

Article

Thermodynamic and Techno-Economic Performance Comparison of Methanol Aqueous Phase Reforming and Steam Reforming for Hydrogen Production

Changsong Hu ¹ , Chao Xu ¹, Xiaojun Xi ¹, Yao He ^{2,*} and Tiejun Wang ^{1,*}

¹ School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China; changsonghu@gdut.edu.cn (C.H.); 2112106186@mail2.gdut.edu.cn (C.X.); 2112306091@mail2.gdut.edu.cn (X.X.)

² School of Environmental Science and Technology, Guangdong University of Technology, Guangzhou 510006, China

* Correspondence: jason301.he@163.com (Y.H.); tjwang@gdut.edu.cn (T.W.)

Abstract: Methanol, which can be derived from sustainable energy sources such as biomass, solar power, and wind power, is widely considered an ideal hydrogen carrier for distributed and mobile hydrogen production. In this study, a comprehensive comparison of the thermodynamic and techno-economic performance of the aqueous phase reforming (APR) and steam reforming (SR) of methanol was conducted using Aspen Plus and CAPCOST software to evaluate the commercial feasibility of the APR process. Thermodynamic analysis, based on the Gibbs free energy minimization method, reveals that while APR and SR have similar energy demands, APR achieves higher energy efficiency by avoiding losses from evaporation and compression. APR typically operates at higher pressures and lower temperatures compared to SR, suppressing CO formation and increasing hydrogen fraction but reducing methanol single-pass conversion. A techno-economic comparison of APR and SR for a distributed hydrogen production system with a 50 kg/h hydrogen output shows that although APR requires higher fixed operating costs and annual capital charges, it benefits from lower variable operating costs. The minimum hydrogen selling price for APR was calculated to be 7.07 USD/kg, compared to 7.20 USD/kg for SR. These results suggest that APR is a more economically viable alternative to SR for hydrogen production.

Keywords: methanol; hydrogen; aqueous phase reforming; steam reforming; thermodynamic analysis; techno-economic analysis



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1. Introduction

The efficient and reliable transportation, distribution, and storage of hydrogen remain technically and economically challenging, hindering the realization of a complete hydrogen economy [1,2]. A promising solution is chemical hydrogen storage with on-demand release via catalytic processes. Methanol can be produced from sustainable energy sources including biomass, solar power, and wind power. It is widely considered to be one of the most favorable hydrogen carriers for distributed and mobile hydrogen production due to several advantages: (1) methanol is a liquid under ambient conditions, making its transportation easier and safer than hydrogen; (2) methanol has a high hydrogen storage density of 18.75 wt.%; and (3) methanol can be activated at relatively low temperatures (150–350 °C) [3–5].

Hydrogen can be produced from methanol via steam reforming (SR) or aqueous phase reforming (APR). APR typically operates at lower temperatures compared to SR

and avoids the tedious and energy-consuming evaporation process; thus, it is ideal for mobile and distributed systems [3]. Experimental results in the literature show APR produces purer hydrogen with lower CO content [6–8]. This facilitates alleviating the challenge of CO removal, as CO can poison the catalysts used in fuel cells and is an undesirable byproduct [9,10].

Over the past few decades, hydrogen production technologies have seen considerable advancements in various areas, including the development of advanced materials (such as novel catalysts, membrane materials, and nanostructured materials) [11], enhanced control systems [12,13], and alternative feedstocks [14]. Methanol SR remains one of the most mature and economically competitive processes for hydrogen generation. In contrast, the methanol APR process has not yet reached commercialization, primarily because of the absence of mature catalysts with commercial competitiveness. The Cu-based catalysts typically used in methanol SR are not suitable for methanol APR, owing to their limited hydrothermal stability [15]. As a result, recent research has predominantly focused on the design and optimization of highly active, thermally stable, and low-temperature catalysts specifically for methanol APR [6,16–19]. Lin et al. [16] found that Pt atoms dispersed on α -MoC are highly effective for hydrogen production via methanol APR at 150–190 °C, achieving an average turnover frequency of 18,046 mol_{H₂}/mol_{Pt}/h. Lin et al. [17] also developed a novel Ni/ α -MoC catalyst with a hydrogen evolution activity of 171 μ mol_{H₂}/gcat/s, nearly six times higher than Pt/Al₂O₃. Li et al. [18] reported that a novel Pt/NiAl₂O₄ catalyst enhanced the conversion of carbon to gaseous products and hydrogen yield by fourfold over Pt/Al₂O₃, reaching 99.9% and 95.7%, respectively. It maintained excellent stability with only a 10% loss in conversion after 600 h on stream. In general, there are two primary issues for the catalysts reported in the literature: (1) most catalysts use precious metals as active components; (2) the low loading of active components (typically less than 10 wt.%) restricts the compact design of hydrogen production units for portable applications [6,16–19]. These factors are also the main reasons why methanol APR has not been commercialized. In recent years, our research group has developed a series of carbon-coated Cu-based catalysts with low cost, high loading, high activity, and high stability for methanol APR, offering a feasible pathway for the commercialization of hydrogen production via methanol APR [20–24]. To gain a deeper understanding of the commercial potential of methanol APR, a comprehensive investigation of its thermodynamic performance is essential, with a particular focus on the distinctions between APR and SR. However, to our knowledge, few studies have focused on the thermodynamic and techno-economic performance of methanol APR [6,25]. There still exists a lack of direct comparisons of thermodynamic and techno-economic performance between methanol APR and SR.

In order to evaluate the commercial potential and feasibility of hydrogen production via methanol APR, comparative thermodynamic and techno-economic analyses of methanol APR and SR were performed in this study. The enthalpy and Gibbs free energy of reaction, as well as chemical and phase equilibrium based on the Gibbs free energy minimization method, were investigated to clarify the thermodynamic performance of APR and SR. A distributed hydrogen production system with a pure hydrogen production capacity of 50 kg/h was modeled to enable a comparative techno-economic analysis of APR and SR. The fixed capital investment (FCI) for both processes was estimated using CAPCOST 2017 rev2 software. The break-even price of hydrogen was calculated through the discounted cash flow method. Additionally, a sensitivity analysis was conducted to evaluate the effects of fluctuations in key parameters on the profitability of the project.

2. Methods

2.1. Thermodynamic Modeling

Thermodynamic analysis was performed using Aspen Plus V11 software with the Peng Robinson cubic equation of state incorporating the Boston-Mathias alpha function (PR-BM). The PR-BM method, renowned for its accuracy and efficiency in describing temperature, pressure, and phase compositions in both binary and multi-component systems, is widely utilized in gas–liquid equilibrium calculations, especially at moderate to high pressures. This method requires only critical properties and the acentric factor for generalized parameters, enabling efficient computation and accurate phase equilibrium prediction [26]. It is well suited for methanol APR and SR [25–28].

