CHEMICAL ENGINEERING TRANSACTIONS
VOL. 94, 2022

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Petar S. Varbanov, Yee Van Fan, Jiří J. Klemeš, Sandro Nižetić

ISBN 978-88-95608-93-8; **ISSN** 2283-9216

DOI: 10.3303/CET2294086

Comparative Life Cycle Analysis and Optimization of Operating Conditions of Hydrogen Production Methods

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Various pathways have been adopted for hydrogen production over the years, with technologies like steam methane reforming, often referred to as the 'brown' or 'blue' hydrogen, being the most prevalent. Different colors correspond to different production pathways, each having its life cycle greenhouse gas emissions. Using process simulation results as the major life cycle inventory data, life cycle impact assessment results for brown and blue hydrogen pathways have been presented. The results of the life cycle analysis study were utilized to determine the set of optimum operating conditions, with the global warming potential (GWP) corresponding to the blue hydrogen pathway at the optimal operating conditions being 33 % less than the optimal brown hydrogen counterpart. The operating cost for the brown hydrogen pathway at the optimal operating conditions can be reduced up to 69 % for the studied range of process operating conditions.

1. Introduction

Hydrogen has various roles in the chemical process industry– processing fossil fuel, producing chemicals like ammonia for fertilizers, hydrochloric acid, and methanol, reducing metallic ores, etc (Gebreslassie et al., 2013). With the rise in pollution levels and decrease in global fossil fuel levels, it is expected that a vast majority of future energy systems will be powered by greener and emerging technologies. Due to its critical role in the energy transition, it is imperative to make the 'hydrogen economy' sustainable both from an economic and environmental point of view (Yue et al., 2021). As the world moves towards a more hydrogen-dependent economy along with the development of new technologies to meet the increasing global hydrogen demand, it is essential to improve the process designs of the current technology variations (brown, blue) to achieve minimum environmental impact under economically competitive costs of production (He et al., 2015). The existing studies present the life cycle impact assessment (LCIA) results for the hydrogen production pathways for one life cycle inventory (LCI) data set, corresponding to a particular set of operating parameters (Tian et al., 2022). From an operating point of view, optimizing process parameters (such as pressure, temperature, and feed inlet ratio of steam to methane) are in accordance with minimizing environmental impacts (Gong and You, 2015). In this work, an optimization model has been developed to find the operating parameters for hydrogen production pathways corresponding to minimum total emissions (direct and indirect emissions from previous and subsequent life cycle stages of plant operation) and operating costs. A process modification to the traditional brown hydrogen pathway has also been proposed where the excess electricity generated from the process is utilized in an Alkaline water electrolysis (AWE) system to increase the total hydrogen from the process and improve the environmental and economic performance of the overall process on a functional unit basis.

2. Process Description and System Boundaries

Figure 1(a) illustrates the process flowsheet for the studied brown hydrogen facility. The first step is the reaction between the incoming natural gas and the produced steam in the reformer. The outlet from the reformer goes into a series of shift reactors, high-temperature shift (HTS) and low-temperature shift (LTS), operating at different temperatures, to maximize the hydrogen production and consume the toxic carbon monoxide (CO) produced. All three reactors operate in a series of decreasing temperatures (reformer > HTS > LTS). Cooling utilities have been used to bring down temperatures. The outlet from the LTS reactor is cooled again and passed into a flash

Paper Received: 12 April 2022; Revised: 23 July 2022; Accepted: 28 July 2022
Please cite this article as: Lal A., You F., 2022, Comparative Life Cycle Analysis and Optimization of Operating Conditions of Hydrogen Production Methods, Chemical Engineering Transactions, 94, 517-522 DOI:10.3303/CET2294086

separator to remove the water from the stream. The vapor stream from the flash separator goes into the pressure swing adsorption (PSA) to recover the hydrogen produced. The cooling utilities from the exit of the heat exchangers are combined with makeup water. The second stream from the PSA system (which does not contain hydrogen) is called the 'tail gas' (Leperi et al., 2016). The tail gas is sent to a furnace system so the heat of the outlet stream from the furnace can operate the reformer at the required temperature. The residual heat in this stream is captured by maximizing the steam generated (Leperi et al., 2019). Some of the generated steam is used as the raw material for the process (which depends on the inlet ratio of steam to methane maintained). Suppose the incoming steam to the reformer is used in excess. In that case, i.e., if the amount is higher than the stoichiometric value– the reforming reaction rate can be improved, and the coke buildup can also be prevented (Rajesh et al., 2000). The other part of the remaining steam (if any) is sent to the turbine to generate electricity. As per the operational limitations and plant cost, the steam to methane ratio is between 3-6. Also, according to the safety limitations, the upper limit on the reforming temperature is set at 900 K (Taji et al., 2018). Figure 1(b) illustrates the subsystems considered for the life cycle analysis (LCA) study.

