Energy and exergy analyses of a solar magnesium-chlorine thermochemical plant for methane production

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Abstract. Solar power as the most available type of renewable energy can be used as a clean driving source in the thermal systems. One of the ways to overcome the intermittency problem of solar energy is to convert it into a chemical that can be used whenever it is required. Hydrogen is a good candidate for using it as a fuel. Thermochemical methods for the production of hydrogen are considered as promising candidates. magnesium-chlorine (Mg-Cl) thermochemical cycle is one of the water-splitting cycles that can be used to produce hydrogen. Due to the problems related to storing hydrogen, it is more convenient if we convert it into another chemical like methane. A novel integrated system has been proposed in this study for the production of methane through the Mg-Cl thermochemical cycle. For the base case, hydrogen can be produced with a mass flow rate of 188.32 kg/h. Energy and exergy efficiencies of the Mg-Cl cycle are calculated as 26.25% and 59.88%, respectively. If the produced hydrogen is converted into methane, the methane production capacity of the plant would be 352.98 kg/h. Our results indicated that the energy and exergy efficiencies of the overall system are 7.04% and 60.28%, respectively.

Keywords: Solar tower, Molten salt, Mg-Cl thermochemical cycle, Hydrogen production, Methane production

1. Introduction

Alternative fuels can be produced by using solar energy and carbon dioxide [1,2]. Hydrogen is a key component of clean fuel production. There are many ways to produce hydrogen from either hydrocarbons or water. Such methods include steam methane reforming, coal gasification, water electrolysis, etc. An environmental benign hydrogen production method can significantly reduce global CO₂ emissions [3]. Solar systems with central receiver units are a good candidate for their integration with various cycles for the production of low-carbon fuels such as hydrogen or even power [4,5].

Some studies investigated the thermodynamic analysis of solar systems with central receiver units. Xu et al. [6] performed a thermodynamic analysis for heliostat sets and solar tower. They employed solar energy as the input of the Rankine cycle to produce power. Their analysis showed that the energy and exergy efficiencies of the cycle of under investigation are 22.89% and 24.48%, respectively. Also, the energy and exergy efficiencies of the solar tower were obtained as 90.02% and 55.48%, respectively [6]. In the other study in this field, Li et al. elaborated on the details of solar tower and formulated the calculations of its heat loss [7]. Toghyani et al. [8] considered a system including solar energy and thermal energy storage (TES) integrated with a Rankine cycle. They investigated the performance of the mentioned cycle using four different nano-fluids in the solar system. They also
studied the effect of various parameters on the performance of the cycle and concluded when solar irradiation increases, the output power of the cycle will grow significantly [8]. A comprehensive analysis containing 4E analysis was conducted by Boukelia et al. They used two different fluids as the working fluid of the solar system and compared the systems with and without the presence of the TES subsystem [9].

Among various hydrogen production methods, thermochemical methods are of interest because they are more environmentally friendly. Ozcan and Dincer [10] studied magnesium-chlorine (Mg-Cl) cycle integrated with solar energy and a Rankine cycle and conducted energy and exergy analyses. They concluded that if the molten salt is employed as the working fluid of the solar system, the rate of hydrogen production will be increased. The energy and exergy efficiencies of the system were reported as 26.9% and 40.7%, respectively [10].

The main problem of renewable energies such as wind and solar energy is their fluctuating nature. Power to gas is one way to store their excess produced energy [11]. For example, methane production can be considered for this purpose. Methane can be used to store energy without any limitation, whereas there are some issues about hydrogen such as its safe storage [12]. Safari and Dincer examined wind-powered system to produce methane. They produced hydrogen through a proton exchange membrane (PEM) electrolyzer and combined it with CO₂ to get methane. The energy and exergy analyses were completed and the rate of methane production was evaluated as 1.68 kg/h [13].

In this study, energy and exergy analyses of an integrated solar-powered Mg-Cl cycle system have been performed. The system investigated here, includes a solar subsystem with a central receiver unit, a sensible TES unit, a three-step Mg-Cl cycle, a regenerative Rankine cycle, and a methanation unit. The solar and TES subsystems are modeled using a quasi-dynamic method with hourly time-steps. Using TES tanks eliminates the problem of intermittency of solar energy. In the Mg-Cl cycle, pinch analysis is used to get the maximum recoverable waste heat in the cycle. The produced hydrogen is then used to produce methane. The rate of methane production and the energy and exergy efficiencies of each part are also evaluated here. Finally, a parametric study is conducted to show the influence of changing important input parameters on system performance.

