1}$ kg$^{-1}$ bar$^{-1}$)</td>
<td>1.07</td>
</tr>
<tr>
<td>$k_1$ (mol s$^{-1}$ kg$^{-1}$ bar$^{-1}$)</td>
<td>1.22 x 10$^{10}$</td>
</tr>
</tbody>
</table>

$$r_{CH_{3}OH} = \frac{k_{3a}K_2K_3K_hP_{CO_2}P_{H_2} \left[ 1 - (1/K_1) \left( P_{H_2}O/P_{CH_{3}OH} \right) \right]^3 \left( 1 + (K_{H_2}O/K_hK_2K_h) \left( P_{H_2}O/P_{H_2} \right) + \sqrt{K_{H_2}P_{H_2} + K_{H_2}O/P_{H_2}O} \right)} \left( 1 + (K_{H_2}O/K_hK_2K_h) \left( P_{H_2}O/P_{H_2} \right) + \sqrt{K_{H_2}P_{H_2} + K_{H_2}O/P_{H_2}O} \right)$$  \hspace{1cm} (11)

$$r_{CH_{3}OH} = \frac{0.91 \exp \left( \frac{36696}{RT} \right) P_{CO_2} P_{H_2} - 3.46 \times 10^{10} \exp \left( -\frac{21933}{RT} \right) \frac{P_{H_2}O P_{H_2}O}{P_{H_2}} - 1.04 \times 10^{10} \exp \left( \frac{-94765}{RT} \right) P_{CO_2} - 0.97 \times 10^{8} \exp \left( -\frac{55125}{RT} \right) \frac{P_{H_2}O P_{H_2}O}{P_{H_2}}}{1 + 3453.38 \exp \left( \frac{0}{RT} \right) \left( P_{CO_2} \right)^{0.5} + 0.499 \exp \left( \frac{17197}{RT} \right) \left( P_{H_2} \right)^{0.5} + 6.62 \times 10^{11} \exp \left( -\frac{124119}{RT} \right) \frac{P_{H_2}O}{P_{H_2}}}$$  \hspace{1cm} (15)

$$r_{RWGS} = \frac{k_1 P_{CO_2} \left[ 1 - K_3^* \left( P_{H_2}O P_{CO_2} / P_{CO_2} P_{H_2} \right) \right]}{(1 + (K_{H_2}O / K_hK_2K_h) (P_{H_2}O / P_{H_2}) + \sqrt{K_{H_2}P_{H_2} + K_{H_2}O/P_{H_2}O})}$$  \hspace{1cm} (12)
For MeOH synthesis, reactors are typically operated in the temperature range of 220–269 °C (Ganesh, 2014) and at high pressures of approximately 50–100 bar (Van-Dal and Bouallou, 2013). In the present study, the MeOH reactor was operated at 70.93 bar and 265 °C. The reactor pressure drop was fixed at 3 bar (Chen et al., 2011) and the CO₂ conversion was approximately 40% in R-1.

2.3. Base case MeOH purification

MeOH and unreacted reactants were separated using a separator. The unreacted components were recycled. Subsequently, the MeOH was purified using the separator tank and distillation column. The target MeOH purity and recovery in the distillation column were 99.5 mol %. For the purification unit, a near-optimum MeOH distillation preliminary design was utilized; moreover, a shortcut column with a reflux ratio of 1.3 times the reflux minimum was used (Chaniago and Lee, 2018). The last separation of the base case process consisted of 49 theoretical stages of distillation to purify the MeOH in the liquid phase of the top product with a reasonable MeOH stream product temperature of approximately 36.3 °C. To calculate the activity coefficient that affects the vapor-liquid equilibrium in the separation that involves water, the non-random two-liquid model (NRTL) was utilized because it is suitable for separation. In the optimization process, the column stages were manually minimized and the column reflux ratio was optimized using the VS algorithm.

3. Exergy analysis

An energy evaluation to determine the benefit of the sustainable energy process for green technology may be inadequate. An exergy analysis was therefore performed to determine the improved efficiency and thermodynamic loss due to the irreversible increase in entropy (Hajjaji et al., 2012). This analysis addresses the loss (destruction) of available useful energy in the system. By considering the 1st and 2nd laws of thermodynamics, the concept can be understood and the tool can be developed i.e., exergy analysis, which is widely employed to analyze the use of energy considering the 1st and 2nd laws of thermodynamics, the concept of the loss (destruction) of available useful energy in the system. By exergy analysis of individual components present in the same dimension, the chemical exergy of component \( i \) and \( eX_{D, i} \) is the standard chemical exergy of component \( i \).

