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Potential of chemical looping for green hydrogen production from biogas: process design and techno-economic-environmental analysis

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ABSTRACT

Hydrogen (H_2), as the promising alternative to fossil fuel-based energy carriers, faces the critical challenge of diversifying its sources and lowering production costs. Biogas, produced from organic waste, offers a renewable and carbon-neutral option for H_2 production, but its high CO_2 content requires a pre-separation process of CO_2 from CH_4 or specialized catalysts for use in existing reforming processes. Chemical looping reforming (CLR), as an advanced H_2 production process, uses an oxygen carrier (OC) as the oxidant, allowing raw biogas to be used directly in the reforming process. Recently, numerous studies on CLR design and analysis have demonstrated their growing economic feasibility. However, deploying the CLR process in the biogas treatment industry requires further research to analyze its technical, economic, and environmental performance under target capacities and H_2 purity. This study proposes biogas-based CLR processes and analyzes the capability of the processes from techno-economic and environmental perspectives: i) chemical looping partial oxidization (CLPO), ii) chemical looping steam reforming (CLSR), iii) chemical looping water splitting (CLWS), and iv) chemical looping CO_2 splitting (CLCS). Evaluation metrics include energy efficiency, exergy efficiency, unit production cost (UPC), and net CO_2 equivalent emission (NCE) to compare technical, economic, and environmental performance, respectively. Each process is simulated in Aspen Plus to obtain mass and energy balance data. The heat exchanger network (HEN) is optimized to maximize heat recovery and achieve autothermal conditions. As a result, we comparatively analyze the economic and environmental capability of the proposed processes by identifying the major cost drivers and CO_2 emission contributors.

Keywords: Renewable and Sustainable Energy, Process Synthesis, Hydrogen, Chemical Looping, Technoeconomic Analysis.

INTRODUCTION

As the demand for sustainable energy systems intensifies, hydrogen (H_2) has emerged as a significant energy carrier capable of decarbonizing in heavy industry and long-distance transportation [1]. Currently, most of the global H_2 production relies on fossil fuel-based processes, notably steam methane reforming (SMR), which emits substantial amounts of CO_2 into the atmosphere [2]. While water electrolysis powered by renewable energy offers a carbon-neutral alternative, its widespread implementation faces significant economic and logistical barriers, particularly due to the high cost and the

intermittent availability of renewable energy sources [3]. As such, innovative reforming technologies that achieve a balance between cost-effectiveness and environmental sustainability are needed to enable a smooth energy transition.

Biogas, a renewable energy source produced through the anaerobic decomposition of organic waste, presents an attractive feedstock for sustainable H_2 production [4]. Unlike natural gas, biogas is composed primarily of CH_4 and CO_2. The high CO_2 content of biogas poses technical challenges for conventional reforming technologies, requiring either costly pre-separation of CO_2 from CH_4 or advanced systems capable of directly

processing CO_2-rich feedstocks [5][6]. However, when its CO_2 content is effectively utilized, biogas can offer a carbon-neutral pathway. Therefore, the need for reforming technologies that can efficiently exploit the potential of biogas without incurring additional separation costs is increasing.

Chemical looping reforming (CLR) has emerged as a next-generation H_2 production technology capable of overcoming many of the limitations associated with traditional reforming technologies. In CLR processes, a solid metal oxygen carrier (OC) facilitates redox reactions, enabling the direct utilization of raw biogas without the need for prior CO_2 removal [7]. This innovative process can achieve autothermal conditions that improve both energy and operational efficiencies while integrating inherent CO_2 capture capabilities that reduce carbon management costs. These combined advantages make CLR processes a cost-competitive pathway for sustainable H_2 production [8].