2. System Description

The layout of the proposed system is illustrated in Figure 1. The working fluid of solar tower, molten salt, enters the solar tower at 290 °C. The solar tower increases the temperature of molten salt to 565 °C. Afterward, a part of molten salt is sent to the Rankine and Mg-Cl cycles, and the remaining is stored in a hot TES tank. When the amount available energy is higher than the required energy of the Mg-Cl and Rankine cycles, the molten salt hot tank is charged, and whenever the required energy is not available, the tank is discharged. The Mg-Cl cycle considered here includes two reactors and an electrolyzer unit. In one of the reactors, an exothermic reaction occurs, and in the other one, an endothermic reaction takes place.

Hydrolysis and Chlorination reactions are shown below:

\[ \text{MgCl}_2(s) + \text{H}_2\text{O}(g) \rightarrow \text{MgO}(s) + 2\text{HCl}(g) \]  \hspace{2cm} (1)

\[ \text{MgO}(s) + \text{Cl}_2(g) \rightarrow \text{MgCl}_2(s) + \frac{1}{2}\text{O}_2(g) \]  \hspace{2cm} (2)

The energy of the endothermic reaction (hydrolysis reaction) is provided by the molten salt flowing through the reactor's shell (i.e., Reactor 1 in Figure 1). Additionally, molten salt supplies the required energy of the heaters 1 to 4, present in the Mg-Cl cycle. Seven heat exchangers are used to recover the excess energy of each stream. The only input of the Mg-Cl cycle is steam and the outputs are oxygen and hydrogen. As mentioned earlier, a regenerative Rankine cycle has been integrated with the system to provide the required power of the electrolyzer. The electrochemical reaction that takes place in the electrolyzer unit is shown below:

\[ 2\text{HCl}(g) \rightarrow \text{H}_2(g) + \text{Cl}_2(g) \]  \hspace{2cm} (3)
The Rankine cycle includes three closed feedwater heater (CFWH) and one open feedwater heater (OFWH) to increase the energy efficiency of the cycle. Also, a multi-stage turbine is used to reach a higher output power. In the steam generator of the Rankine cycle, water is heated from state 48 to 49 by stream 8. It is noted that all of the power that is generated in the Rankine cycle is used in the electrolyzer unit to produce hydrogen, and therefore, no excess power is generated here. The produced hydrogen at state 22 is sent to the methanation unit where it will react with CO$_2$ to produce methane. The Sabatier reaction takes place in the methanation unit at a constant temperature of 300 °C, and methane is produced at state 64. The produced methane can be stored in a tank or can be consumed directly.

![Figure 1. Schematic of the integrated system for methane production.](image)

3. Thermodynamic Modeling
The main assumptions which have been used in this study are:
- A dynamic model is developed to investigate the variation of solar radiation over time.
- Kinetic and potential energies are negligible.
- The temperature and pressure of the dead state are 25°C and 101 kPa, respectively.

In order to complete the energy and exergy analyses, the energy and exergy rate balances must be written for all the system components. These equations are written as follows [14]:

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This content is extracted from a technical document related to the thermodynamic modeling of a system involving solar energy conversion, feedwater heaters, turbines, and methanation processes. The focus is on enhancing energy efficiency through the Rankine cycle and integrating solar energy for hydrogen production, with subsequent methanation. The diagram illustrates the flow of processes, including solar radiation collection, steam generation, power generation, hydrogen production, and methanation.
\[ \dot{Q} + \dot{w} = \sum (\dot{m} h)_{\text{out}} - \sum (\dot{m} h)_{\text{in}} \]  
\[ \dot{E}_{\text{heating}} - \dot{w} = \sum \dot{E}_{\text{out}} - \sum \dot{E}_{\text{in}} + \dot{E}_{\text{dest}} \]  

where \( \dot{Q} \) and \( \dot{w} \) represent the rates of heat and work, respectively. Also, \( \dot{E}_{\text{dest}} \) is the rate of exergy destruction, and \( \dot{E}_{\text{heating}} \) is the rate of exergy transfer accompanying heat transfer calculated by:

\[ \dot{E}_{\text{heating}} = \sum \dot{Q} \left(1 - \frac{T_0}{T}\right) \]

here, \( T_0 \) is the dead state and \( T \) is the source/sink temperature.