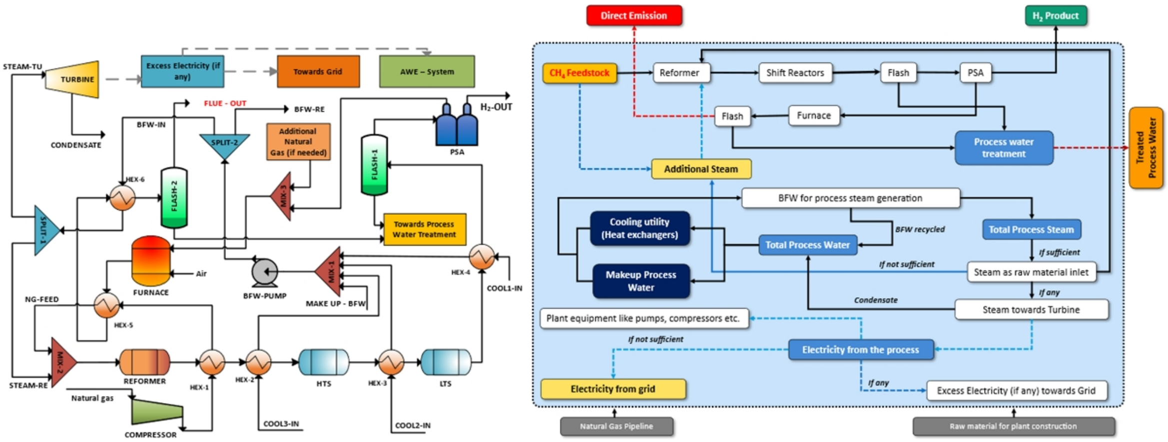

Figure 1: Process flowsheet for the brown hydrogen pathway (left) and system boundary for the LCA study of the brown hydrogen pathway (right)

The functional unit chosen is '1kg of hydrogen produced' for a fair comparison as in comparative LCA studies (Yang 2018). The subsystems considered for the LCA study are 'direct emissions from the process', 'natural gas feedstock', 'process water treatment', 'additional process steam requirement', and 'electricity requirement.' It has been assumed that the construction required for the plant and other necessities such as the pipeline required to transport the natural gas is already in place. They have been placed outside the system boundary, as depicted above. The other steam methane reforming (SMR)-based process in this study combines brown hydrogen production with carbon capture and storage (CCS). The carbon dioxide (CO_2) generated from the process is compressed and then transported to other sites for storage or utilization (Yancy et al., 2020).

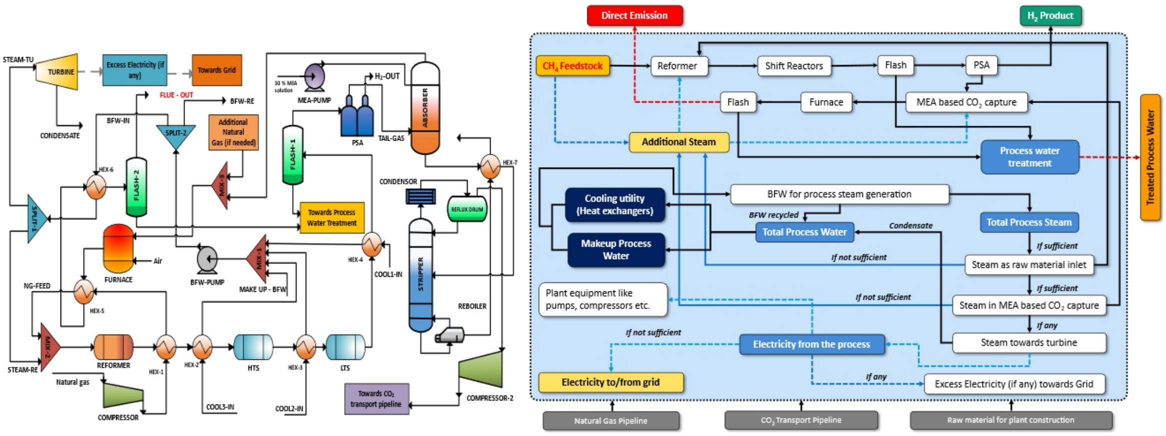

Figure 2: Process flowsheet for studying blue hydrogen process (left) and system boundary for the LCA study of blue hydrogen process (right)