Despite the promising characteristics of CLR process, its practical application in the biogas industry remains limited. Further research is necessary to evaluate the performance of CLR processes under various configurations and operating scales. This study aims to evaluate the performance of four different CLR process configurations: i) chemical looping partial oxidation (CLPO), ii) chemical looping steam reforming (CLSR), iii) chemical looping water splitting (CLWS), and iv) chemical looping CO_2 splitting (CLCS). Through a comprehensive analysis of their technical, economic, and environmental performance, this research seeks to identify viable processes for integrating CLR processes into sustainable H_2 production systems, while also identifying key cost drivers and key environmental impact variables.

TECHNOLOGY OVERVIEW AND METHODOLOGY

Technology overview

Chemical looping partial oxidization (CLPO)

The CLPO process consists of two reactors: a reducer and a combustor. In the reducer, biogas is partially oxidized with the OC, producing syngas while reducing the OC. The reduced OC is then transported to the combustor, where it is fully regenerated with air, releasing significant heat. This heat is used to sustain the endothermic reactions in the reducer as the OC circulates back, ensuring efficient heat transfer. The overall thermal balance is maintained by an optimized heat exchanger network (HEN). The reducer employs a moving bed reactor design, which facilitates countercurrent contact between the biogas and the OC, thereby enhancing reaction efficiency and maximizing syngas yield [9]. Conversely, the combustor utilizes a fluidized bed reactor to
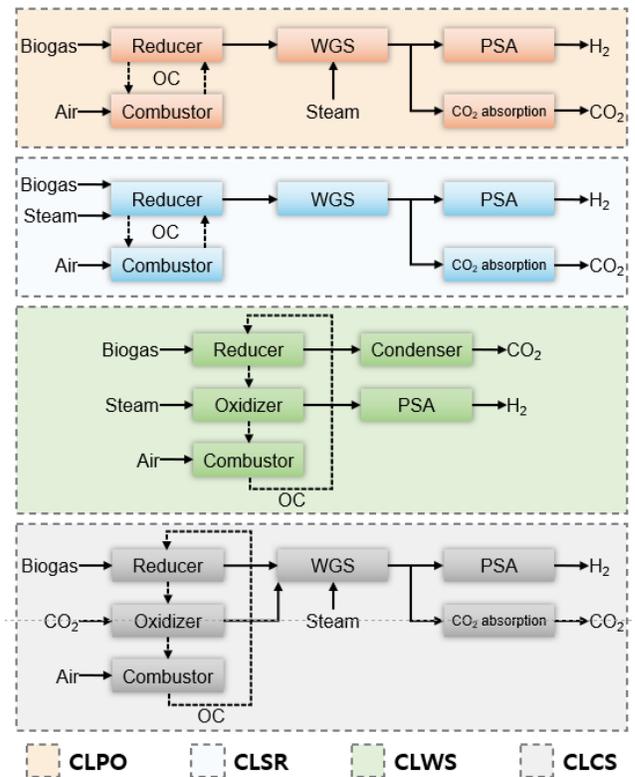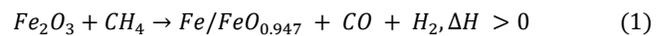

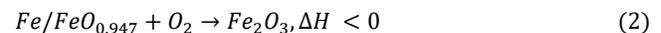**Figure 1.** Process flow diagram of CLR processes.

ensure uniform temperature distribution and efficient heat transfer [10]. Downstream of the reducer, the syngas undergoes a water-gas shift (WGS) reaction to increase its H_2 content. A monoethanolamine (MEA)-based CO_2 absorption process is then used to capture CO_2 and reduce greenhouse gas emissions, followed by pressure swing adsorption (PSA) is employed to produce high-purity H_2.
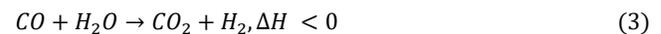
Key reactions in the CLPO process:
Reducer:

$$Fe_2O_3 + CH_4 \rightarrow Fe/FeO_{0.947} + CO + H_2, \Delta H > 0 \qquad (1)$$

Combustor:

$$Fe/FeO_{0.947} + O_2 \rightarrow Fe_2O_3, \Delta H < 0 \qquad (2)$$

WGS reactor:

$$CO + H_2O \rightarrow CO_2 + H_2, \Delta H < 0 \qquad (3)$$

Chemical looping steam reforming (CLSR)