\( \dot{E}_{\text{out}} \) and \( \dot{E}_{\text{in}} \) are the exergy rates of the outlet and inlet streams. To obtain these parameters, specific exergy must be known for each stream. The specific exergy is expressed as [14]:

\[ ex = ex^{ph} + ex^{ch} \]

where \( ex^{ph} \) and \( ex^{ch} \) are the specific physical and chemical exergies, respectively. Specific physical exergy is evaluated by:

\[ ex^{ph} = (h - h_0) - T_0(s - s_0) \]

The amount of solar radiation which strikes the heliostats is evaluated as:

\[ \dot{Q} = A_h \dot{q} \]

where \( A_h \) is the area of heliostat mirrors and \( \dot{q} \) is the solar radiation per unit area.

By knowing the heliostat efficiency, the amount of heat loss from this component can be obtained. The energy balance in the solar tower is written as follows:

\[ Q_{re} = Q_{re,abs} + Q_{loss,tot} \]

where \( Q_{re,abs} \) is the absorbing heat by the working fluid. Also, \( Q_{loss,tot} \) is the total heat loss of solar tower which includes four terms, namely convection, conduction, radiation, and reflection heat losses. The following equation can be applied for estimating convection heat loss:

\[ Q_{\text{conv}} = (h_{air,fc} \times A_{ape} \times (T_{\text{re,sur}} - T_a)) + (h_{air,nc} \times A_{re,sur} \times (T_{\text{re,sur}} - T_a)) \]

\( h_{air,fc} \) and \( h_{air,nc} \) are the forced and natural convection heat transfer coefficients, respectively. Also, \( A_{re,sur} \) and \( T_{\text{re,sur}} \) are the area and temperature of the receiver surface and \( A_{ape} \) represents the aperture area of the receiver.

The conduction heat loss that should be found by an iterating method is represented as:

\[ Q_{\text{cond}} = A_{re,sur} \frac{(T_{\text{re,sur}} - T_{\text{ins,w}})}{\frac{\delta_{\text{ins}}}{\lambda_{\text{ins}}}} = A_{re,sur} \frac{(T_{\text{ins,w}} - T_a)}{\frac{1}{h_{air,o}}} \]

where \( T_{\text{ins,w}} \) is the insulation wall temperature and \( h_{air,o} \) is the heat transfer coefficient in the outside of insulation layer. Also, \( \delta_{\text{ins}} \) and \( \lambda_{\text{ins}} \) are the thickness and conductivity of insulation.

Two remaining heat losses can be estimated by the following equation:
\[ Q_{rad} = \varepsilon_{avg} \times \sigma \times A_{resur} \times F_r \times (T_{resur}^4 - T_a^4) \]  

\[ Q_{ref} = Q_{re} \times F_r \times \rho \]  

(13)  

(14)

where \( \varepsilon_{avg} \) and \( \rho \) are the receiver emissivity and reflectivity, respectively. Also, \( F_r \) is the view factor and \( \sigma \) denotes the Stefan-Boltzmann constant which is equal to \( 5.67 \times 10^{-8} \text{ (W/m}^2 \times \text{K}^4) \). The Sabatier reaction that produces methane is an exothermic reaction which releases 165.02 kJ/mol CH\(_4\) under standard condition [15]. It is shown in the following equation:

\[ \text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H = -165.02 \text{ kJ/mole} \]  

(15)

Finally, the overall energy and exergy efficiencies of the cycle are obtained by

\[ \eta_{en} = \frac{(m \text{LHV})_{CH_4}}{Q_{in}} \]  

\[ \eta_{ex} = 1 - \frac{E_{x\text{dest}}}{E_{x\text{in}}} \]  

(16)  

(17)

The main assumptions for the base case of this study have been listed in Table 1 [6,10].

| Parameter                  | Value | Parameter                  | Value |
|----------------------------|-------|----------------------------|-------|
| Single heliostat area (m\(^2\)) | 100   | Hydrolysis temperature (°C) | 500   |
| Heliostat efficiency (%)   | 75    | Chlorination temperature (°C) | 450   |
| Heliostats numbers         | 1000  | TES height (m)             | 12    |

4. Results and discussion

4.1. Comparison with past studies

The results for selected parts of the system are compared with those of past studies. Figure 2 illustrates the results of the solar tower compared with those reported by Xu et al. [6]. Also, the results of the Mg-Cl cycle are compared with those presented by Ozcan and Dincer [10] in Table 2. Conversion ratio of the CO\(_2\) to CH\(_4\) in the Sabatier reaction is compared with the results of Ohya et al. [16] in Figure 3. As can be seen, our results are in good agreement with those presented in past studies.
Figure 2. Receiver efficiency of the solar tower versus the direct normal irradiation.