For a system that includes electrical and mechanical work, the exergy of the work is given as:

\[
E_{W} = W 
\]  

(20)

Exergy analysis of individual components present in the same system can be performed using the following equation:

\[
E_{X_{i}} = \sum_{i} E_{X_{i,i}} 
\]  

(21)

where, \( E_{X_{i,i}} \) can be calculated as:

\[
E_{X_{i,i}} = E_{X_{in,i}} - E_{X_{out,i}} 
\]  

(22)

4. Optimization algorithm

The non-optimized process with a recuperator can be optimized using vortex search optimization (VSO) after exergy analysis. VSO is a meta-heuristic type algorithm and is superior to other heuristic types such as pattern search (PS) and random search (RS) algorithms. It has the advantage of using an adaptable instead of a fixed step size during search tasks. This algorithm optimizes the exploration and exploitation of the search region to provide the best results. Therefore, several highly non-linear processes have been successfully optimized using the VSO approach (Qyyum et al., 2019a). In VSO, the initial guess solution search space can be calculated using the mean value of the bounds provided, as follows:

\[
\mu_{a} = \frac{upper \_ bound + lower \_ bound}{2} 
\]  

(23)

Further, \( n \) candidate solutions are randomly generated using a multivariate Gaussian methodology (Equation (24)), where \( d \) is the dimension, \( \zeta \) is the \( d \times 1 \) vector of a randomly generated variable, \( \mu \) is the \( d \times 1 \) vector of the sample mean (taken as the center), and \( v \) is the covariance matrix.

\[
p(\zeta | \mu, v) = \frac{1}{\sqrt{2\pi}v} \exp \left( -\frac{1}{2} \frac{(\zeta - \mu)^{T}(\zeta - \mu)}{v} \right) 
\]  

(24)

\( v \) can be computed from \( v = s^{2} |I_{d \times d}| \), where \( s^{2} \) represents the variance of the distribution and \( I \) represent the \( d \times d \) identity matrix. The initial standard deviation (\( s_{0} \)) can be calculated as follows:

\[
s_{0}(=r_{a}) = \frac{\text{max}(upper \_ bound) - \text{min}(lower \_ bound)}{2} 
\]  

(25)

In this case, \( s_{0} \) can also be considered as the initial radius \( r_{a} \) and is selected to have a large value initially, for full coverage of the search space. The VSO flow diagram is shown in Fig. 6. The radius step-size, which is one of the main features of VSO is vital to the adjustments that are performed. A further explanation of the VS algorithm with an emphasis on the details of its implementation for the optimization of highly non-linear and complex systems is provided in the literature (Doğan and Ölmez, 2015).

The constrained were handled for the optimization problem by the exterior penalty function method (EPF) (Qyyum et al., 2018), which involves folding the constraints into the objective function. The reformulation of this problem is represented by Eqn. (26) and the minimum and upper bounds for each decision variable are...
defined in Equation (27).

\[ F(X, p, r_h, g_h) = f(X, p) + P(X, p, r_h, g_h) \]  

(26)

\[ X_i^f \leq X_i \leq X_i^u \quad i = 1, 2, ..., n \]  

(27)

In (26), \( r_h \) and \( r_g \) are the penalty constants (multipliers), and \( P(X, p, r_h, r_g) \) is the penalty function, expressed in (28).

\[ P(X, p, r_h, r_g) = r_h \left[ \sum_{k=1}^{l} h_k(X, p)^2 \right] + r_g \left[ \max_{j=1}^{m} \left\{ g_j(X, p) \right\} \right]^2 \]  

(28)

\( h_k \) represents the equality constraint and \( g_k \) is the inequality constraint. The present study does not include any equality constraints; hence, \( r_h \) is assumed to be zero. HYSYS and MATLAB were interfaced using component object model technology for this.
optimization process. In the proposed study, among the key constraints, feasible and realistic MITA values of approximately 20 °C for fluid temperatures exceeding 300 °C and 10 °C for low fluid temperatures were chosen (Harvego and McKellar, 2011). The details of the HYSYS and MATLAB linking procedure is provided in the supporting information.

This study focused on improving the overall energy and exergy efficiency of MeOH production using retrofitted recuperators. The process attempts to optimize the single objective function for each part of the process; hence, there are three objective functions
involved in the optimization (Table 2). The range of optimization is illustrated in Fig. 7.

5. Results and discussions

Exergy analysis was performed to identify the exergy loss in all individual equipment items in the process. In this work, exergy analysis was performed for each piece of equipment engaged in co-electrolysis and MeOH production. The physical exergy was calculated for every stream, while the chemical exergy was only calculated for equipment where reactions occurred. The equations used for physical and exergy loss calculations in the equipment that are associated with co-electrolysis and MeOH production are provided in Tables 3 and 4, respectively.