Building on the CLPO configuration, the CLSR process introduces steam into the reducer to enable simultaneous SMR reaction. While the addition of steam requires more energy, it substantially increases the H_2 yield due to the SMR reaction. The reduced OC is subsequently regenerated in the combustor, as in CLPO, while the syngas undergoes WGS to enhance H_2 content, MEA-based CO_2 absorption for carbon capture, and PSA for H_2 purification. Similar to CLPO, the CLSR process uses a

moving bed reducer for enhanced biogas and steam reactions, paired with a fluidized bed combustor for efficient heat recovery.

Key reaction in the CLSR process:
SMR reaction in reducer:

$$CH_4 + H_2O \rightarrow CO + 3H_2, \Delta H > 0 \tag{4}$$
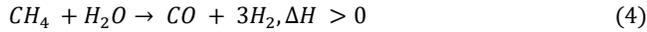
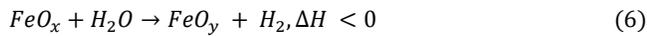## Chemical looping water splitting (CLWS)

In addition to the reducer and combustor, the CLWS process introduces a third reactor, the oxidizer. In the reducer, the biogas undergoes complete oxidization with the OC, producing flue gas containing only N_2, CO_2 and H_2O. The water in the flue gas is removed by condensation, leaving CO_2, which is then captured at a relatively low quality. The reduced OC is partially re-oxidized with steam in the oxidizer, directly producing H_2. By enabling water splitting, the CLWS process eliminates the need for a WGS and MEA-based CO_2 absorption process and simplifies the downstream H_2 purification steps to just a condenser and a PSA unit. The oxidizer is designed as a moving bed reactor, ensuring an efficient water splitting reaction. The OC is fully regenerated in the combustor before being returned to the reducer.

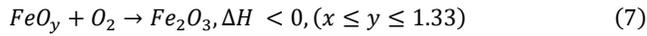Key reactions in the CLWS process:
Reducer:

$$Fe_2O_3 + CH_4 \rightarrow FeO_x + CO_2 + H_2O, \Delta H > 0 \tag{5}$$

Oxidizer:

$$FeO_x + H_2O \rightarrow FeO_y + H_2, \Delta H < 0 \tag{6}$$

Combustor:

$$FeO_y + O_2 \rightarrow Fe_2O_3, \Delta H < 0, (x \leq y \leq 1.33) \tag{7}$$

Chemical looping CO_2 splitting (CLCS)

The CLDR process, like the CLWS process, consists of a reducer, oxidizer, and combustor, but differs in that CO_2 is used as the oxidant in the oxidizer, allowing for a CO_2 splitting reaction. In the reducer, biogas goes through partial oxidation, to produce syngas, while CO_2 in the oxidizer partially regenerate the OC, producing CO. The resulting syngas and CO are sent to the WGS reactor along with steam, which increases the H_2 production by converting H_2O and CO into H_2 and CO_2. The H_2-rich stream undergoes MEA-based CO_2 absorption for carbon capture, followed by PSA for further H_2 purification. Unlike other CLR processes, the CLDR process involves a highly endothermic CO_2 splitting reaction, using CO_2 as an oxidant in the oxidizer. Thus, to maintain autothermal conditions, heat generated in the combustor is recovered and transferred to the oxidizer through a jacketed reactor. This ensures that the energy required for oxidizer is supplied efficiently, providing stable and energy-efficient operation.