Table 2. Comparison of the results for the Mg-Cl cycle

| Parameter                                 | Present study | Ozcan and Dincer study [10] |
|-------------------------------------------|---------------|-----------------------------|
| Energy efficiency (%)                    | 56.45         | 51.6                        |
| Exergy efficiency (%)                    | 62.89         | 67.6                        |
| Requirement heat for the endothermic reactor (kJ/mol) | 93.1          | 97.59                       |
4.2. Base case results

The results of the base case of the proposed system are shown in Table 3. According to our results, the energy and exergy efficiencies of the overall system are obtained as 7.04% and 60.28%, respectively. Also, the exergy destruction of the overall cycle is equal to 24.27 MW. As it is shown, the mass flow rate of hydrogen production in the Mg-Cl cycle is calculated as 188.32 kg/h. For this amount, the electrolyzer unit will require 7.99 MW of electricity. After performing the thermodynamic analysis for all the system components, the amount of methane can be evaluated as 352.98 kg/h.

Figure 4 shows the percentage of exergy destruction of each section in the overall cycle. The heliostat field has the main effect on the overall exergy destruction. On the other hand, the minimum contribution to exergy destruction belongs to the TES tank which is zero, approximately. Mg-Cl cycle, solar tower, Rankine cycle, and methanation unit are the other sections with occupying 17, 10, 9, and 1 percent of this pie chart, respectively.
The effect of various parameters on the performance of the cycle has been investigated here. The influence of increasing the number of heliostats on system performance is shown in Figure 5. When the number of heliostats is increased, both the exergy destruction rate and the mass flow rate of methane will be increased. To be more specific, by increasing the number of heliostats from 1000 to 10000, the mass flow rate of methane and exergy destruction rate are increased from 352.98 kg/h and 24.27 MW to 3535.95 kg/h and 247.6 MW, respectively. As mentioned earlier, the heliostat field has a major influence on the rate of exergy destruction. Therefore, an increase in the overall exergy destruction rate is expected with an increase in the number of heliostats. Besides, when the number of heliostats is increased, higher rates of energy can be extracted from molten salt. Consequently, the input energy of the Mg-Cl cycle will be higher, and the rate of both hydrogen and methane production will be increased.

Figure 4. Distribution of exergy destruction among the various subsystems in the integrated model.
Figure 5. Effect of the number of heliostats on the rate of exergy destruction and mass flow rate of methane.

Inlet pressure of the high-pressure turbine is another parameter that is investigated and the effect of that on the energy efficiency and rate of exergy destruction are shown in Figure 6. By changing the pressure from 8 to 16 MPa, energy efficiency increases from 6.8% to 7.15%, respectively. In this situation, the output power of the Rankine cycle is improved, and therefore, the rate of hydrogen production will be increased. As a result, the increase in the energy efficiency of the overall system is reasonable. Also, by an increase of the Rankine cycle’s net power output, the required mass flow rate of molten salt for the production of a constant amount of electricity for the electrolyzer unit is reduced, and thus, the rate of exergy destruction will be reduced, too.

Figure 7 shows the influence of the inlet temperature of the high-pressure turbine on the mass flow rate of methane and the exergy efficiency of the system. By increasing the temperature it is expected to achieve more power in the Rankine cycle. Hence, the required power of the electrolyzer is improved, and therefore, the mass flow rate of hydrogen will be increased. As a result, the mass flow rate of the produced methane will also increase. Additionally, the exergy efficiency of the system is experiencing an upward trend with the increase of the inlet temperature of the high-pressure turbine. It is due to the decrease in the amount of molten salt that was required in the steam generator unit. At a constant flow rate of hydrogen, by increasing the inlet energy of the electrolyzer, less molten salt is required to provide the energy of the electrolyzer. Reducing the mass flow rate of the molten salt will decrease the exergy destruction rate, and increase the exergy efficiency of the system, subsequently.
Figure 6. Impact of the inlet pressure of the high-pressure turbine on the energy efficiency and exergy destruction rate of the system.