Figure 2 represents the process flowsheet of the blue hydrogen process. Most of the process flow is consistent with the previous diagram on the brown hydrogen process, except that a Monoethanol Amine (MEA)- based CO_2 capture system has been applied to the tail gas to capture the CO_2 in this stream. MEA solvent absorption is one of the relatively mature technologies available to capture CO_2 from effluent streams (Husebye et al., 2012). The tail gas enters the bottom of an absorber, and a 30 % MEA solution enters from the top. Depending on the flow rate of the MEA solution, the percentage capture of the CO_2 in the tail gas stream varies from 60 to 90 %. The vapor from the top of an absorber is sent to the furnace. The rich MEA solution (containing the captured CO_2) is sent to the stripper to recover the MEA. Energy consumption for solvent regeneration is an important parameter that must be considered for an effective CO_2 absorption process from an economic and environmental point of view (Yue et al., 2015). The energy consumption here refers to the reboiler heat duty because the energy for the solvent generation is provided by steam passing through a reboiler at the bottom of the generation column (Sakwattanapong et al., 2005).

3. Problem Statement and Model Formulation

The operating conditions of any process play a crucial role in the overall efficiency of the process. These conditions are mainly referred to as the process parameters like temperature, pressure, inlet molar ratio, etc. (He et al., 2014). Generally, these parameters are optimized considering various economic (least operating cost), safety, and heuristical constraints. In this study, using the Aspen Plus flowsheet developed for the process flowsheets described, the operating conditions were varied to generate different values of LCI data (He and You, 2016). These different sets of LCI data were eventually utilized to study how varying the operating conditions affect the GWP for the process (Gong et al., 2018). For the case of the brown hydrogen process, the varied operating parameters are the temperature of the inlet feed (reforming) $\in$ [700 K, 900 K], operating pressure $\in$ [7 bar, 25 bar], inlet molar ratio of steam to methane $(\frac{H_2O}{CH_4}) \in [3, 6]$. An additional operating parameter of the percentage of CO_2 capture has been included in the blue hydrogen process with tail gas capture, which varies $\in$ [60 %, 90 %]. The equipment in the plant which utilized electricity was used at respective isentropic efficiencies (0.6 for pumps and 0.7 for compressors). The turbine generated electricity from excess steam (if any) and was also set at an isentropic efficiency of 0.7. The rate law kinetics for both reforming and shift reactions were obtained from the literature. Based on the study by Amran et al. (2017), the reformer has been modeled as an isothermal reactor. The shift reactors were operated at two temperatures and were modeled as an adiabatic reactor (Amran et al., 2017). The MEA solution utilized has a 30 % concentration for each set of simulations. The maximum number of trays in the absorber column for each simulation run was 15. In the brown hydrogen process using an alkaline electrolyzer, it was assumed that the electrolyzer would be run at the optimal operating conditions (temperature, pressure, current density). Figure 3 describes the methodology used to develop the framework to get optimum operating conditions:

