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Preliminary Examination of the Biogas-to-Hydrogen Conversion Process

Hegwon Chung[a], Minseong Park[a], and Jiyong Kim[a]*

[a] Sungkyunkwan University, School of Chemical Engineering, Suwon, Gyeonggi-do, South Korea
* Corresponding Author: jiyongkim@skku.edu.

ABSTRACT

Biogas is a promising energy source for sustainable hydrogen production due to its high concentration of CH_4. However, determining the optimal process configuration is challenging due to the uncertainty of the fed biogas composition and the sensitivity of the operating conditions. This necessitates early-stage evaluation of the biomass-to-hydrogen process's performance, considering economics, energy efficiency, and environmental impacts. A data-driven model was introduced for early-stage assessment of hydrogen production from biogas without whole process simulation and optimization. The model was developed based on various biogas compositions and generated parameters for mass and energy balance. A database of unit processes was created using simulation models. Sensitivity analysis was performed under four techno-economic and environmental evaluation criteria: Unit Production Cost (UPC), Energy Efficiency (EEF), Net CO_2 equivalent Emission (NCE), and Maximum H_2 Production (MHP). The early-stage evaluation of the biogas-to-hydrogen process can guide the establishment of biogas utilization strategies and propose effective biogas enhancement process development solutions to respond to market disturbances.

Keywords: Hydrogen, Biosystems, Optimization, Environment, Technoeconomic Analysis, Data-driven model

1. INTRODUCTION

Continuous concerns over global warming and the depletion of fossil fuels have spurred research into efficient technologies and sustainable energy generation. Currently, hydrogen is gaining increasing attention as a substantial energy carrier, primarily due to its environmental advantages and high calorific value. Although hydrogen is a potentially valuable material especially for the environment as a fuel, the conventional steam methane reforming plant, responsible for 50% of conventional hydrogen production emits 13.7 kg eq. CO_2 per kg of net H_2 produced [1]. Biogas is a viable alternative raw material for hydrogen production, as the methane within biogas can be utilized to prevent greenhouse gas emissions into the atmosphere [2]. There are various sources from which biogas can be obtained, such as sewage sludge digesters, organic waste digesters, or landfills. The biogas typically comprises 55 – 75% of methane, 25-45% of CO_2, and trace elements like nitrogen (N_2), oxygen (O_2), hydrogen sulfide (H_2S), siloxanes, and some dust particles [3]. Before constructing a biogas utilization plant, an early-stage assessment of the biogas-to-hydrogen process is necessary. Zhao X, et al investigated various biogas reforming technologies utilizing different catalysts to convert biogas to syngas. They conducted techno-economic analysis of biogas conversion technologies [4]. However, the previous research has not explored and evaluated the most efficient pathways for biogas utilization.

In this study, we have presented a superstructure-based data-driven model that can provide optimal strategies for biogas-to-hydrogen conversion. We carried out a comprehensive analysis of economic, environmental, and technological aspects by generating mass and energy balance data for every possible pathway and operating conditions from the superstructure. The main operating variables include the types of reformers and each operating conditions for various criteria. The techno-

