Investigation of an integrated solar thermochemical plant for hydrogen production using high-temperature molten salt

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Abstract. One of the most promising methods for producing hydrogen is the use of a water splitting process utilising the copper-chlorine (Cu-Cl) thermochemical cycle. The Cu-Cl cycle uses heat and electricity to produce hydrogen and oxygen from the decomposition of water molecules. In this paper, a new solar-powered integrated system is proposed which utilises (LiNaK)₂CO₃ high-temperature carbonate molten salt as both a heat transfer fluid and a thermal energy storage medium to provide the required heat for the Cu-Cl cycle reactors and heat exchangers. The system is integrated with a supercritical regenerative steam Rankine cycle (SRC) which produces the required electricity for the electrolyser unit. Thermodynamic and economic analyses were conducted to evaluate the proposed system in terms of hydrogen production cost and system performance. For the base case, the integrated system was found to be capable of producing 823.71 kg/h of hydrogen. The system is optimised for two objective parameters, overall system thermal efficiency and the levelized cost of hydrogen. The results of optimisation analysis indicated that, for the optimal Pareto solution, the overall system thermal efficiency and levelized cost of hydrogen were 29.17%, and $7.58/kg of H₂, respectively.

Keywords: Hydrogen production, Thermochemical cycle, Solar energy, Economic analysis, Optimisation, Molten salt

1. Introduction

Due to the increasing awareness of climate change-related problems, extra attention is now being paid to the production of low carbon fuels [1]. Hydrogen, as a carbon-free fuel with high energy density, is a good candidate for such study [2], and there are various ways in which this substance can be produced. These methods include steam reforming, coal gasification, and water splitting processes [3]. Recently, water splitting processes that dissociate water molecules into hydrogen and oxygen have attracted the attention of many researchers. These processes utilise heat, electricity, or both to produce hydrogen [3]. Water electrolysis is the main water splitting process that uses electric power, while thermolysis and many thermochemical cycles utilise heat as their power source; however, few thermochemical cycles effectively use both heat and electricity [4].

The copper-chlorine (Cu-Cl) thermochemical cycle uses electricity and thermal power, and this is one of the most promising available options for the clean production of hydrogen. This cycle utilises a series of reactions to produce hydrogen from the splitting of water, and all of the chemicals used in the cycle can be recycled, with no catalysts required for the chemical reactions [5]. This cycle has four main steps: hydrolysis, thermolysis, drying, and electrolysis. The first three steps require heat, while the final step uses electricity. H₂O and CuCl₂ react in the hydrolysis step to produce HCl and Cu₂OCl₂, a reaction that occurs at temperatures around 400 °C [6]. The Cu₂OCl₂ produced in this step then goes
through the second reactor, where it is dissociated to produce CuCl and O₂. This reaction takes place at temperatures around 530 ℃. The CuCl produced in the second step and the HCl produced in the first step then react in the electrolyser unit to produce H₂ and aqueous CuCl₂. Finally, dry CuCl₂ is produced in the drying phase, allowing the cycle to be repeated [6].

Various aspects of this cycle have been investigated and analysed by numerous authors in the past decade. Rabbani et al. [7] investigated the possibility of using a shell and tube heat exchanger to recover the heat from the O₂ leaving the second reactor, analysing various parameters including the type of fluid and mass flow rate using Bella Delaware software. Energy and exergy analyses of a lab-scale Cu-Cl cycle were performed by Razi et al. [8], who determined the overall energy and exergy efficiencies to be 6.8% and 10.4%, respectively. The thermodynamic feasibility of a new type of three-step Cu-Cl cycle was investigated by Khalid et al. [9], and the thermal efficiency of the proposed system was evaluated as 32%. Chandehariun et al. [10] investigated the reduction of hazards from copper-chloride in the Cu-Cl cycle, positing that the best possible case for hazard reduction occurred whenever CuCl vapour was absorbed by the Cu₂OCl₂ [10].

One of the main challenges of producing hydrogen from the Cu-Cl cycle is its integration with energy sources. Various sources that produce heat at a temperature higher than 550 ℃ can be used for this cycle, including solar, nuclear, and fossil fuel energy sources [11]. However, as the most readily available renewable energy source, solar energy can be used to produce clean hydrogen utilising this cycle. Chandehariun et al. [12] thus also investigated the coupling of parabolic trough collectors with the Cu-Cl cycle, concluding that the thermal efficiency of the integrated system was 49%.

Solar power tower systems appear to be more suitable for integration with the Cu-Cl cycle than other alternatives. These systems are therefore one of the most economically feasible, technologically available, and relatively high-performance systems to be applied to this process [13]. Either air or molten salt can be used in such plants to harness solar heat. Sadeghi and Chandehariun [14] investigated the coupling of a solar power tower with air as its heat transfer fluid with an integrated Cu-Cl cycle. The thermal efficiency of their system was 45.07%, and the main problem of the proposed system was the fact that it required larger heat exchangers, making it more complex and expensive.