Key reaction in the CLDR process:

Oxidizer:

$$FeO_x + CO_2 \rightarrow FeO_y + CO, \Delta H > 0, (x \leq y \leq 1.33) \tag{8}$$
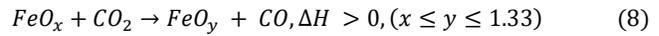
Model description

For process simulation and optimization, the commercial process simulator Aspen Plus is used as the primary modeling tool. The Peng-Robinson-Boston-Mathias (PR-BM) equation of state is selected to accurately represent the thermodynamic properties of all units. The CLR reactions are simulated using the Gibbs free energy minimization method, to achieve equilibrium-based calculations for the redox reactions. The CLR reactors are designed to operate near atmospheric pressure. All processes are designed to operate under heat-neutral conditions. To ensure thermal balance and enhance H_2 yield, heat integration is performed using an optimized HEN. The HEN is designed using Aspen Energy Analyzer to ensure efficient energy recovery and the autothermal operating conditions. Product specifications are set for high-purity H_2 and CO_2 streams at industrially relevant pressures. In all configurations, biogas and other feed streams, such as water and air, are preheated to the same temperature before entering the reforming reactors to ensure consistent evaluation criteria, with feedstock and OCs also having identical compositions.

Evaluation method

The performance of the CLR processes is evaluated from three perspectives: thermodynamic efficiency, economic performance, and environmental impact. From a thermodynamic perspective, energy efficiency and exergy efficiency are calculated to assess the ability of the process to convert input energy to useful H_2 with minimal losses. Energy efficiency, expressed as η_{energy}, is defined as the ratio of the chemical energy in the H_2 product to the total energy input, including feedstock and external utilities.

$$\eta_{energy} = \frac{\dot{P}_i \times LHV_i}{\sum(\dot{F}_i \times LHV_i) + \sum U_j} \tag{9}$$

Here, $\dot{P}_i$ represents the molar flow rate of the H_2 product, while LHV_i denotes the lower heating value of each material. Similarly, $\dot{F}_i$ corresponds to the molar flow rate of the feedstock, and $\sum U_j$ indicates the total external energy input.

Exergy efficiency, denoted as η_{Exergy}, measures the capacity of the process to minimize the loss of energy during the conversion processes.

$$\eta_{Exergy} = \frac{\dot{Ex}_{in,total} - \dot{Ex}_{des,total}}{\dot{Ex}_{in,total}} = \frac{\dot{Ex}_{out,total}}{\dot{Ex}_{in,total}} \tag{10}$$

In eq. 10, $\dot{Ex}_{in,total}$ is the total input exergy, $\dot{Ex}_{out,total}$, is the total output exergy, and $\dot{Ex}_{des,total}$ represents the exergy destroyed within the process.

The economic performance of the processes is evaluated using the unit production cost (UPC) of H₂. The total investment cost includes both capital expenditure (CAPEX) and operating expenditure (OPEX). CAPEX is calculated from the annualized capital investment (ACI), which is derived from the total capital investment (TCI). TCI comprises direct plant cost (DC), indirect plant cost (IDC), and working capital (WC). The capital recovery factor (CRF), calculated using Eq. 11, is used to annualize the capital costs.

$$CRF = \frac{i \times (1 + i)^r}{(1 + i)^r - 1} \tag{11}$$

Where i is the interest rate and r is the plant lifetime. Using the CRF, the ACI is calculated based on eq. 12.

$$ACI = TCI \times CRF \tag{12}$$

OPEX accounts for both variable operating costs (VOC) and fixed operating costs (FOC). Finally, the UPC of H₂ is determined by dividing the total annualized cost by the annual H₂ production (P_{H_2}).

$$UPC = \frac{ACI + VOC + FOC}{P_{H_2}} \tag{13}$$

From an environmental perspective, the processes are analyzed based on their net CO_2 equivalent emission (NCE), which reflects the total CO_2 emissions per kilogram of H₂ produced. NCE includes direct CO_2 emissions (DCE) from the process, indirect CO_2 emissions (ICE) associated with energy inputs, and carbon credits (CC). The CC is calculated as the net difference between the CO_2 reduction effect of biomass and the CO_2 emissions from biogas production [11]. The NCE is calculated using eq. 14.