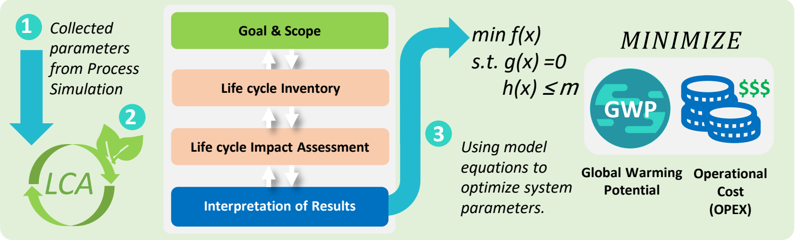

Figure 3: Methodology used to get optimization framework equations

An NLP model is formulated for each technology alternative studied to optimize the operating condition. In the SMR technology alternatives studied (brown, blue), the inlet feed of the methane feedstock to the reformer was fixed at each operating condition. The flows obtained from the converged flowsheets (i.e., hydrogen production rate, CO_2 emission rate, tail gas flow rate, cooling utilities) and the other parameters required (power requirement for the equipment) were used as the LCI data after converting the obtained values to the functional unit basis. The values needed for the brown hydrogen technology included the mass of carbon dioxide released as direct emissions from the process ($GWP^{direct\ emission}$), the mass of the natural gas feedstock needed ($GWP^{natural\ gas\ feedstock}$), process water treatment required ($GWP^{treatment}$), electricity generated/needed (GWP^{elec}), additional natural gas needed to generate steam (for the additional steam subsystem). The environmental impact of generating additional steam if required from the process has been included in the calculations for the subsystem of natural gas production and direct emission. Depending on the brown hydrogen technology being investigated, the GWP equivalent of the electricity mixture or the amount of additional hydrogen generated using the AWE is needed. The blue hydrogen tail gas capture technology also needs the same values. However, the key difference is the presence of an additional input variable (i.e., % of carbon capture in the tail gas). The formulated constraints are different due to how the LCI data is changed. For example, the mass of CO_2 released would be less than the brown hydrogen counterpart under the same conditions due to carbon capture. Another example would be the additional steam required as part of the reboiler duty requirement in the process. The operating cost for the process includes the feedstock cost (FC), operations and maintenance cost (OM), utility costs (UC), and carbon tax (c^{tax}) associated with emissions.

$$min\begin{cases} GWP = GWP^{direct\ emission} + GWP^{natural\ gas\ feedstock} + GWP^{treatment} + GWP^{elec} \\ OPEX = FC + OM + UC + c^{tax} \end{cases} \tag{1}$$

s.t. Equality constraints to estimate LCI parameters
Heuristical constraints on bounds of operating parameters (input variables)
LCIA impact category estimation equality constraint
Economic evaluation constraint

4. Results and Discussion

Figure 4 depicts that different operating conditions could drastically impact the GWP equivalents for the subsystems, as described in the previous section. For the first set of operating conditions in the brown hydrogen pathway (temperature = 900 K, inlet ratio = 6, pressure = 7 bar), the subsystems of 'additional process steam' and 'electricity generation' have positive values and still have a lower value of total GWP (total 11.755 kg CO_{2}-eq) than the second set (temperature = 900 K, inlet ratio = 4.5, pressure = 25 bar) which has no contribution from the 'additional steam' subsystem and also has a negative contribution from 'electricity requirement' subsystem because at this operating condition additional electricity over the requirement can be generated. A similar conclusion can be drawn for the blue hydrogen technologies with varying degrees of MEA-CO_2 capture in the tail gas.

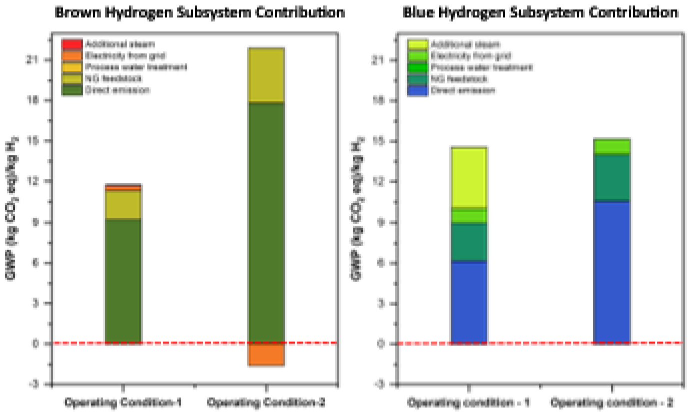

Figure 4: Comparison of GWP at two different operating conditions for brown hydrogen and blue hydrogen

The first set of conditions (temperature = 900 K, inlet ratio = 6, pressure = 16 bar) has a CO_2 capture of 90 %. It would require more steam to maintain the reboiler duty requirement. Accordingly, it has a high positive value for this subsystem and the electricity generation subsystem. However, for the second set (temperature = 900 K, inlet ratio = 6, pressure = 25 bar), since the % capture in tail gas is comparatively less (60%), no additional steam is required (and zero contribution). Electricity from the grid is still needed (since the electricity produced by the residual steam is not sufficient) and a positive contribution from this subsystem. Two versions of brown hydrogen production have been studied in this study. One involves using excess electricity to produce additional hydrogen. The other involves supplying additional electricity to the grid. It was observed that different combinations of conditions could have different choices for the suitable option. This can be implied with the help of Figure 5, which represents the difference in GWP for both versions of brown hydrogen. For the chosen operating temperature (900 K), when the inlet ratio maintained is on the lower side, it is more suitable at all operating pressures to supply electricity to the grid from an emission point of view.