Conventional molten salt is usually used in solar thermochemical hydrogen production plants. Commonly, molten salt is a binary mixture of KNO₃ and NaNO₃, offering a stability limit of 565 ℃ [15]. Due to the low thermal stability of such salts, they are not suitable candidates for use in integrated solar Cu-Cl cycles, as the minimal difference between the thermolysis reactor temperature and the maximum operating temperature of this salt could result in high flow rates of molten salt which would reduce the performance of the integrated system. Additionally, if a plant used a Rankine cycle to produce the required power for the electrolysis step, the low upper temperature of the Rankine cycle would also reduce the performance of the integrated system. To deal with this, a more suitable salt with a series of particular traits, including low cost, high thermal stability, and a high range of operating temperatures, must be utilised [16]. (LiNaK)₂CO₃, which is a ternary carbonate salt with an operating temperature of 400 to 800 ℃ and a purchase cost of around $2/kg is thus suitable option [16].

In this paper, economic and thermodynamic analyses are performed for an integrated solar Cu-Cl cycle that produces the required electricity and uses a ternary mixture of Li₂CO₃ (32.1%)-Na₂CO₃ (33.4%)-K₂CO₃ (34.5%) molten salt, referred to as (LiNaK)₂CO₃, for both heat transfer fluid and thermal energy storage (TES). The objective is to calculate the levelized cost of producing hydrogen and to determine the thermal efficiency of the proposed system. A Genetic Algorithm (GA) is utilised to achieve the optimal design for the cycle.

2. System Description

An illustration of the solar-driven standalone thermochemical cycle investigated in this work is shown in Figure 1. The solar radiation reflected by the heliostats is received by the receiving tower, which heats the molten salt. The salt then enters the hot tank, where it is stored until radiation levels are low. The salt is then divided into two streams to provide the required heat for both the Cu-Cl reactors and heater 1, and to produce superheated steam for the production of electricity. The salt at state 32 sequentially enters the thermolysis reactor, hydrolysis reactor, heater 1, and drying unit while at state 37, the salt flows through the steam generator unit to produce superheated steam. To reduce the exergy destruction
of the system, salt streams from states 36 and 38 are mixed at the same temperature. This mixed salt then enters the cold salt tank, and the process is repeated.

As mentioned, in the Cu-Cl cycle, four steps, hydrolysis, thermolysis, electrolysis, and drying, are required. The products of each step then go through internal heat exchangers, heaters, or coolers to achieve the required temperature for the next chain reaction to proceed. The steam Rankine cycle considered here includes three closed feedwater heaters and one open feedwater heater to increase the performance of the cycle. The steam turbine is bled four times to provide the required thermal power for the feedwater heaters, and the Rankine cycle produces the required electricity for the electrolyser unit only, with no excess electricity.

![Figure 1. Schematic of the investigated solar Cu-Cl thermochemical cycle.](image)

3. Modelling and Optimisation

To conduct thermodynamic analysis, it is necessary to evaluate the thermophysical properties of each stream, including its temperature, pressure, enthalpy, and entropy values. MATLAB is applied with the help of the REFPROP 9 library to calculate these properties for various streams. However, the properties of several substances used in the Cu-Cl cycle are not present in the REFPROP software, making it necessary to use Shomate equations and constants to calculate these properties. The enthalpy and entropy of the substances are calculated based on the following equations [17]:

\[
\Delta h^0 = At + B \frac{t^2}{2} + C \frac{t^3}{3} + D \frac{t^4}{4} - \frac{E}{t} + F - H
\]
\[ S^0 = \ln(t) + C + \frac{D}{2} \frac{t^2}{2} + \frac{E}{3} \frac{t^3}{3} + G \]  

where \( t \) is the temperature of a selected stream divided by 1,000, and \( A, B, C, D, E, F, G, \) and \( H \) are the Shomate constants as discussed in [17]. Additionally, mass and energy conservation equations are used for each component to complete the thermodynamic modelling [18]:

\[ \sum m_i = \sum m_e \]  
\[ \sum (\dot{m} h)_e + \dot{Q} = \sum (\dot{m} h)_i + \dot{W} \]

The input assumptions for the thermodynamic analysis of the base case are presented in Table 1.