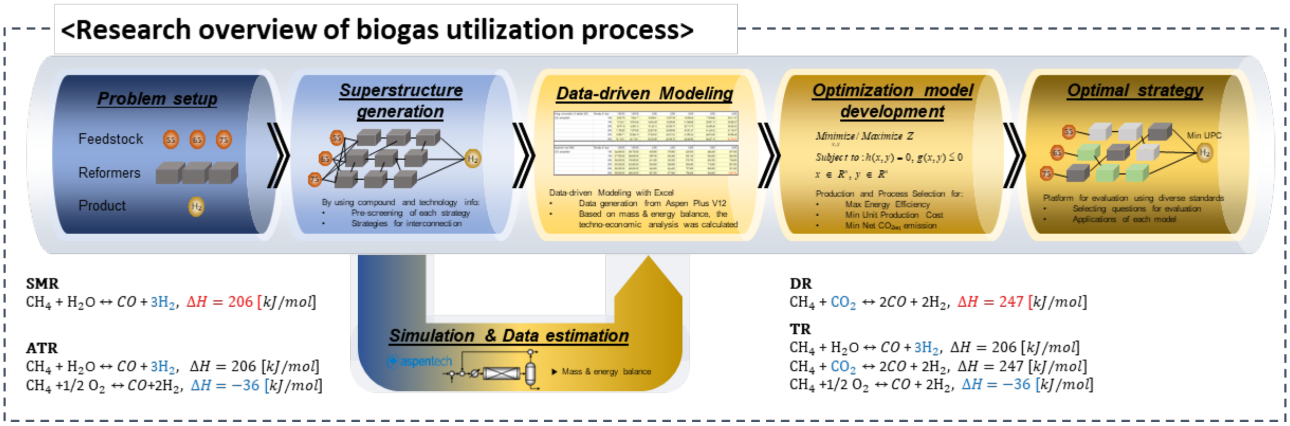


Figure 1: Research overview of biogas utilitzation process.

economic analysis and sensitivity analyses were conduced prior to optimization to assess the overall process parameters. As a result of the optimization, we can recommend the appropriate technologies with defined operating conditions for the process.

2. RESEARCH OVERVIEW AND METHODOLOGY

Research Overview

The section demonstrates the conceptual framework for hydrogen production through the reforming of biogas. Figure 1 provides an overall view of the research on the utilization of biogas, which comprises five steps: Problem setting, superstructure generation, data-driven modelling, development of optimization models, and optimal strategy formulation. To begin the process, we identify the feedstock, types of reformers, and product. The superstructure for the biogas-to-hydrogen process can be generated via various pathways, each involving different types of reformers and operating conditions for the applied technologies. Afterwards, data generated from the process simulation can be utilised to estimate additional mass and energy balance. This is done using the Excel-based data-driven model and is key to calculating techno-economic and environmental parameters. Prior to recommending optimal strategies, an optimization model was created based on diverse evaluation criteria evaluating the impact of economic and environmental factors. The optimization outcomes enable the recommendation of appropriate strategies for the distinct elements of biogas.

We considered three biogas compositions, comprising 55%, 65%, and 75% CH_4. To attain the best pathways for each composition, we evaluated four reformers: Steam Methane Reforming (SMR), Dry Reforming (DR), Auto-Thermal Reforming (ATR), and Tri-Reforming (TRI). In the case of conventional hydrogen production from natural gas, SMR is typically employed in conjunction with water gas shift reactions to maximize hydrogen production. However, the significant quantity of CO_2 emissions produced by the conventional process necessitates the assessment of the biogas utilization process on various parameters. Steam methane reforming, which has a 3:1 H_2/CO ratio, is highly endothermic, whereas dry reforming reduces CO_2 by consuming it as a reactant. Nonetheless, DR is also an extremely high endothermic process. To reduce the consumption of the reforming process, the ATR that employs partial oxidation with steam methane reforming has emerged. The TRI, which simultaneously employs partial oxidation and dry reforming with steam methane reforming, is a viable technology for biogas utilization. Both ATR and TRI can minimise energy consumption for the reforming process, although H_2/CO ratio may decrease to less than 3. Prior to constructing a biogas utilization process, it is crucial to assess the advantages and disadvantages of various technologies. Table 1 showcases the operating limits of each reformer under atmospheric pressure.

Table 1: Types and operating conditions of biogas reforming technologies at atmospheric pressure [5-8].