Methanol APR and SR processes can be considered as consisting of the two main thermodynamic equilibrium reactions, as follows [29]:



Methanol is cracked into CO and H₂, followed by the conversion of CO to CO₂ in the WGS reaction, producing additional H₂ [30–33]. Based on the analysis of product distribution in bench-scale experiments [20–23,34,35], only the primary compounds involved in methanol APR and SR (CH₃OH, H₂O, CO, CO₂, and H₂) were taken into account in this work, consistent with the established parameters in the relevant thermodynamic literature [27,32,33]. Some studies have reported introducing C and CH₄ as additional products, showing unreasonably high yields of C and CH₄. The results are inconsistent with the severe inhibition of C and CH₄ formation observed in methanol reforming experiments with Cu-based catalysts [27,36,37]. Therefore, C and CH₄ were excluded as products in the calculation model for this study.

The bubble point temperature (BPT), bubble point pressure (BPP), dew point temperature (DPT), and dew point pressure (DPP) of methanol–water mixtures were determined using a Flash 2 separator [38,39]. The enthalpy and Gibbs free energy of the substances were derived using enthalpy departure or Gibbs free energy departure based on the state equation, in conjunction with temperature-dependent ideal gas properties. The RGibbs reactor was utilized in the calculation of chemical equilibrium and phase equilibrium, applying the Gibbs free energy minimization method [27,40].

Assuming constant pressure and temperature, the equilibrium of the system can be expressed as follows:

$$G^t = \sum_{i=1}^N n_i \bar{G}_i = \sum_{i=1}^N n_i \mu_i = \sum_{i=1}^N n_i G_i^0 + RT \sum_{i=1}^N n_i \ln \frac{\hat{f}_i}{f_i^0} \quad (3)$$

The minimization of G^t in the equation above can be achieved by determining the optimal set of n_i values. This process is subject to the constraint of maintaining the elemental balance across all components of the mixture.

$$\sum_i n_i a_{ik} = A_k, \quad k = 1, 2, \dots, M \quad (4)$$

The Lagrange multiplier method is used to construct the combination function ψ , as outlined in the following expression:

$$\psi = G^t + \sum_{k=1}^M \lambda_k a_{ik} \quad (5)$$

The minimum value of ψ corresponds to the primitive function G^t , and the constant value of the Lagrange multiplier, λ_k , can be calculated. At equilibrium, the derivative of ψ with respect to n_i is zero, the equation is expressed as follows:

$$\frac{\partial \psi}{\partial n_i} = \sum_{i=1}^N n_i \left(\Delta G_{fi}^0 + RT \ln \frac{y_i \hat{\Phi}_i P}{P^0} + \sum_{k=1}^M \lambda_k a_{ik} \right) = 0 \quad (6)$$

The constraint in Equation (4) results in a set of $(N + M)$ equations, which allows the determination of the values for n_i and λ_k under the minimization condition.

To evaluate the performance of the methanol reforming system, the conversion rate of methanol and the molar fractions of H_2 , CO and CO_2 were defined as follows:

$$\text{Methanol conversion rate} = \frac{F_{\text{methanolin}} - F_{\text{methanolout}}}{F_{\text{methanolin}}} \times 100\% \quad (7)$$

$$H_2 \text{ molar fraction} = \frac{F_{H_2\text{out}}}{F_{H_2\text{out}} + F_{CO\text{out}} + F_{CO_2\text{out}}} \times 100\% \quad (8)$$

$$CO \text{ molar fraction} = \frac{F_{CO\text{out}}}{F_{H_2\text{out}} + F_{CO\text{out}} + F_{CO_2\text{out}}} \times 100\% \quad (9)$$

$$CO_2 \text{ molar fraction} = \frac{F_{CO_2\text{out}}}{F_{H_2\text{out}} + F_{CO\text{out}} + F_{CO_2\text{out}}} \times 100\% \quad (10)$$

where $F_{\text{methanolin}}$ and $F_{\text{methanolout}}$ are the molar flow rates of methanol at the inlet and outlet of the reactor, and $F_{H_2\text{out}}$, $F_{CO\text{out}}$, and $F_{CO_2\text{out}}$ are the molar flow rates of H_2 , CO, and CO_2 at the outlet, respectively.

2.2. Techno-Economic Modeling

The process flow diagrams for methanol SR and APR, designed for the production of 50 kg/h of pure hydrogen, are illustrated in Figures 1 and 2, respectively. The flow-sheets presented in these figures closely align with the descriptions found in the relevant literature [41–44], ensuring the reliability of the system design. Considering that the produced hydrogen is typically stored in high-pressure containers, the outlet pressure of hydrogen in both processes is set at 4 MPa to facilitate a meaningful comparison. According to previous studies, the operating conditions for the APR process are set at 200 °C and 4 MPa, whereas the SR process operates with the reformer set to 300 °C and 1 bar. A commercial catalyst Cu/ZnO/Al₂O₃ is applied for the SR process [34,35]. The APR process is designed based on the Cu@C catalyst developed by our research group, with data for this study derived from laboratory-scale experiments, as the methanol APR process has not yet been industrialized [20–24]. Both the SR and APR catalysts were assumed to have a lifetime of 1 year [42,45]. Due to the low cost and long lifetime (exceeding 10 years) of the adsorbent material in PSA, the cost of replacing the adsorbent material is negligible and is not included in the economic analysis of either process. The APR process is equipped with two stages of flash drums, each operating at different pressures. Flash drum 1 operates at a pressure of 4 MPa and is responsible for separating the high-pressure gas products after reforming. The liquid phase separated in Flash drum 1 is then depressurized to atmospheric pressure, which causes partial vaporization. This gas–liquid mixture is further separated in Flash drum 2, which operates at atmospheric pressure, to recover unconverted liquid reactants (methanol and water). The mass and energy balances of the SR and APR processes were analyzed using the PR-BM method in Aspen Plus software. Table 1 outlines the detailed specifications of the units employed in the conceptual design and simulation of the methanol reforming systems.

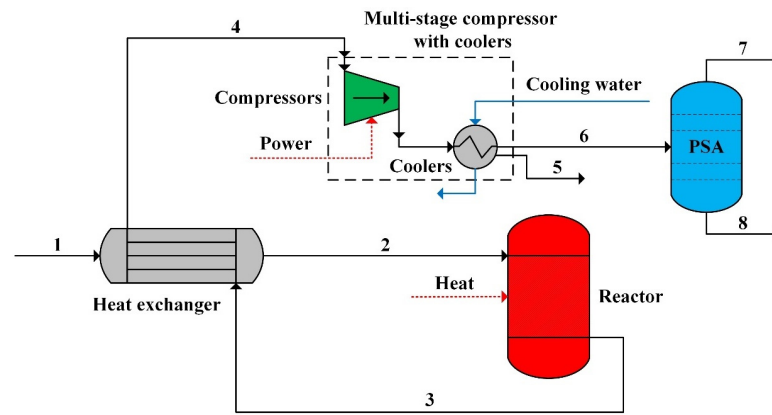


Figure 1. Process flow diagram for hydrogen production via methanol SR.