| Parameter                              | Value       |
|----------------------------------------|-------------|
| Irradiation level (W/m\(^2\))         | 1,000       |
| Hydrolysis temperature (\(^\circ\)C)  | 390         |
| Thermolysis temperature (\(^\circ\)C) | 530         |
| Drying temperature (\(^\circ\)C)       | 80          |
| Molten salt inlet temperature (\(^\circ\)C) | 400     |
| Molten salt outlet temperature (\(^\circ\)C) | 700    |
| Mirror numbers                         | 2,500       |
| Turbine inlet temperature (\(^\circ\)C) | 580        |
| SRC - boiler pressure (kPa)            | 23,000      |
| SRC - first bleed pressure (kPa)       | 4,500       |
| SRC - second bleed pressure (kPa)      | 1,300       |
| SRC - third bleed pressure (kPa)       | 310         |
| SRC - fourth bleed pressure (kPa)      | 170         |
| Isentropic efficiencies of pumps (%)   | 88          |
| Pinch temperature difference           | 8           |

The total revenue requirement (TRR) method is used for the economic analysis in this study. The TRR for the \( j \)th year of plant operation is calculated as follows [19]:

\[ TRR_j = TCR_j + ROI_{j,d} + ROI_{j,ce} + ROI_{j,ps} + ITX_j + OTX_j + FC_j + OMC_j \]

where \( TCR, ROI, ITX, OTX, FC, \) and \( OMC \) denote total capital recovery, return on investment, income tax, other taxes and insurance, fuel costs, and operation and maintenance costs, respectively. Subsequently, the levelized cost of hydrogen (LCOH) is evaluated using the following equation [19]:

\[ LCOH = \frac{CRF \sum_{j=1}^{n} \frac{TRR_j}{(1 + \text{ieff}_j)^j} - \text{BPV}}{\text{MPQ}} \]

where \( CRF, MPQ, \) and \( BPV \) are the capital recovery factor, main product quantity, and by-product value, respectively. The input economic assumptions and breakdown of capital investment costs are presented in Tables 2 and 3, respectively.
Table 2. Input economic assumptions for the base case.

| Parameter                  | Value |
|----------------------------|-------|
| Plant lifetime (years)     | 30    |
| Inflation rate (%)         | 2     |
| Interest rate (%)          | 6     |
| O&M factor (%)             | 2     |
| Economic year              | 2020  |

Table 3. Breakdown of capital investment costs for the base case.

| Component                                | Cost (million U.S.D) |
|------------------------------------------|----------------------|
| Primary equipment costs                  | 84.75                |
| Piping, Control, and electrical equipment| 51.59                |
| Equipment installation                   | 33.16                |
| Land and buildings                       | 40.53                |
| Working capital fee                      | 66.32                |
| Construction costs                       | 36.85                |
| Service, engineering, and contractor’s expenses | 88.43            |
| Others                                   | 33.16                |

To optimise the system, multi-objective optimisation using a Genetic Algorithm is applied. The algorithm selected was a stochastic algorithm that determines optimal solutions as a curve, known as the Pareto Frontier [20]. The variable ranges for the optimisation study are presented in Table 4.

Table 4. The lower and upper bounds of selected parameters for the optimization study.

| Selected parameters                  | Lower bound | Upper bound |
|--------------------------------------|-------------|-------------|
| Mirror numbers                       | 1,000       | 10,000      |
| Molten salt outlet temperature (°C)  | 620         | 700         |
| Hydrolysis temperature (°C)          | 380         | 400         |
| Thermolysis temperature (°C)         | 510         | 530         |
| Turbine inlet temperature (°C)       | 500         | 600         |
| SRC - boiler pressure (kPa)          | 10,000      | 25,000      |
| SRC - first bleed pressure (kPa)      | 1,900       | 7,000       |
| SRC - second bleed pressure (kPa)     | 900         | 1,600       |
| SRC - third bleed pressure (kPa)      | 200         | 600         |
| SRC - fourth bleed pressure (kPa)     | 60          | 180         |
| Isentropic efficiencies of pumps and turbines (%) | 75 | 90 |
| Pinch temperature difference         | 8           | 12          |
4. Results and Discussion
The results of the thermodynamic and economic modelling for the base case are shown in Table 5. The thermal efficiencies of the solar subsystem, Cu-Cl cycle, and SRC are evaluated as 60.39, 40.53, and 46.47%, respectively. Additionally, the solar to hydrogen efficiency is calculated as 28.91%. The power consumption of the electrolyser unit and the hydrogen production rate are 11.50 MW and 823.71 kg/h, respectively. Finally, the LCOH is determined to be $8.34/kg H₂.

| Parameter                                      | Value  |
|-----------------------------------------------|--------|
| Solar subsystem thermal efficiency (%)        | 60.39  |
| Cu-Cl cycle thermal efficiency (%)            | 40.53  |
| SRC thermal efficiency (%)                    | 46.47  |
| Solar to hydrogen efficiency (%)              | 28.91  |
| Hydrogen production rate (kg/h)               | 823.71 |
| Electrolyser power consumption (MW)           | 11.50  |
| Levelized cost of hydrogen ($/kg H₂)          | 8.34   |