On the contrary, when the maximum inlet ratio is used (i.e., 6), it is more beneficial to use an AWE system to consume any additional electricity produced. Similarly, different operating temperatures can change the favorable choice here. For example, when the operating temperature is reduced (i.e., 800 K), the proposed modification becomes beneficial at higher than moderate operating pressures (> 16 bar) even for low inlet ratios maintained in the reformer. However, when the inlet ratio increases at this temperature, the proposed modification is useful only at high operating pressures (i.e., 25 bar).

From an operating cost point of view, it was observed that increasing the operating pressures leads to an increase in operating costs for both the technology alternatives. However, at 900 K, it is more economical to send the electricity to the grid and vice versa for 800 K, as depicted in **Error! Reference source not found.**.

The optimal operating conditions predicted by the model applied for the technology alternatives described above for the site location to be in Texas. The critical factor is the electricity mixture in Texas, which corresponds to a GWP equivalent of 0.556 kgCO_2-eq /kWh consumed. Commercial electricity prices have been assumed to be \$0.0933/kWh (Zhao and You, 2020). It has also been assumed that no-cost benefits will be accounted for if any additional electricity is provided to the grid. However, the credit for the GWP equivalent corresponding to the electricity provided has been considered. Figure 7 clearly shows that the GWP value is lesser for the blue hydrogen pathway than for the brown hydrogen counterpart. In both technology alternatives, the two significant contributors are the direct emissions released from the process and the indirect emissions due to natural gas feedstock utilization.

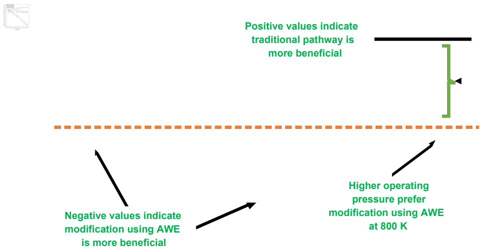

Figure 5: GWP for the optimized brown hydrogen pathway at different combinations of operating parameters

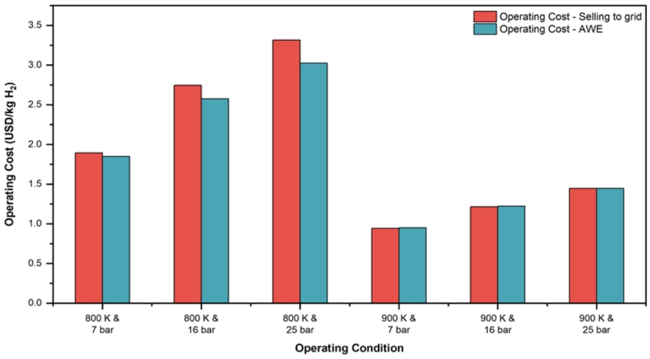

Figure 6: Operating cost for both versions of brown hydrogen pathway at different operating conditions

5. Conclusion

Two technology alternatives for the SMR process have been analyzed: brown and blue. It was observed that not all the subsystems contribute towards GWP at all operating conditions. The subsystems of 'additional steam requirement' and 'electricity from the grid' have a non-zero impact only at some operating parameters. Two versions of the brown hydrogen technology can be adopted depending on how the process's excess electricity (if any) is utilized. It is possible that depending on the operating condition, different versions of the brown hydrogen technology are more beneficial from an economical and environmental point of view. At their respective optimal operating conditions, the brown hydrogen technology alternative is more economical than blue hydrogen, with an operating cost of 1.19 \$/kg of hydrogen. Future work should consider uncertainty analysis of the optimized hydrogen pathways and processes following the life cycle perspective (Yue et al., 2012).

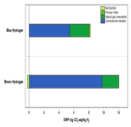

Figure 7: Comparison between the GWP for optimized process at the Texas site

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