The standard molar chemical exergies for the investigated components are summarized in Table 5. The calculated physical and chemical exergy losses for the base case are listed in Table 6.

Optimal results were obtained after the three optimization steps listed in Table 2 were applied. For co-electrolysis, H2O was automatically adjusted during the optimization process, while maintaining \( S(H_2/CO) = 2, 2181 \text{ kmol/h H}_2O \) as required for 1000 \( \text{ kmol/h CO}_2 \). There was not a significant reduction of the electrolysis power; it decreased by only 1195.82 kW from 206,175.79 kW, due to the fixed conversion reaction and hard constraints. However, the optimization achieved its purpose in terms of finding the applicable variable ofHX. Another important decision variable was the stream return to co-electrolysis from T-1. The ratio of the stream return to co-electrolysis was determined to be 0.15. A significant change was obtained for the R-1 temperature, which was lower than that of the base case R-1. The optimal recycling ratio was 3.722, which resulted in more MeOH production.

The MeOH reaction for this process was based on CO. The compositions of CO and MeOH during the reaction are compared in Fig. 8. The optimized solution alongside the reactor shows a molar composition for given reactor lengths. The expressions for the physical and chemical exergy losses in Table 6 and 8 were utilized. By applying the recuperators, the exergy destruction via the coolers, \( E (\text{air/water-based}) \), could be

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Equations for physical exergy loss calculation for equipment associated with co-electrolysis and MeOH production.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equipment</td>
<td>( E_{\text{ph,loss}} = -\sum m_i(H_{\text{in}} - H_{\text{out}}) )</td>
</tr>
<tr>
<td>Compressor (K)</td>
<td></td>
</tr>
<tr>
<td>Pump (P)</td>
<td></td>
</tr>
<tr>
<td>Cooler exchanging heat with ambient (E)</td>
<td></td>
</tr>
<tr>
<td>Phase separator (F)</td>
<td></td>
</tr>
<tr>
<td>Throttle valve (JT valve)</td>
<td></td>
</tr>
<tr>
<td>Mixer (M)</td>
<td></td>
</tr>
<tr>
<td>Tree (T)</td>
<td></td>
</tr>
<tr>
<td>Recuperator (HX)</td>
<td></td>
</tr>
<tr>
<td>Water gas shift reactor (WGS)</td>
<td></td>
</tr>
<tr>
<td>MeOH reactor (R-1)</td>
<td></td>
</tr>
<tr>
<td>Co-Electrolysis unit (Co-E)</td>
<td></td>
</tr>
<tr>
<td>Tee (T)</td>
<td></td>
</tr>
<tr>
<td>Cooler exchanging heat with ambient (E)</td>
<td></td>
</tr>
<tr>
<td>Compressor (K)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Equations for chemical exergy loss calculation for equipment associated with co-electrolysis and MeOH production.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equipment</td>
<td>( E_{\text{ch,loss}} = \sum y_i(H_{\text{loss}} - H_{\text{in}}) + \sum P_i(H_{\text{loss}} - H_{\text{out}}) )</td>
</tr>
<tr>
<td>WGS; Co-E; R-1</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 5</th>
<th>Standard molar chemical exergies from (Im-orb et al., 2018) and (De Alwis et al., 2009).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
<td>( \epsilon_{x_i} )</td>
</tr>
<tr>
<td>H2O(g)</td>
<td>9.50</td>
</tr>
<tr>
<td>O2</td>
<td>3.97</td>
</tr>
<tr>
<td>CO2</td>
<td>19.48</td>
</tr>
<tr>
<td>CO</td>
<td>274.71</td>
</tr>
<tr>
<td>H2</td>
<td>236.09</td>
</tr>
<tr>
<td>CH3OH</td>
<td>754.69</td>
</tr>
</tbody>
</table>
significantly reduced (Fig. 9).

The detailed exergy losses of each equipment for the recuperator-integrated optimal process are shown in Fig. 9. The overall exergy loss was reduced to $9425.57 \times 10^5$ kJ/h, or 15.9%, compared to the non-optimal process. Fig. 9 shows that approximately 82% of the exergy loss occurred in the co-electrolysis unit. The remaining processes accounted for 18% of the exergy loss; however, the majority of this loss occurred in the coolers i.e., 49% of 18%. The optimal system with self-heat recuperation significantly reduced the exergy loss from $2785.20 \times 10^5$ kJ/h to $1067.84 \times 10^5$ kJ/h for the overall heat transfer of the heat exchanger.