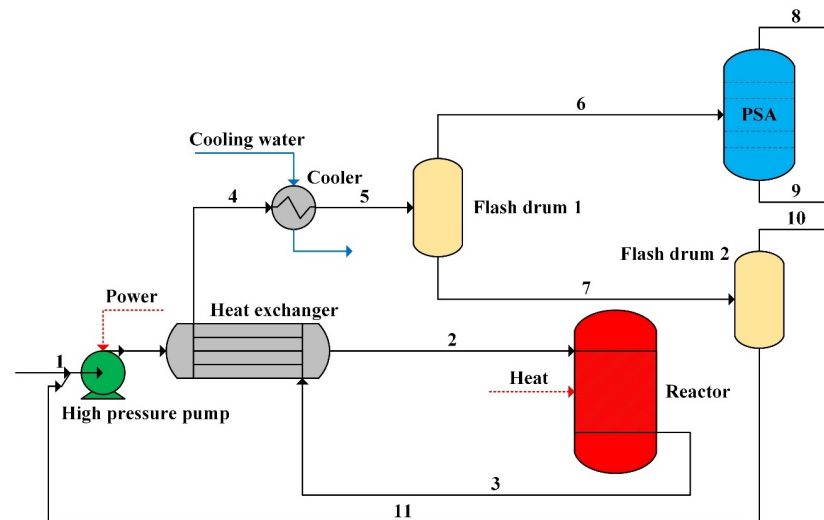


Figure 2. Process flow diagram for hydrogen production via methanol APR.

Table 1. Specifications of the units of methanol SR and APR processes.

Equipment	SR	APR
Pump	–	Discharge pressure: 4 MPa
Heat exchanger	Temperature differential between hot outlet and cold inlet: 30 °C	Temperature differential between hot outlet and cold inlet: 30 °C
Compressor	Multi-stage (4 stage with 2.51 per stage) isentropic compressor	–
Cooler	Cooling water inlet temperature: 30 °C Cooling water outlet temperature: 40 °C	Cooling water inlet temperature: 30 °C Cooling water outlet temperature: 40 °C
Reactor	Isothermal Reaction in gaseous phase Operating temperature: 300 °C Operating pressure: 0.1 MPa Catalyst: Cu/ZnO/Al ₂ O ₃	Isothermal Reaction in liquid phase Operating temperature: 200 °C Operating pressure: 4 MPa Catalyst: Cu@C
Flash drum	–	Operating pressure (flash drum 1): 4 Mpa Operating pressure (flash drum 2): 0.1 MPa
PSA	Operating temperature: 40 °C Operating pressure: 4 Mpa Purity of H ₂ -rich product: 99.999% Recovery: 80%	Operating temperature: 40 °C Operating pressure: 4 Mpa Purity of H ₂ -rich product: 99.999% Recovery: 80%

The FCI was assessed using the CAPCOST software [46], which estimates the purchase costs for each individual unit by integrating design parameters such as operating conditions (e.g., pressure and temperature), system capacity, required heat transfer area, construction materials, and other relevant factors within the program. This cost estimation starts with a base unit cost and includes additional expenses for materials, equipment installation, labor, and indirect costs. These elements together constitute the bare module cost (C_{BM}), which accounts for both direct and indirect costs associated with equipment procurement and installation. The CAPCOST software calculates the C_{BM} by combining the bare module cost for equipment under base conditions (C_{BM}^0) (representing units constructed from standard materials, such as carbon steel, and designed to operate at near-ambient pressure) with a multiplication factor that accounts for the specific design pressures and construction materials. In this study, all equipment units are assumed to be constructed using stainless steel as the material.

Typically, the purchase costs of equipment rise over time due to inflation. In the CAPCOST software, the chemical engineering plant cost index (CEPCI) is used to update equipment cost estimates to the current year (2023, $CEPCI_{2023} = 797.9$), according to the following formula [46,47]:

$$Cost_{2023} = Cost_{base\ time} \times \frac{CEPCI_{2023}}{CEPCI_{base\ time}} \quad (11)$$

The CAPCOST software was utilized for the cost estimation of most process units, with the exception of the reactor and PSA. The costs of the reactor and PSA were determined based on publicly available commercial data from the literature [42,47] and adjusted for different capacities using the six-tenths rule, as shown below [46]:

$$\frac{C_a}{C_b} = \left(\frac{A_a}{A_b} \right)^n \quad (12)$$

where A is the equipment cost attribute, C is the purchased cost, and n is the cost exponent, which varies depending on the class of equipment. The value of n for different items of equipment is often around 0.6.

The FCI is calculated as the sum of C_{BM} , contingency and fee costs (assumed to be 15% and 3% of C_{BM}), and auxiliary facilities costs (estimated at 50% of C_{BM}^0). Fixed operating costs are determined as a percentage of FCI [46], whereas variable operating costs are derived from consumable expenses. The annual capital charge is the total of annualized C_{BM} and the rest of the investment cost.

Hydrogen is considered the sole valuable product in revenue calculations. The minimum hydrogen selling price is calculated using the discounted cash flow method, with a 10% rate of return, ensuring that the cumulative net present value (NPV) at the end of the project is zero [46].

$$\sum_{n=1}^{n=t} \frac{CF_n}{(1+i')^n} = 0 \quad (13)$$

where CF_n is the cash flow in year n , t is the project life in years, and i' is the discounted cash-flow rate of return (percent/100).

The FCI is distributed over the first year, with 50% allocated at the beginning and the remaining 50% at the end, under the assumption of a 20-year project lifetime and a 1-year construction period. The project lifetime is the sum of the operational period (plant lifetime) and the construction period of the plant. A summary of the raw materials and utilities costs is provided in Table S1.

3. Results and Discussion

3.1. Thermodynamic Analysis

3.1.1. Impact of Temperature and Pressure on Enthalpy and Gibbs Free Energy of Reaction

The phase state of reactants in methanol reforming is primarily controlled by reaction pressure, with additional influence from temperature and the molar ratio of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$. In the following discussion, the assessment of the phase state of reactants is based on the bubble and dew point data for the methanol–water mixture provided in Table S2.