Steam reforming (Ni/Mg Al_2O_4 spinel)	Temperature: 600-900℃ H_2O/CH_4: 1-3
Dry reforming (Rh/Al_2O_3)	Temperature: 600-1,000℃ CO_2/CH_4: 0.4-1
Auto-thermal reforming (Ni/Mg Al_2O_4)	Temperature: 600-1,000℃ H_2O/CH_4: 1-5 O_2/CH_4: 0-0.5
Tri-reforming (Ni/Mg Al_2O_4)	Temperature: 600-1,000℃ H_2O/CH_4: 1-2 O_2/CH_4: 0.1-1

Process Analysis Method

The process was assessed using multiple criteria, including unit production cost (UPC), Net CO_2-equivalent emissions (NCE), and energy efficiency (EEF), as demonstrated in Eqs. (1)-(3). In the economic evaluation, capital expenditures (CAPEX) and operating expenses (OPEX) were divided by the quantity of produced hydrogen. The UPC was estimated using an interest rate of 7% over a 25-year plant lifespan.

$$UPC = \frac{CAPEX+OPEX}{Amount\ of\ hydrogen}, (\$/kg_{H_2}) \qquad (1)$$

In order to calculate the environmental parameters, we considered the net CO_2-equivalent emissions (NCE). The term 'direct CO_{2eq}' refers to greenhouse gas emissions during process operations, whilst 'indirect CO_{2eq}' pertains to the emissions caused by the consumption of utilities for the consumption of electricity and heating sources in the process operation. The 'carbon credit' (CC) represents the decrease in the amount of CO_2 achieved by utilizing CO_2 as a reactant.

$$NCE = \frac{Direct\ CO_{2e}+Indirect\ CO_{2e}-CC}{Amount\ of\ hydrogen}, (kg_{CO_{2-eq}}/kg_{H_2})(2)$$

For the assessment of the technical aspects of the biogas-to-hydrogen process, energy efficiency (EEF) serves as an assessment parameter. To determine the EEF of the process, the heat generated by the product (hydrogen) is divided by the energy used by utilities and the heat introduced by the fed feedstock (biogas).

$$EEF = \frac{Heat\ of\ hydrogen}{Heat\ of\ fed\ biogas+\ E_{utilities}} \times 100\%, (\%)\ (3)$$

3. RESULTS AND DISCUSSION

Techno-economic analysis

For the purpose of economic evaluation, we analysed the breakdown of overall production cost and operational cost for producing hydrogen.

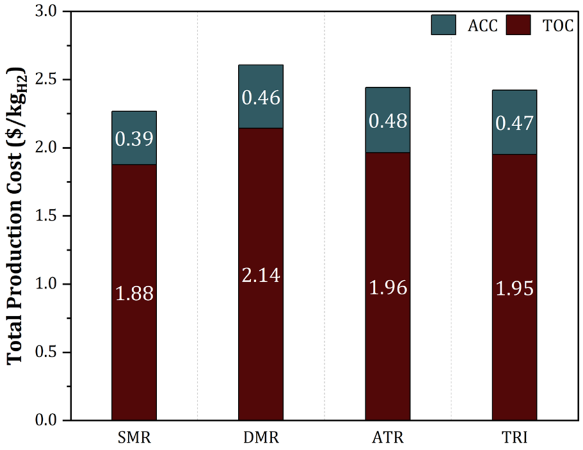


Figure 2: Total production cost analysis of biogas-to-hydrogen processes with different reformers.

To address different strategies, we initially studied the optimal operating conditions for each type of reformers. Figure 2 presents the cost breakdown of hydrogen production, indicating that the total operating cost (TOC) represents more than 80% of the total cost for all technologies. To evaluate the impact of OPEX, which is a significant factor in this research, we analysed the specific breakdown of the total operating cost, which is displayed in Figure 3.

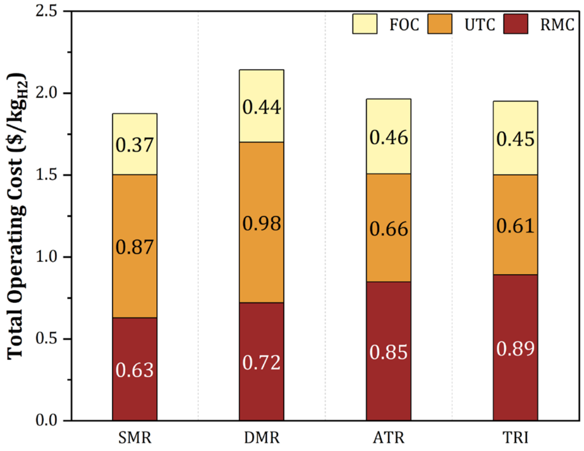


Figure 3: Analysis of total operating cost of the biogas-to-hydrogen processes.