After optimizing the self-recuperative, high-temperature, and co-electrolysis-based MeOH synthesis process, the energy-saving opportunities corresponding to exergy efficiency enhancement can be illustrated via analysis of the composite curves (temperature differences between composite curves (TDCC), and temperature-flow between composite curves (THCC)) within the heat exchangers, HX-1 and HX-2. Fig. 10(a) and (b) present the TDCC and THCC curves for HX-1, while Fig. 11(a) and (b) present the TDCC and THCC curves for HX-2, respectively.

TDCC analysis provides information on the internal approach temperatures along the length of the recuperators. The recuperators can be more effective when the approach temperature (peak of the TDCC) lies between the defined range. TDCC analysis also addresses the impact of all the design variables on the overall performance with respect to the available energy utilization. In HX-1, the peak of the TDCC curve varied from 20.0°C to 98.0°C, which ultimately led to different temperature gradients inside the exchanger and explains the exergy losses. However, the peak remained above 20.0°C, which could be further reduced by employing a more robust strategy.

Exergy losses can also be evaluated by observing the distance between the THCC curves. Fig. 10(b) shows that the warmer and colder ends of recuperator HX-1 strictly follow the constrained approach temperature i.e., 20.0°C to 98.0°C, which ultimately led to different temperature gradients inside the exchanger and explains the exergy losses. However, the peak remained above 20.0°C, which could be further reduced by employing a more robust strategy.

Table 7a
Optimization of CO and H2 unit for proposed stream and equipment schemes (Step 1).

<table>
<thead>
<tr>
<th>CO and H2 unit Process</th>
<th>1</th>
<th>2</th>
<th>E-1</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>30.0</td>
<td>43.9</td>
<td>102.5</td>
<td>51.1</td>
<td>102.5</td>
<td>800.0</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>1.01</td>
<td>1.80</td>
<td>1.11</td>
<td>1.11</td>
<td>1.11</td>
<td>1.11</td>
</tr>
<tr>
<td>Mole Flow (kmole/h)</td>
<td>2181.00</td>
<td>1000.00</td>
<td>2239.72</td>
<td>1563.73</td>
<td>2239.72</td>
<td>2239.72</td>
</tr>
<tr>
<td>Vapor Fraction</td>
<td>1.00</td>
<td>1.00</td>
<td>0.86</td>
<td>1.00</td>
<td>0.86</td>
<td>1.00</td>
</tr>
<tr>
<td>Duty (kW)</td>
<td>25,437.43</td>
<td>25,437.43</td>
<td>25,437.43</td>
<td>25,437.43</td>
<td>25,437.43</td>
<td>25,437.43</td>
</tr>
</tbody>
</table>

Table 7b
Optimal findings for the proposed MeOH synthesis streams and equipment schemes (Step 2).

<table>
<thead>
<tr>
<th>MeOH Synthesis Process</th>
<th>32</th>
<th>33</th>
<th>E-6</th>
<th>34</th>
<th>35</th>
<th>36</th>
<th>R-1</th>
<th>E-7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>75.9</td>
<td>204.0</td>
<td>225.0</td>
<td>225.0</td>
<td>221.0</td>
<td>110.6</td>
<td>221.0</td>
<td>40.0</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>70.93</td>
<td>70.93</td>
<td>70.93</td>
<td>70.93</td>
<td>67.93</td>
<td>67.93</td>
<td>67.93</td>
<td>67.93</td>
</tr>
<tr>
<td>Mole Flow (kmole/h)</td>
<td>13,993.18</td>
<td>13,993.18</td>
<td>13,993.18</td>
<td>13,993.18</td>
<td>12,102.78</td>
<td>12,102.78</td>
<td>12,102.78</td>
<td>12,102.78</td>
</tr>
<tr>
<td>Vapor Fraction</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>0.97</td>
<td>1.00</td>
<td>0.91</td>
<td>0.91</td>
</tr>
<tr>
<td>Duty (kW)</td>
<td>2395.38</td>
<td>2395.38</td>
<td>2395.38</td>
<td>2395.38</td>
<td>2395.38</td>
<td>2395.38</td>
<td>2395.38</td>
<td>2395.38</td>
</tr>
</tbody>
</table>
The HX-2 THCC curves behaved differently, with only the warmer end following the constrained approach temperature, i.e., 10°C (Fig. 11(b)). The colder side of HX-2 results in composite curves with large separation distances, indicating that the exergy loss in this region is higher compared to that of the warmer side. The HX-2 TDCC curves peaked at a maximum of 35.0°C and varied between 10.0°C and 35.0°C (Fig. 11(a)). This is still significantly higher than the specified value, i.e., 10.0°C. However, analysis of the composite curves for the proposed recuperators revealed that it is possible to achieve further minimization of the distance between the TDCC composite curves, as well as the peaks. This could significantly improve the overall performance of the proposed self-recuperative high-temperature co-electrolysis based-MeOH synthesis process.