Figure 3a,b present the impact of temperature and pressure on the enthalpy of the WGS and methanol reforming reactions. Both reactions exhibit similar trends in enthalpy, with changes in temperature and pressure. As the reaction temperature rises from ambient (25°C) to the BPT of the methanol–water mixture, the reaction enthalpy gradually decreases. When temperature exceeds the BPT, reaction enthalpy sharply decreases until reaching the DPT, then increases slightly as the temperature rises further. The significant decrease in reaction enthalpy observed between the BPT and DPT represents the heat of evaporation of the reactants [48]. When the reactants are in the liquid phase, the enthalpy of both the WGS and methanol reforming reactions decreases with increasing pressure, whereas in the gas phase, it decreases with decreasing pressure. The WGS reaction is exothermic with gas phase water but becomes endothermic at lower temperatures with liquid phase water. Across the studied temperature and pressure ranges, the methanol reforming reaction remains endothermic. Additionally, the enthalpy of both the WGS and methanol reforming reactions is significantly higher when the reactants are in the liquid phase compared to the gas phase. This is primarily due to the heat of evaporation of the reactants.

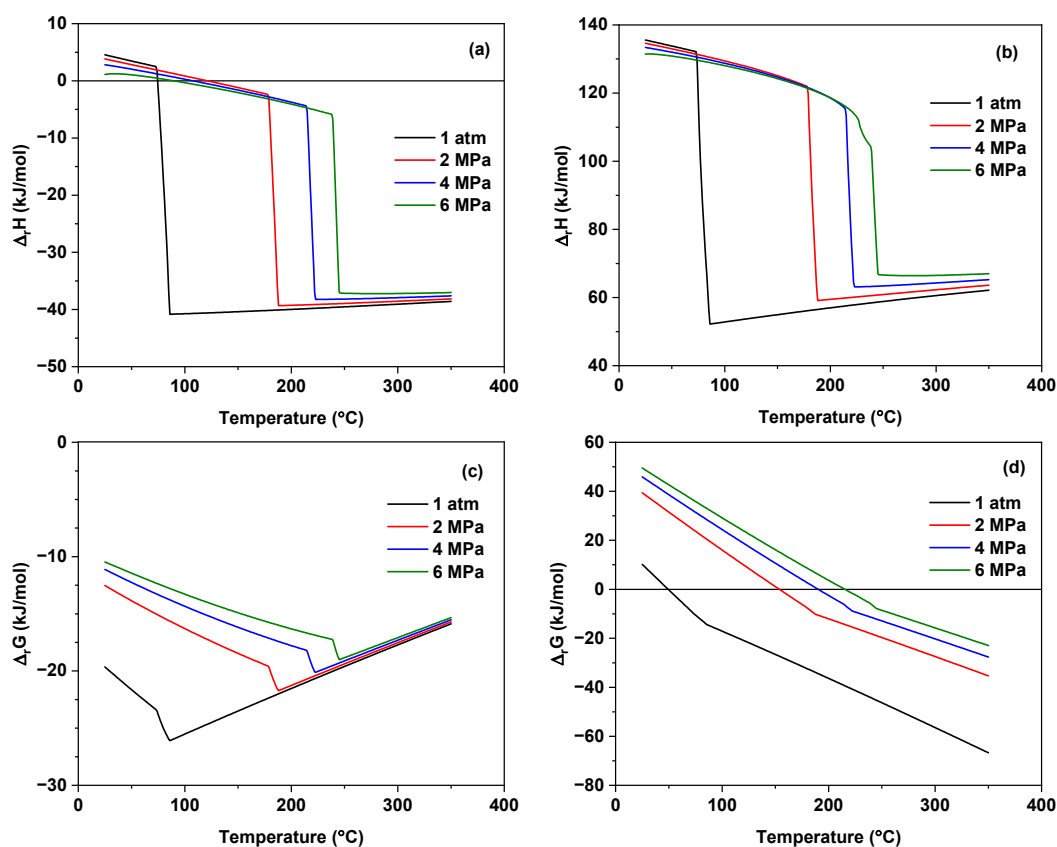


Figure 3. Enthalpy and Gibbs free energy of reaction as a function of temperature and pressure: (a,c) the WGS reaction and (b,d) methanol reforming reaction.

The impact of temperature and pressure on the Gibbs free energy of the WGS and methanol reforming reactions is given in Figure 3c,d. Similar to the reaction enthalpy,

the Gibbs free energy of both the WGS and methanol reforming reactions shows a rapid decrease between the BPT and DPT because of the heat of evaporation of the reactants. The Gibbs free energy of the WGS and methanol SR reactions consistently shows negative values, indicating that these reactions can proceed spontaneously. For methanol SR at temperatures above the DPT, the reaction enthalpy increases with increasing temperature while the Gibbs free energy of reaction decreases, suggesting an increase in entropy. The Gibbs free energy of the methanol APR reaction starts positive at low temperatures, decreases with increasing temperature until it becomes negative. For a typical methanol APR conducted at 4 MPa [23,24], the reaction is spontaneous, between 190.24 °C and 214.79 °C, with reactants in the liquid phase and a negative Gibbs free energy of reaction. Both the Gibbs free energy of the WGS and methanol reforming reactions rise with increasing pressure, indicating reduced spontaneity. Therefore, excessively high pressure is not advisable for methanol APR. A pressure slightly above the BPP of the reactants is favorable.

3.1.2. Impact of Temperature and Pressure on the Thermodynamic Equilibrium

Figure 4 shows the impact of temperature and pressure on methanol conversion rate and gas product distribution with a $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ ratio of 1:1. The results demonstrate that increasing reaction pressure at constant temperature promotes a transition from SR to APR, resulting in smooth changes in methanol conversion rate and gas product molar fractions. This suggests that the phase transition of the reactants does not directly affect methanol conversion rate and product distribution. Instead, these parameters vary smoothly with temperature, pressure, and other operating conditions.