The analysis of total operating costs indicates that utility costs (UTC) dominate the process that employs SMR and DMR for reforming, while raw material costs (RMC) are the most influential parameter for the process using ATR and TRI reactions. It has been determined that highly endothermic reforming reactions yield a relatively larger amount of hydrogen than processes utilizing partial oxidation reactions. Furthermore, we have observed that the process which adopts highly endothermic reforming reactions can produce a greater quantity of hydrogen compared to the partial oxidation reaction process. However, the high heat consumption rate has led to an increased proportion of utility costs in the total operating costs.

Sensitivity analysis

The sensitivity analysis of the hydrogen UPC was conducted by examining the impact of a 20% change in major economic parameters, as displayed in Figure 4. Optimal conditions for every biogas composition and type of reformer were analyzed, with results presented as a range distribution. The bar graph demonstrates the average values obtained across all cases. Technical abbreviations have been explained within the text.

The results of the sensitivity analysis indicate that the price of biogas (feedstock) has the largest impact on the UPC, decreasing and increasing by 20.1% and 18.1%, respectively. The price of fired heat and electricity are the second and third most sensitive parameters, resulting in UPC changes of around 5% and 3%, respectively.

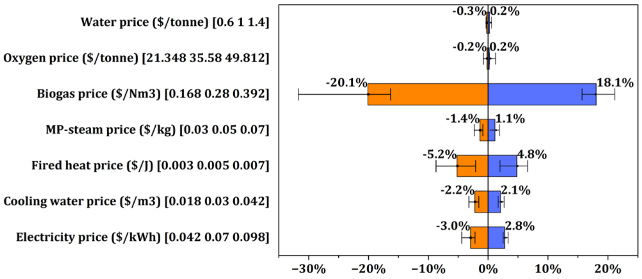


Figure 4: Sensitivity analysis for the unit production cost of total biogas-to-hydrogen processes.

Other factors have a minor impact on UPC, staying below 2%. Accordingly, we scrutinized that the cost of generating hydrogen is significantly linked to OPEX, particularly the expenses concerning raw materials, fired heat, and electricity. Thus, these costs have a trade-off relation with respect to economic and environmental factors.

Optimization model

To identify the optimal pathways of biogas-to-H₂, we developed optimization models using a mixed-integer linear programming (MILP) technique. Here, we considered various evaluation criteria as objective functions to identify the viable biogas utilization strategies. Eq. (1) identifies the minimum unit production cost for a fixed capacity of biogas as a feedstock, which represents the most economic strategy.

$$MinUPC = \sum_{j} \alpha_j + \sum_{j} \varphi_j + \sum_{i \in I^F} \phi_i F_{ij} + \sum_{i \in I^U} \pi_i U_{ij} \tag{1}$$

where α_j is the total capital investment cost of pathway j, φ_j is the fixed operating cost factor of pathway j, and π_i and ϕ_i are the unit costs for utilities and feedstock, respectively. F_{ij} and U_{ij} is the amount of feedstock $i \in I^F$ and utilities $i \in I^U$, respectively.
Eq. (2) seeks for the most eco-friendly process, which is minimum net CO₂ emission strategy for the same amount of process capacity.

$$MinNCE = \sum_{j} \delta_j + \sum_{i \in I^F} \varepsilon_i U_{ij} - \sum_{i \in I^F} \gamma_i F_{ij} \tag{2}$$

where δ_j is the amount of directly emitted CO₂ by technology j. ε_i is the amount of indirect CO₂ emission by using utility $i \in I^U$, and γ_i is the CO₂ inventory for feedstock $i \in I^F$.
Finally, maximum energy efficient process is identified via Eq. (3), which is maximum energy stored in product with a certain input energy to process.

$$MaxEE = \sum_{j} \rho_i P_{ij} \tag{3}$$

where ρ_i is the heating value of final product $i \in I^P$. P_{ij} is the amount of product of pathway j.