6. Conclusions

This study presents a progressive implementation of the superior heuristic VS algorithm for innovative optimization to address the heat recovery issues associated with co-electrolysis and exothermic MeOH reactors to improve the process efficiency, resulting in cleaner MeOH production. The base case exergy analysis revealed that the highest exergy destruction rate was associated with the process involving thermochemical reactions, with a

<table>
<thead>
<tr>
<th>Equipment</th>
<th>$E_{\text{ex,loss}}$ ($\times 10^5$)kJ/h</th>
<th>$E_{\text{ex,bas}}$ ($\times 10^5$)kJ/h</th>
<th>Total ($\times 10^5$)kJ/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>WGS</td>
<td>-1576.26</td>
<td>0.51</td>
<td>-1575.74</td>
</tr>
<tr>
<td>Co-E</td>
<td>8998.29</td>
<td>-0.21</td>
<td>8998.09</td>
</tr>
<tr>
<td>R-1</td>
<td>239.98</td>
<td>-0.11</td>
<td>239.88</td>
</tr>
<tr>
<td>C-1</td>
<td>487.81</td>
<td>0.00</td>
<td>487.81</td>
</tr>
<tr>
<td>$\Sigma$ (F)</td>
<td>30.18</td>
<td>0.00</td>
<td>30.18</td>
</tr>
<tr>
<td>$\Sigma$ (M, T and J valve)</td>
<td>83.20</td>
<td>0.00</td>
<td>83.20</td>
</tr>
<tr>
<td>$\Sigma$ (K and P)</td>
<td>94.32</td>
<td>0.00</td>
<td>94.32</td>
</tr>
<tr>
<td>$\Sigma$ (E)</td>
<td>991.72</td>
<td>0.00</td>
<td>991.72</td>
</tr>
<tr>
<td>HX-1</td>
<td>62.32</td>
<td>0.00</td>
<td>62.32</td>
</tr>
<tr>
<td>HX-2</td>
<td>13.79</td>
<td>0.00</td>
<td>13.79</td>
</tr>
<tr>
<td>Whole Process</td>
<td>($\times 10^5$)kJ/h</td>
<td></td>
<td>9425.57</td>
</tr>
</tbody>
</table>

Fig. 9. Exergy loss comparison for major equipment items, with and without the recuperator.

Fig. 10. Optimal curves for recuperator HX-1: (a) TDCC, (b) THCC.
A metaheuristic approach was implemented in the co-electrolysis case. The total exergy loss of approximately 82%. The remaining processes involved 18% exergy loss, most of which occurred at the coolers i.e., 49% of 18%. The VS metaheuristic approach searched for optimal values of performance parameters for high-temperature co-electrolysis-based MeOH production with appropriate operational MTA of the self-heat recuperation. It was successfully implemented in the retrofitted case. The exergy loss from the energy transfer process system was significantly reduced, by 61.7% and achieved an overall exergy efficiency enhancement of 15.9%. Specifically, the VSO could reduce the required energy for steam generation at E-1 and the co-electrolysis power. The exergy loss in the co-electrolysis process was reduced from 9129.95 to 8998.09 kJ/h. Optimum gas recycling from T-1 was achieved. This is considered to be among the influential variables in self-electrolysis that affects H2O and co-electrolysis performance under self-heat recuperation enhancement. The H2O requirement was reduced to 2181 kmol/h from 2191 kmol/h to maintain S(H2/O) while increasing the energy efficiency. Optimization of the self-heat recuperation sequence for co-electrolysis and MeOH synthesis not only improved the process exergy efficiency, but also increased MeOH production from 936.53 to 940.23 kmol/h, with reduced the C-1 reboiler duty.

These results suggested that the improved performance of methanol production in the proposed recuperated process could be achieved via the implementation of appropriate optimization and by exploiting the maximum potential benefit of the retrofitting recuperators. This implies that the proposed solution of self-recuperation with the implementation of appropriate optimization is a potential solution to the problem of CO2 emission utilization, which is occasionally hindered by process complexity. Moreover, this method is a flexible approach that can be directly implemented for the enhancement of co-electrolysis and MeOH synthesis in a system that requires heat recovery to improve the efficiency and final product.

Declaration

The authors declare no competing financial interest.

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Appendix A. Supplementary data

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References