$$NCE = \frac{DCE + ICE - CC}{P_{H_2}} \tag{14}$$

RESULT AND DISCUSSION

Techno-economic and environmental analysis

The energy and exergy efficiencies of the four CLR processes are shown in Fig. 2. The CLSR process demonstrates the highest thermodynamic performance, achieving energy and exergy efficiencies of 49% and 47%, respectively, due to its high H₂ yield from SMR reaction and effective heat recovery strategies via the HEN. Closely following CLSR, the CLCS process achieve comparable efficiencies of 48% and 47%. Although its high H₂ production contributes significantly to performance, the strong heat demands of the CO_2 splitting reaction slightly limits its overall efficiency. In contrast, the CLPO process shows the lowest performance, with efficiencies of 23% and 22%, mainly due to the imbalance between endothermic heat in the reducer and excessive heat

generation in the combustor, resulting in significant thermal losses. The CLWS process shows intermediate performance, with efficiencies of 43% and 42%, respectively. While its effective heat recovery strategy supports reasonable performance, its lower H₂ yield limits its thermodynamic efficiency compared to CLSR and CLCS.

Taken together, the CLR processes, except CLPO, exhibit similar process efficiencies due to HEN designs optimized for autothermal conditions. The CLPO process exhibits lower efficiency due to heat imbalance, suggesting that advanced heat recovery strategies such as combined heat and power plant can effectively address this limitation and improve performance.
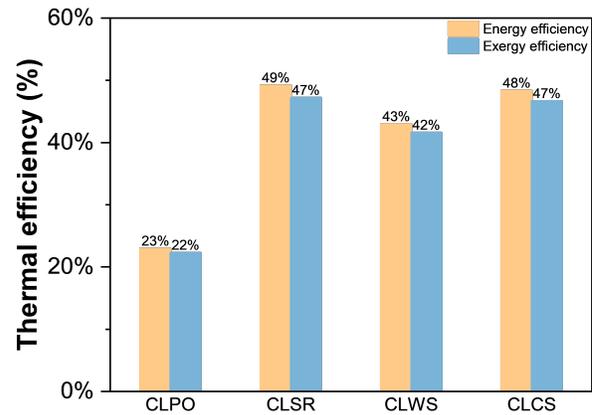

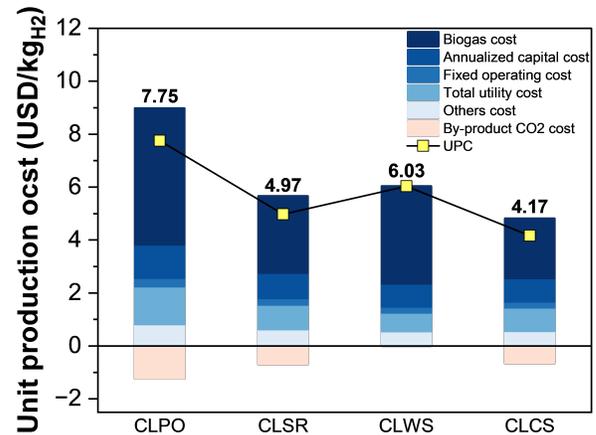**Figure 2.** Thermal efficiencies of CLR processes.

Figure 3. Unit production costs of CLR processes.

The economic performance of the four CLR processes is evaluated based on their UPC (USD/kg_{H₂}), as shown in Fig 3. Among the processes, the CLCS process achieves the lowest UPC of 4.17 USD/kg_{H₂}, benefiting from reduced biogas cost by producing additional H₂ through the utilization of CO. In contrast, the CLPO process has the highest UPC at 7.75 USD/kg_{H₂}, primarily due to its higher operating energy requirements and lower H₂ yield. The CLSR and CLWS processes show mid-range

UPC of 4.97 USD/kg$_{H_2}$ and 6.03 USD/kg$_{H_2}$, respectively. The relatively lower cost of CLSR can be attributed to the integration of steam reforming, which enhances the H$_2$ yield. On the other hand, the CLWS process has higher UPC due to a lack of by-product CO$_2$ credit, attributed to the relatively low-quality of the captured CO$_2$. A comprehensive evaluation of the results shows that biogas cost, energy inputs, and capital expenditures emerge as the primary cost drivers for all processes.