The optimization model with proper corresponding constraints is developed as follows.

Flow conservation: Eq. (4) is used to balance the amount of flows between the utilized feedstock and the total amount of processed feedstock in pathway j.

$$\sum_{j_1}^{j_n} F_{ij} = \sum_{j_1}^{j_n} Q_{ij}^{in} \quad \forall i \in I^F \tag{4}$$

where Q_{ij}^{in} is the flow rate of the feedstock input to technology j.
Similaryly, the flow rate of the feedstock input to the technology must be identical to the sum of the three output flow rates for the final product, by-product, and waste, as illustrated in Eq. (5)

$$Q_{ij}^{in} = P_{i'j} + B_{i'j} + W_{i''j} \quad \forall i \in I^F,\; i' \in I^P,\; i'' \in I^W,\; j \in J \tag{5}$$

where P_{ij}, $B_{i'j}$, and $W_{i''j}$ are the amount of product, byproduct and wate from pathway j, respectively.

Feed availability: The amount of feedstock should be bounded by an upper limit (i.e., availability) and a lower limit (i.e., minimum purchase for realistic technology operation) as shown in Eq. (6)

$$r_i \le \sum F_{ij} \le \omega_i \quad \forall i \in I^F \tag{6}$$

where r_i and ω_i are the minimum purchase and feed availabiltiy, respectively.

Logistic constraint: In case an input can be processed by various technologies, only one technology that can satisfy the objective function should be selected using binary variables.

$$\sum_{j_1}^{j_n} X_{j_n} \le 1 \;\; \forall \{j_1, \cdots, j_n\} \in J \tag{7}$$

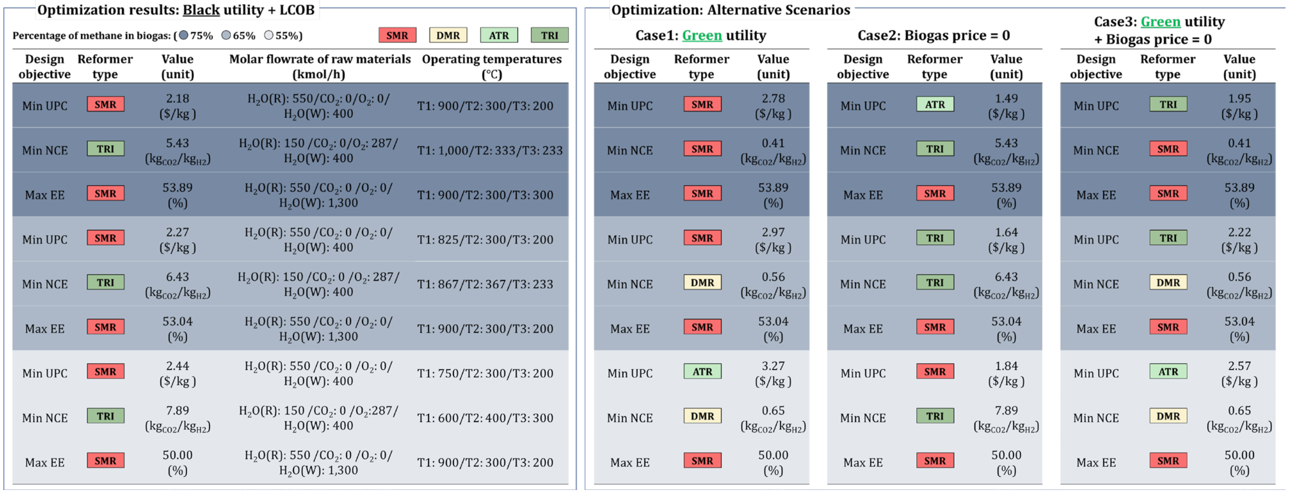
where X_{j_n} is a binary variable that represents the pathway selection.