The influence of increasing the hydrolysis reaction temperature on LCOH and hydrogen production rate are demonstrated in Figure 2. By increasing the hydrolysis temperature from 653 to 673 K, the hydrogen production rate increases from 916.03 to 921.45 kg/h. Increasing the hydrolysis temperature has no significant effect on the solar-to-hydrogen efficiency of the cycle, though reducing the hydrolysis temperature from 653 to 670 K reduces LCOH. An optimal point is found at 670.5 K, with a value of $8.33/kg H₂, and this starts rising again as the hydrolysis temperature begins to increase. The reason for this increase in performance and reduction in cost is that whenever the hydrolysis temperature increases, less heat is required to heat the Cu₂OCl₂; additionally, when the flow rate of molten salt passing through the hydrolysis reactor remains constant, any increase in hydrolysis temperature will result in a lower temperature drop of molten salt, increasing system performance.

Iran has a great deal of solar potential, with many provinces such as Sistan and Baluchestan, Fars, and Kerman having direct normal irradiation levels that exceed 1,100 W/m² between May and August [21]. The influence of varying solar radiation levels on the hydrogen production rates and LCOH are presented in Figure 3. When the solar radiation increases from 600 to 1,100 W/m², the LCOH reduces from $13.10 to $7.72/kg H₂, while the hydrogen production rate increases from 470.80 to 911.79 kg/h,. Intensification of solar radiation results in higher input heat for the cycle, and thus higher performance in the solar subsystem with regard to thermal efficiency. The appropriate selection of a site for such a thermochemical hydrogen production plant is thus a necessary aspect of designing such as system.
Figure 2. Influence of increasing hydrolysis temperature on LCOH and hydrogen production rate.

Figure 3. Influence of varying solar radiation level on LCOH and hydrogen production rate.

The influence of variations in pinch temperature difference on hydrogen production rate and LCOH are presented in Figure 4. When the pinch temperature difference increases, the heat recovery that takes place in the Cu–Cl cycle reduces. Moreover, the capital investment costs for heat exchangers are also reduced. By increasing the pinch temperature difference from 5 to 15, the hydrogen production rate reduces from 919.55 to 916.8 kg/h. Generally, when the pinch temperature difference is increased, the hydrogen production rate, and hence, the system performance reduces. The LCOH reaches an optimal point at a pinch temperature difference of 12, mainly due to the reduction of capital investment costs.
Figure 4. Influence of variations in pinch temperature difference on LCOH and hydrogen production rate.

The influence of increasing the SRC boiler pressure on solar to hydrogen efficiency and LCOH are presented in Figure 5. By increasing the boiler pressure from 14,000 to 24,000 kPa, the solar-to-hydrogen efficiency increases from 28.48 to 28.93%. However, at the pressures of around 21,000 kPa, the LCOH reaches its minimum value of $8.34/kg H_2$, as at a pressure higher than 21,000 kPa, the purchase cost of the steam turbines increases drastically, making it uneconomical to increase the pressure further.

Figure 5. Influence of variations of SRC boiler pressure on solar to hydrogen efficiency and LCOH.

The Pareto Frontier of optimal solutions for the multi-objective optimisation in this study is shown in Figure 6. By applying the Linear Programming Technique for Multidimensional Analysis of Preference (LINMAP) method, the optimal Pareto solution is determined. The solar to hydrogen efficiency and LCOH of this solution are evaluated as 29.17% and $7.58/kg H_2$, respectively. The optimal input design parameters for the solution are presented in Table 6. The cost of large-scale
hydrogen production from solar energy is not currently competitive with most fossil fuel-based hydrogen production methods such as steam methane reforming or coal gasification [3]. However, due to an increase in concern about environmental issues and the likely imposition of carbon dioxide taxes, along with the current depletion of fossil fuels, the cost of renewable energies is likely to be more competitive in the future, causing the cost of solar-based hydrogen to drop.

5. Conclusion
Thermodynamic and economic analyses of a novel high-temperature molten salt hydrogen production system were undertaken and reported. The system investigated in the study was divided into three main subsystems: solar power tower, the Cu-Cl hydrogen production cycle, and the steam Rankine cycle. The modelling results indicated that the system produces 823.71 kg/h of hydrogen, and that to maintain the production of hydrogen at this rate, the SRC cycle needs to produce 11.50 MW of electricity. The thermal efficiencies of solar, the Cu-Cl, and SRC subsystems were evaluated as 60.39, 40.53, and
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