The environmental performance of the CLR processes is evaluated based on their NCE (kg$_{CO_2eq}$/kg$_{H_2}$), as shown in Fig. 4. Among the processes, the CLWS process demonstrates the most environmentally favorable

Figure 4. Net CO$_2$ equivalent emissions of CLR processes.

outcome, achieving a negative emission of -7.25

kg$_{CO_2eq}$/kg$_{H_2}$. This carbon-negative result stems from the ability to capture CO$_2$ internally without the need for an MEA-based CO$_2$ absorption process, thereby significantly reducing both indirect and direct CO$_2$ emissions. In contrast, the CLCS process exhibits the highest emissions at 3.18 kg$_{CO_2eq}$/kg$_{H_2}$, primarily due to the significant thermal energy required for CO$_2$ capture. The CLSR and CLPO processes show moderate results, with net emissions of 1.99 kg$_{CO_2eq}$/kg$_{H_2}$ and 2.79 kg$_{CO_2eq}$/kg$_{H_2}$, respectively. The results highlight the significant environmental benefits of the CLWS process and demonstrate its potential for carbon-negative H$_2$ production. It is also observed that the presence or absence of an MEA-based CO$_2$ absorption process has the greatest impact on the overall CO$_2$ equivalent emissions of the process. Therefore, further in-depth research on CO$_2$ separation technologies is essential to improve the environmental performance of CLR processes.

Sensitivity analysis

A comprehensive techno-economic assessment of the four CLR processes identify biogas cost, energy inputs, and capital expenditures as critical factors influencing the UPC of H$_2$. To quantify their economic impact, a sensitivity analysis is conducted on key parameters, including biogas price, interest rate, plant lifetime, and utility prices.