Technology capacity: The involved technology is limited by its capacity (ψ_j).

$$Q_{j_n}^{in} \le \psi_j X_{j_n} \quad \forall j_n \in J \tag{8}$$

Optimal strategies of biogas-to-hydrogen process

The most efficient hydrogen production methods from diverse biogas compositions are evaluated using Figure 5, based on three different criteria. The first column of Figure 5, representing the optimization results, takes into account black utility and levelized cost of biogas (LCOB). According to the estimated process cost by UPC, SMR utilization strategies show the most cost-effective pathways for all the examined biogas



Optimization results: Black utility + LCOB

Percentage of methane in biogas: (● 75% ● 65% ○ 55%) 🟥 SMR 🟨 DMR 🟩 ATR 🟩 TRI

Design objective	Reformer type	Value (unit)	Molar flowrate of raw materials (kmol/h)	Operating temperatures (℃)
Min UPC	SMR	2.18 ($/kg)	H_2O(R): 550/CO_2: 0/O_2: 0/ H_2O(W): 400	T1: 900/T2: 300/T3: 200
Min NCE	TRI	5.43 (kg_{CO2}/kg_{H2})	H_2O(R): 150 /CO_2: 0/O_2: 287/ H_2O(W): 400	T1: 1,000/T2: 333/T3: 233
Max EE	SMR	53.89 (%)	H_2O(R): 550 /CO_2: 0 /O_2: 0/ H_2O(W): 1,300	T1: 900/T2: 300/T3: 300
Min UPC	SMR	2.27 ($/kg)	H_2O(R): 550 /CO_2: 0 /O_2: 0/ H_2O(W): 400	T1: 825/T2: 300/T3: 200
Min NCE	TRI	6.43 (kg_{CO2}/kg_{H2})	H_2O(R): 150 /CO_2: 0 /O_2: 287/ H_2O(W): 400	T1: 867/T2: 367/T3: 233
Max EE	SMR	53.04 (%)	H_2O(R): 550 /CO_2: 0 /O_2: 0/ H_2O(W): 1,300	T1: 900/T2: 300/T3: 200
Min UPC	SMR	2.44 ($/kg)	H_2O(R): 550 /CO_2: 0 /O_2: 0/ H_2O(W): 400	T1: 750/T2: 300/T3: 200
Min NCE	TRI	7.89 (kg_{CO2}/kg_{H2})	H_2O(R): 150 /CO_2: 0 /O_2:287/ H_2O(W): 400	T1: 600/T2: 400/T3: 300
Max EE	SMR	50.00 (%)	H_2O(R): 550 /CO_2: 0 /O_2: 0/ H_2O(W): 1,300	T1: 900/T2: 300/T3: 200

Optimization: Alternative Scenarios

Case1: Green utility			Case2: Biogas price = 0			Case3: Green utility + Biogas price = 0		
Design objective	Reformer type	Value (unit)	Design objective	Reformer type	Value (unit)	Design objective	Reformer type	Value (unit)
Min UPC	SMR	2.78 ($/kg)	Min UPC	ATR	1.49 ($/kg)	Min UPC	TRI	1.95 ($/kg)
Min NCE	SMR	0.41 (kg_{CO2}/kg_{H2})	Min NCE	TRI	5.43 (kg_{CO2}/kg_{H2})	Min NCE	SMR	0.41 (kg_{CO2}/kg_{H2})
Max EE	SMR	53.89 (%)	Max EE	SMR	53.89 (%)	Max EE	SMR	53.89 (%)
Min UPC	SMR	2.97 ($/kg)	Min UPC	TRI	1.64 ($/kg)	Min UPC	TRI	2.22 ($/kg)
Min NCE	DMR	0.56 (kg_{CO2}/kg_{H2})	Min NCE	TRI	6.43 (kg_{CO2}/kg_{H2})	Min NCE	DMR	0.56 (kg_{CO2}/kg_{H2})
Max EE	SMR	53.04 (%)	Max EE	SMR	53.04 (%)	Max EE	SMR	53.04 (%)
Min UPC	ATR	3.27 ($/kg)	Min UPC	SMR	1.84 ($/kg)	Min UPC	ATR	2.57 ($/kg)
Min NCE	DMR	0.65 (kg_{CO2}/kg_{H2})	Min NCE	TRI	7.89 (kg_{CO2}/kg_{H2})	Min NCE	DMR	0.65 (kg_{CO2}/kg_{H2})
Max EE	SMR	50.00 (%)	Max EE	SMR	50.00 (%)	Max EE	SMR	50.00 (%)