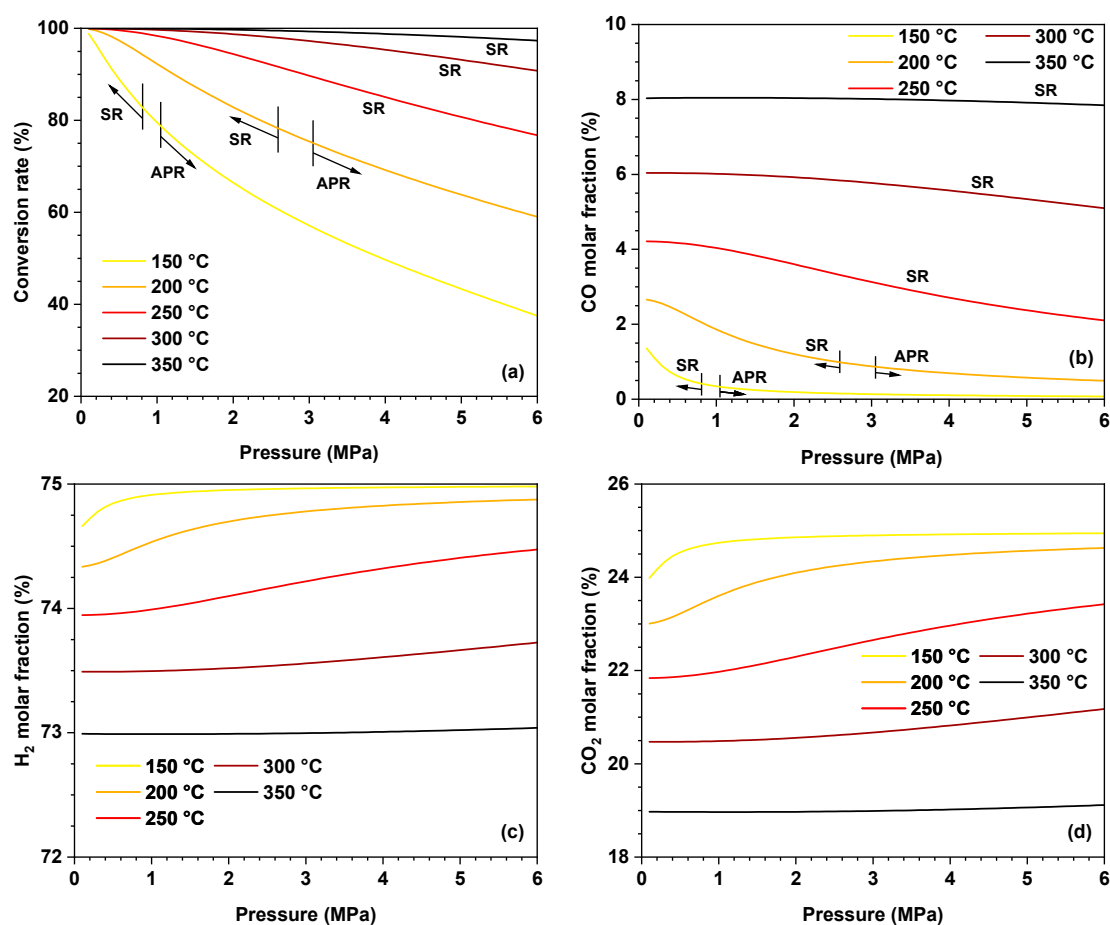


Figure 4. Methanol conversion rate and gas product distribution in methanol reforming as a function of temperature and pressure: (a) methanol conversion rate; (b) CO molar fraction; (c) H₂ molar fraction; and (d) CO₂ molar fraction.

Increasing temperature and decreasing pressure improve methanol conversion rate but also promote the formation of CO, resulting in a reduction in the H_2 molar fraction in gas products. This implies the enhancement of the methanol cracking reaction. At temperatures above $250\text{ }^\circ\text{C}$ and pressures below 6 MPa, the reactants are entirely in the gas phase. Low temperature and high pressure are required to maintain APR and decrease the CO molar fraction in gas products. Decreasing temperature is more effective in suppressing CO formation compared to adjusting pressure, whereas enhancing reaction rates at low temperatures is extremely challenging in practical applications. Under APR operating conditions, a further increase in the reaction pressure results in a significant decrease in the methanol conversion rate. Therefore, the reaction pressure should be kept slightly above the BPP of the reactants. This is consistent with the conclusions previously drawn from the analysis of the Gibbs free energy of reforming reactions.

3.1.3. Impact of CH_3OH/H_2O on the Thermodynamic Equilibrium

Figure 5 illustrates the impact of the molar ratio of CH_3OH/H_2O on methanol conversion rate and gas product distribution at a reaction temperature of $200\text{ }^\circ\text{C}$. As shown in the figure, decreasing the CH_3OH/H_2O ratio significantly improves the conversion rate of methanol and inhibits the formation of CO, resulting in an increased H_2 molar fraction. It also decreases the minimum pressure required to maintain the reactants in the liquid phase.