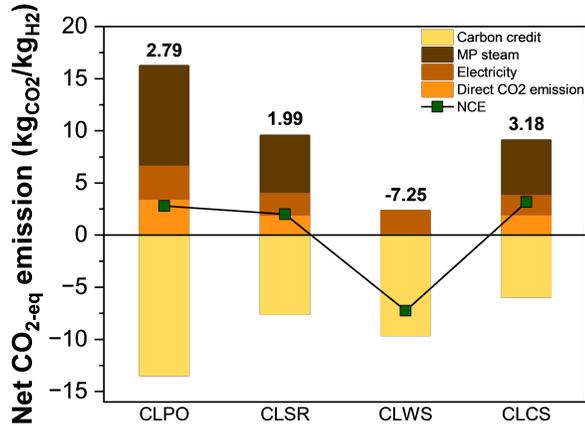The sensitivity analysis results for the four CLR processes (Fig. 5) highlight that biogas price is the most
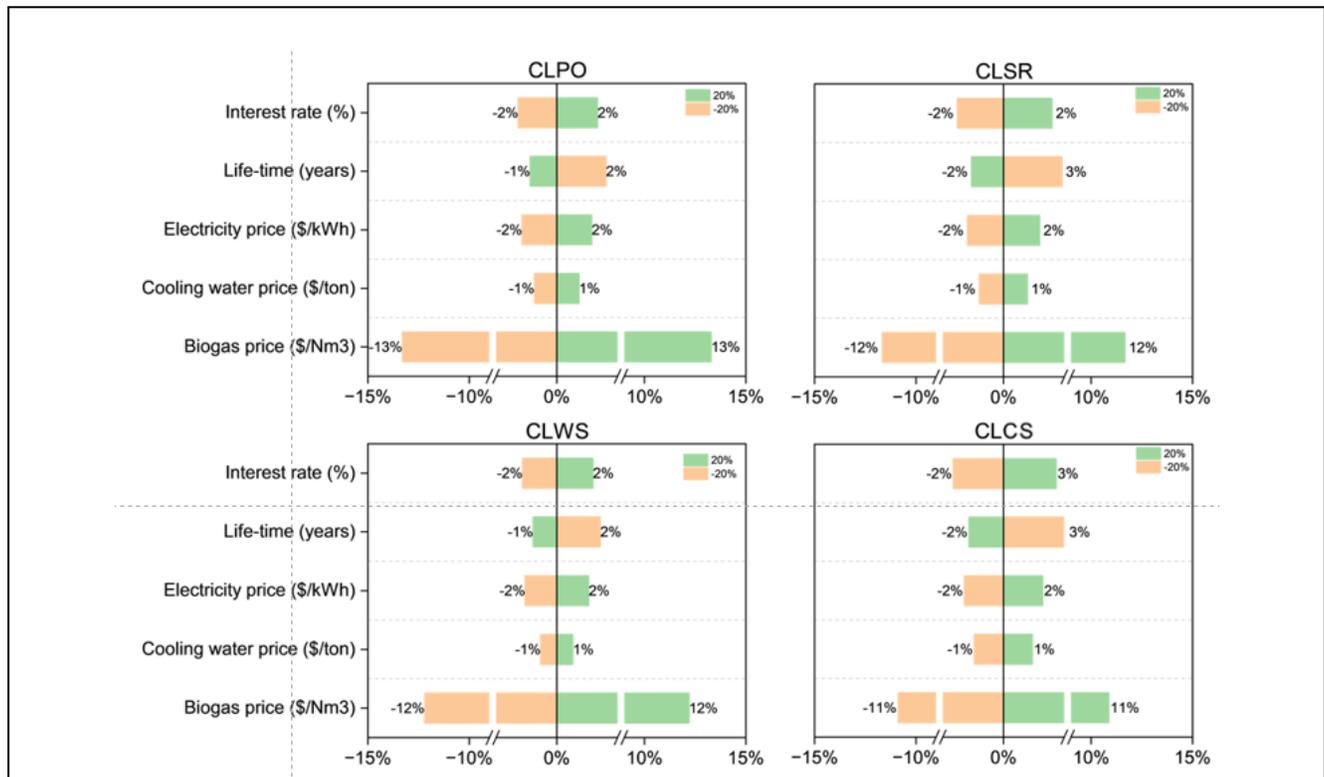

Figure 5. Sensitivity anlaysis results of CLR processes.

influential factor affecting the UPC of H_2. A 20% increase in the biogas price leads to a corresponding UPC rise of approximately 11-13% across all processes, highlighting the critical role of the biogas price in the economics of H_2 production. Moreover, capital related parameters such as interest rate and plant lifetime have an impact. A 20% increase in the interest rate increases UPC by about 2% while extending the plant lifetime by 5 years decreases it by 2%. Similarly, operational parameters such as electricity price and cooling water price show effects, with UPC variations of ±2% and ±1%, respectively. The analysis identify biogas price, capital related parameters, and utility prices as the dominant factors influencing the economics of CLR processes. Prioritizing strategies to reduce biogas costs and optimize capital and operating expenditures will be essential for improving economic viability of CLR processes.

CONCLUSION

This study evaluated four CLR processes: CLPO, CLSR, CLWS, and CLCS for H_2 production from biogas, focusing on their techno-economic and environmental performance. Among the processes, CLCS emerged as the most promising option, offering a balanced performance with thermal efficiency and economic benefits due to effective CO_2 utilization and reduced biogas costs. The CLSR process showed strong potential with competitive production costs and high H_2 yields. The CLWS process achieved carbon reduction, demonstrating its potential as a negative carbon emission technology, although its higher cost remains a challenge. In contrast, the CLPO process had the lowest performance across all criteria, indicating the need for further advancement to enhance its feasibility and performance. To enable the industrial application of CLR processes in the biogas industry, advances in CO_2 capture technologies, heat integration, and process optimization are essential. This study demonstrates the feasibility of biogas-based CLR processes for scalable, sustainable H_2 production, providing a pathway toward carbon-neutral energy solutions.

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