Figure 5: Optimal strategies for different evaluation scenario by considering different biogas compositions.

compositions. The utilization process for low-concentration methane within biogas resulted in an increase in UPC due to the limited production of hydrogen caused by the low levels of methane. By comparing the operating conditions of strategies aimed at minimizing UPC, we can determine that a relatively low-temperature reforming process was utilized for low-concentration methane within biogas. When considering the environmental impact, the TRI utilization strategies exhibit the lowest NCE for all biogas compositions evaluated. The TRI reaction has the potential, in theory, to use CO_2 as a reactant via partial oxidation, thereby supporting the highly endothermic steam methane reforming reaction. The process has the potential to reduce utility consumption through partial oxidation while also reducing CO_2 in the feedstock.

Based on the results of the sensitivity analysis, three parameters that potentially present a trade-off between UPC and NCE when modified can be viewed as constraints for the optimization process. In Case 1, we opted for the use of a green utility with a low $CO_{2\text{-eq}}$ value despite its higher utilization cost instead of a black utility. Remarkably, the optimal pathway for hydrogen production from biogas has been altered. For all evaluation values (UPC, NCE, and EEF), the utilization of SMR process displays the most viable option for converting biogas-to-hydrogen. The SMR utilization strategy generates significant hydrogen production with minimal CO_2 emissions from the utilities, which is the best pathway for minimizing NCE when the biogas contains 75% concentrated methane. Optimal pathway changes when biogas contains less than 65% methane. The DMR strategies were selected for their eco-friendly nature, reducing significant CO_2 emissions by using CO_2 as a feedstock. Consumption of sustainable, 'green' utilities can reduce the significant CO_2 emissions generated from traditional utilities. In case 2, we assumed a biogas price of 0, which can be obtained from upcycling waste. There is no significant change in the optimization results, but the utilization processes of ATR and TRI could be more cost-effective pathways compared to the SMR process for biogas with methane concentrations of 55% and 65%, respectively.

Finally, if we consider both assumption that are used in Case 1 and Case 2, the optimization results can be drastically altered. In terms of cost-effectiveness, strategies utilizing partial oxidation reactions to reduce energy consumption are preferred, while SMR and DMR may be the most environmentally friendly processes by reducing CO_2 emissions from utility consumption and utilizing CO_2 as a feedstock. For technology, the SMR-based process remains the most energy-efficient option.

4. CONCLUSIONS

In this study, we analysed the process of converting biogas directly to hydrogen and optimised it for three evaluation criteria: UPC, NCE, and EEF. This was achieved by constructing a superstructure that considered multiple variables and evaluation parameters. We determined the economic, environmental, and technical feasibility and suggested optimal pathways for the process. The major findings and contributions of this research are as follows:

- To solve the problem of multi variables and evaluation parameters, the superstructure based data driven-modeling was conduced.
- Before the optimization process, we conducted techno-economic evaluation and sensitivity analysis that identified major cost drivers (i.e., price of feedstock, price of electricity and fired heat).
- For the case of process which utilizes black utilities and LCOB, the SMR based process is economically and technically optimal while TRI

based process shows the best results for environmental parameters for every biogas compositions.

- The analysis for different assumptions which showed trade-off relationship between economical and environmental parameters were conducted.
- By considering every assumptions for alternative scenarios which was shown in Case 3, we can analyze that ATR and TRI based process is cost-effective process for each biogas compositions while SMR and DMR can be the technically effective and eco-friendly process.

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