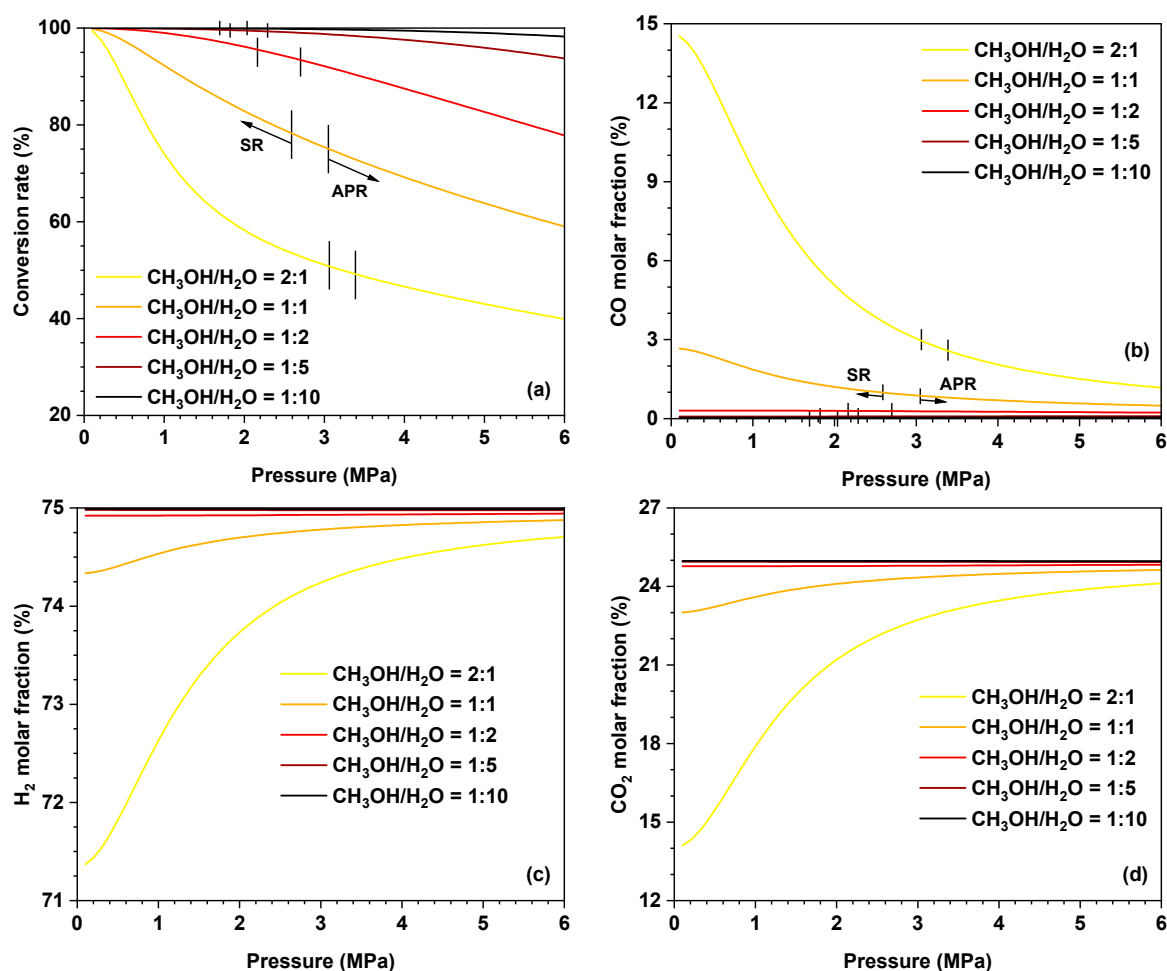


Figure 5. Methanol conversion rate and gas product distribution in methanol reforming as a function of CH_3OH/H_2O ratio and pressure: (a) methanol conversion rate; (b) CO molar fraction; (c) H_2 molar fraction; and (d) CO_2 molar fraction.

When the $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ ratio is kept at 1:1, the pressure must exceed 3.05 MPa to maintain the reactants in the liquid phase, resulting in a maximum methanol conversion rate of 75.06% and a CO molar fraction between 0.49% and 0.87%. As the $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ ratio decreases to 1:10, the BPP drops to 2.04 MPa, and the maximum methanol conversion rate increases to 99.90% with a CO molar fraction between 0.04% and 0.05%. For a typical methanol reforming reaction at 4 MPa, the methanol conversion rate significantly increases from 46.59% to 99.47%, and the CO molar fraction sharply decreases from 2.05% to 0.04% as the $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ ratio decreases from 2:1 to 1:10. From the results, it is clear that decreasing $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ ratio is an effective way to improve methanol conversion rate and inhibit CO generation [49].

However, it must be pointed out that introducing more water will increase the sensible heat carried by unreacted water, which places higher demands on sensible heat recovery and may lead to increased energy losses. Considering the stoichiometric ratio of reactants in the methanol reforming reaction, an optimal $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ ratio between 1:1 and 1:2 appears most suitable.

3.1.4. Comparison of Thermodynamic Performance of Methanol APR and SR

As previously mentioned, the enthalpy of the WGS and reforming reactions is significantly higher when the reactants are in the liquid phase compared to the gas phase. However, in gas phase WGS and SR, methanol and water must be vaporized initially, necessitating the inclusion of their respective heat of evaporation in the comprehensive energy balance calculation. As shown in Figure 6, the enthalpy of the WGS reaction in SR is 7.13 kJ/mol, including the heat of evaporation of the reactants. This value is notably similar to the calculated reaction enthalpy of WGS in APR (6.51 kJ/mol). Figure 7 depicts a comparative analysis of the reaction enthalpy of methanol APR (4 MPa, 200 °C) and SR (1 atm, 200 °C). It reveals that the sum of the heat of evaporation of the reactants and the reaction enthalpy of methanol SR (117.92 kJ/mol) is also close to the reaction enthalpy of APR (118.57 kJ/mol). It is well known that enthalpy, being a state function, is solely contingent upon the current state of the system rather than the specific pathway pursued to attain that state [50]. Therefore, the energy requirements for methanol APR and SR are nearly identical, with minor variations due to different pressures. However, from a full-process perspective, APR is more energy-efficient than SR, as it avoids energy losses from reactant evaporation and gas compression (from atmospheric to reaction pressure) for purification [51,52].

According to the calculated Gibbs free energy of reactions, methanol APR requires a threshold temperature to proceed spontaneously and is not spontaneous at lower temperatures. SR is expected to be more efficient than APR at the same temperature due to a more negative Gibbs free energy.

The difference in the phase states of the reactants imposes distinct demands on the heat and mass transfer process. In SR, the reactants exist entirely in the gas phase, and both the cracking and WGS reactions proceed as two-phase processes between gaseous reactants and a solid catalyst. In contrast, in APR, the WGS reaction becomes a more intricate three-phase process involving liquid water, gaseous CO, and a solid catalyst. Although the cracking reaction in APR also remains a two-phase reaction, it occurs between liquid reactants and a solid catalyst. As a result, APR requires higher heat and mass transfer efficiency compared to SR [48].

Simulations based on the Gibbs energy minimization method show that APR typically has a lower CO molar fraction in gas products and a lower methanol single-pass conversion rate compared to SR. Thus, effective recovery of sensible heat from unreacted reactants is essential for methanol APR to enhance the overall energy efficiency.

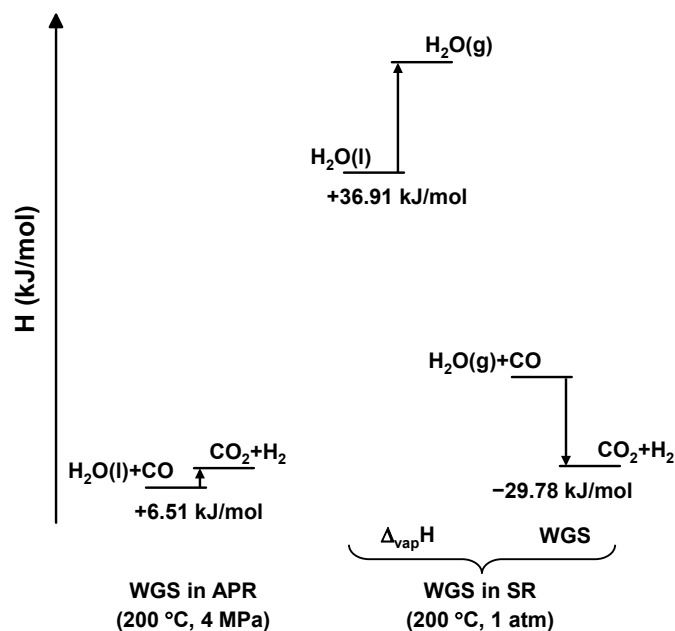


Figure 6. Reaction enthalpy of the WGS in methanol APR (4 MPa, 200 °C) and SR (1 atm, 200 °C).