Figure 7. Variation of the mass flow rate of methane and exergy efficiency of the system with respect to the inlet temperature of the high-pressure turbine.
Sabatier reaction which is an exothermic process to produce methane is usually happening in the range of 300-400 °C. The equilibrium constant of this reaction has an inversely-related relationship with the temperature. Also, when the temperature of the reaction is increased the conversion ratio of carbon dioxide to the methane is starting to drop. Therefore, by changing the temperature of the Sabatier reaction from 300 to 400 °C, the mass flow rate of the methane is expected to experience a reduction. The results are consistent with what is pointed out. Figure 8 illustrated the variations of the mass flow rate of methane and the exergy efficiency of the methanation unit with the reaction’s temperature. Also, the exergy efficiency of the methanation unit will be reduced. It is due to the reduction of specific physical exergy of the products compared with the reactants.

![Graph](image)

**Figure 8.** The effect of temperature of the Sabatier’s reaction on the mass flow rate of methane and exergy efficiency of the methanation unit.

The exergy efficiency of each subsystem of the integrated system are shown in Figure 9. The exergy efficiency of the TES tank is very close to 100%, it is mostly due to the insulation of this unit. That means, TES tank has been insulated very well and the heat loss of the TES tank is low, therefore, the existing exergy in the inlet stream of the TES tank is almost equal to the outlet stream of that. The lowest exergy efficiency belongs to the Mg-CI cycle which is equal to 59.88%. The exergy efficiency of the heliostat field has been shown as 75%. This efficiency was predictable because the energy efficiency of the heliostat field is also 75%. As it is evident, the exergy efficiency of the methanation unit, Rankine cycle, and solar tower are calculated as 88.06%, 80.75%, and 94.88%, respectively.
Figure 9. The exergy efficiency of various subsystems in the proposed integrated system.

5. Conclusion
An integrated system including heliostat field, solar tower, TES tank, Mg-Cl cycle, Rankine cycle, and methanation unit was proposed and investigated to produce methane as a power to gas technology. Energy and exergy analyses for each subsection and overall system were performed in detail. Also, a parametric study was carried out to realize the effect of the various parameters on the performance of the system. The main findings of the present study are shown below:

- Energy and exergy efficiencies of the overall system are calculated as 7.04% and 60.28%, respectively.
- The mass flow rate of hydrogen was attained by 188.32 kg/h. If this hydrogen is used in the methanation unit, the system is capable of producing 352.98 kg/h methane through the Sabatier reaction.
- The main contribution to the exergy destruction rate of the overall system belongs to the heliostat field with a value of 63%.
- By increasing the number of heliostats, the rate of exergy destruction, and the mass flow rate of methane are increased.
- Energy and exergy efficiencies of the cycle improved by the increase of the pressure and temperature of the high-pressure turbine inlet.
- The high-temperature condition for Sabatier's reaction was an undesired situation because it will lead to a drop in the mass flow rate of methane.

6. Nomenclature

| Symbol | Definition |
|--------|------------|
| A      | Area (m²)  |
| ex     | Specific exergy (W/kg) |
| Ex     | Rate of exergy (W) |
| F_r    | View factor |
| h      | Heat transfer coefficient (W/(m².K)) |
| LHV    | Lower heating value (J/kg) |
| ṁ      | Mass flow rate (kg/s) |
| ṗ̇      | Solar radiation (W/m²) |
\( \dot{Q} \) Rate of energy (W)

\( s \) Specific entropy (J/(kg.K))

\( T \) Temperature (K)

\( \dot{w} \) Rate of Work (W)

Subscripts

0 Dead state

a ambient

ape aperture

avg average amount

ch chemical

cond conduction

conv convection

dest destruction

cy forced convection

h heliostat mirrors

in inlet

ins insulation

nc natural convection

out outlet

ph physical

rad radiation

re receiver

ref reflection

sur surface

tot total

w wall

Greek symbols

\( \eta_{en} \) Energy efficiency

\( \eta_{ex} \) Exergy efficiency

\( \Delta \) Difference

\( \varepsilon \) emissivity of receiver

\( \sigma \) Stefan-Boltzmann constant (W/(m².K⁴))

\( \lambda \) Conductivity (W/(m.K))

\( \delta \) Thickness (m)

\( \rho \) Reflectivity of receiver

7. References

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