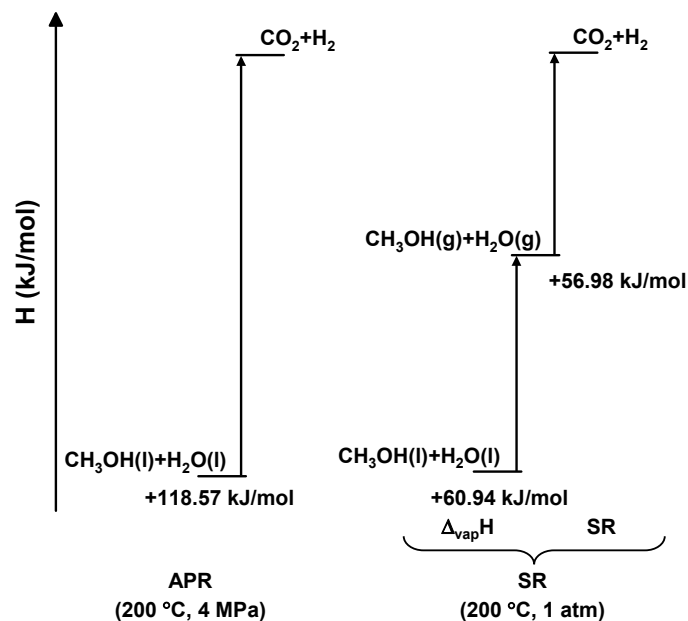


Figure 7. Reaction enthalpy of methanol APR (4 MPa, 200 °C) and SR (1 atm, 200 °C).

3.2. Techno-Economic Analysis

3.2.1. Material and Energy Balance Results

The mass balance calculation results for the methanol SR and APR processes are presented in Tables 2 and 3, respectively. For a system with a pure hydrogen production rate of 50 kg/h, the methanol consumption in the SR process is 358.36 kg/h, while the APR process consumes only 343.18 kg/h. This is consistent with the thermodynamic analysis presented in the previous sections, which indicates a higher hydrogen yield in the APR product. Table 4 outlines the primary energy inflows and outflows for both the SR and APR processes. It is apparent that the SR process requires higher electricity and cooling water consumption due to the need for compressing and cooling the gaseous products. This indicates that the APR option offers a slight advantage in terms of energy efficiency.

Table 2. Mass balance for methanol SR.

Stream Number	Temperature (°C)	Pressure (MPa)	Mass Flow (kg/h)				
			CH ₃ OH	H ₂ O	H ₂	CO	CO ₂
1	25	0.1	358.36	201.48	0	0	0
2	75.83	0.1	358.36	201.48	0	0	0
3	300	0.1	0.01	45.89	62.5	71.35	380.09
4	55	0.1	0.01	45.89	62.5	71.35	380.09
5	40	–	0	44.13	0	0	0
6	40	4	0.01	1.76	62.5	71.35	380.09
7	40	4	0	0	50	0	0
8	40	4	0.01	1.76	12.5	71.35	380.09

Table 3. Mass balance for methanol APR.

Stream Number	Temperature (°C)	Pressure (MPa)	Mass Flow (kg/h)				
			CH ₃ OH	H ₂ O	H ₂	CO	CO ₂
1	25	0.1	343.18	183.89	0	0	0
2	170	4	483.12	271.63	0	0	0.32
3	200	4	148.83	88.87	62.51	8.07	446.76
4	97.19	4	148.83	88.87	62.51	8.07	446.76
5	40	4	148.83	88.87	62.51	8.07	446.76
6	40	4	8.29	1.05	62.5	8.07	443.05
7	40	4	140.54	87.82	0.01	0	3.71
8	40	4	0	0	50	0	0
9	40	4	8.29	1.05	12.5	8.07	443.05
10	39.78	0.1	0.6	0.08	0.01	0	3.39
11	39.78	0.1	139.94	87.74	0	0	0.32

Table 4. Power entering and leaving the methanol SR and APR systems.

Power (kW)	SR	APR
Reactor	459.79	455.57
Pump	–	3.8
Compressor	183.46	–
Cooler	–220.8	–61.82

3.2.2. Economic Analysis Results

The estimated investment and operating costs for methanol SR and APR are presented in Table 5. It is assumed that both processes operate for 8000 h annually. The C_{BM} were derived using the CAPCOST software. The operating costs are classified into fixed and variable operating costs, and are estimated using a similar method described in the reference literature [46,47].

Table 6 presents the total annual costs for both processes, assuming the total capital costs are annualized at a 7% real rate over the 20-year project lifetime. For both the SR and APR processes, the variable operating cost accounts for the largest proportion of the total annual cost, approximately 50% in each case. For the APR process, both fixed operating costs and annual capital charges are higher than those of the SR process, owing to the greater FCI required for APR. However, due to the higher methanol feedstock and electricity consumption associated with the SR process, the APR process results in a lower total annual cost compared to the SR process.

Table 5. Summary of investment and operating cost calculations for methanol SR and APR.

	SR	APR
Capital Cost (kUSD)		
C_{BM}^0 (bare module cost for base case conditions)	1086.18	1037.88
C_{BM} (bare module cost)	3127.92	3420.39
Auxiliary facilities	543.09	518.94
Contingency and fee	563.03	615.67
FCI(fixed capital investment)	4234.04	4555
Fixed operating costs (kUSD/year)		
Operating labor	150	150
Supervisory	27	27
Maintenance and repairs	254.04	273.3
Local taxes and insurance	135.49	145.76
Plant overhead costs	258.63	270.18
Total	825.16	866.24
Variable operating costs (kUSD/year)		
Methanol	1146.75	1098.18
Deionized water	1.61	1.47
Electricity	113.75	2.36
Cooling water	2.18	0.61
Fuel	79.45	78.72
Catalyst	20	40
Total	1363.75	1221.34
Total operating cost	2188.9	2087.58

Table 6. Summary of annual costs for methanol SR and APR.

	SR		APR	
	Annual Cost (kUSD)	Percentage	Annual Cost (kUSD)	Percentage
Variable operating cost	1363.75	52.68%	1221.34	48.51%
Fixed operating cost	825.16	31.88%	866.24	34.41%
Annual capital charge	399.66	15.44%	429.96	17.08%
Rest of investment cost	104.41	4.03%	107.10	4.25%
Bare module cost	295.25	11.41%	322.86	12.82%
Total annual cost	2588.57	100%	2517.54	100%

A discounted cash flow analysis was conducted to determine the minimum selling price of the pure hydrogen product. Several assumptions were incorporated into the analysis: (1) the construction and operational periods were set at 1 and 19 years, respectively; (2) the required rate of return for the project was 10%; (3) the straight-line depreciation method was applied, with a depreciation period of 10 years and a negligible salvage value; (4) the plant was assumed to operate for 8000 h annually; (5) initial investments included the cost of land, which accounted for 6% of FCI, and working capital, equivalent to 1 month of operating expenses; and (6) the tax rate was set at 30% [46,47].

The discounted cash flow analysis indicates that hydrogen produced via the SR and APR processes must be priced at a minimum of 7.20 and 7.07 USD/kg, respectively, to meet all financial requirements. This suggests that the processes become profitable once the hydrogen selling price surpasses these break-even thresholds. Consequently, the analysis concludes that the APR process is more cost-competitive than the SR process.

Figure 8 depicts the cumulative non-discounted and discounted cash flows for the methanol SR and APR processes. It is assumed that any necessary land acquisitions are made at time zero, which corresponds to the initiation of the project and the commencement of plant construction. During the 1-year construction phase, substantial capital expenditures

are incurred, representing FCI in the procurement and installation of equipment and auxiliary facilities essential for plant operation. In this work, the FCI is allocated in two phases: 50% of the total investment is made at time zero, while the remaining 50% is allocated near the time of the plant's start-up. The plant is completed and begins operation at the end of the first year. At this time, an additional investment in working capital is necessary to support the first month's operation. This one-time cost is incurred at start-up and will be fully recouped by the project's conclusion.

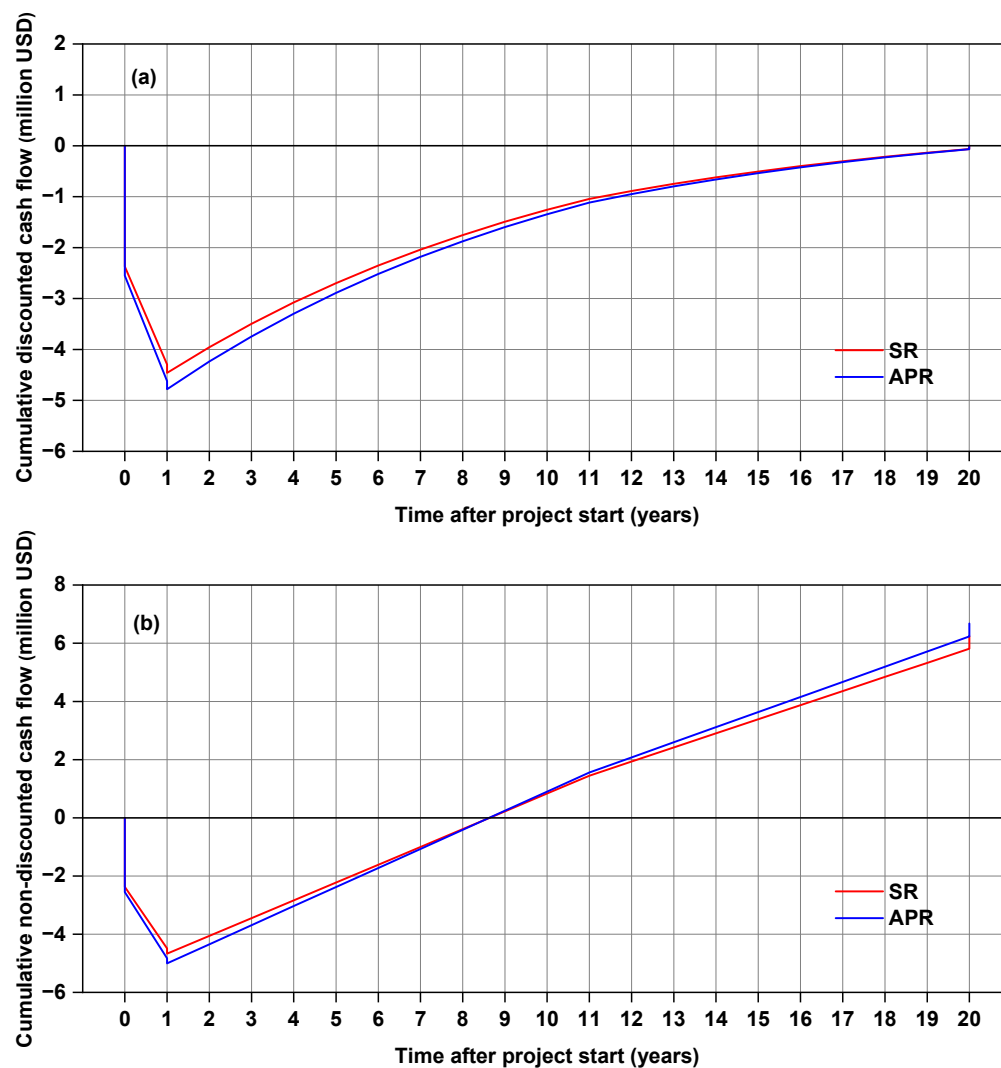


Figure 8. Cumulative cash flow diagrams for the methanol SR and APR processes: (a) cumulative discounted cash flow and (b) cumulative non-discounted cash flow.

Upon start-up, the process initiates hydrogen production for sale, leading to positive annual cash flows. This is evidenced by the upward slope of the cumulative cash flow diagram. It can be observed that the cash flows during the initial ten years following start-up are higher than those in the subsequent years. This is mainly attributed to the impact of depreciation allowances, which are no longer factored into financial calculations once the depreciation period has concluded. Initially, the SR process exhibits a higher non-discounted cash flow compared to the APR process due to its lower initial FCI. However, the APR process ultimately achieves a higher final cumulative cash position with the same rate of return.

The payback period is the duration needed after the plant's start-up to recover the FCI, excluding land cost and working capital. A shorter payback period indi-

cates a more profitable project. The calculation results show that the simple (non-discounted) payback period (SPB) and discounted payback period (DPBP) for the SR process are 6.92 and 14.81 years, respectively. For the APR process, the SPB and DPBP are 6.94 and 14.94 years, respectively.

Therefore, it can be concluded that, at hydrogen prices of 7.20 and 7.07 USD/kg for the SR and APR processes, respectively, the payback periods of the two processes are almost identical. It follows that if the hydrogen product selling price for the APR process is increased to match that of the SR process, the APR process would result in a shorter payback period compared to the SR process.

Considering that fluctuations in key parameters within the economic analysis may influence the project's profitability, the effects of uncertainty ($\pm 50\%$) in parameters such as FCI, methanol purchase price, and rate of return on the minimum hydrogen selling price were evaluated relative to the base scenario. The results are presented in Figure 9. A $\pm 50\%$ change in FCI and methanol purchase price leads to a variation in the minimum hydrogen selling price of ± 1.69 and ± 1.45 USD/kg for methanol SR and ± 1.81 and ± 1.40 USD/kg for APR. An increase in FCI diminishes the profitability advantage of the APR process relative to SR, while an increase in methanol purchase price enhances the profitability advantage of APR. With a $\pm 50\%$ change in the rate of return, the minimum hydrogen selling price varies from -0.66 to $+0.78$ USD/kg for the SR process, and from -0.70 to $+0.83$ USD/kg for the APR process. This indicates that FCI and methanol purchase price have a significantly stronger impact on the project's profitability compared to the rate of return.

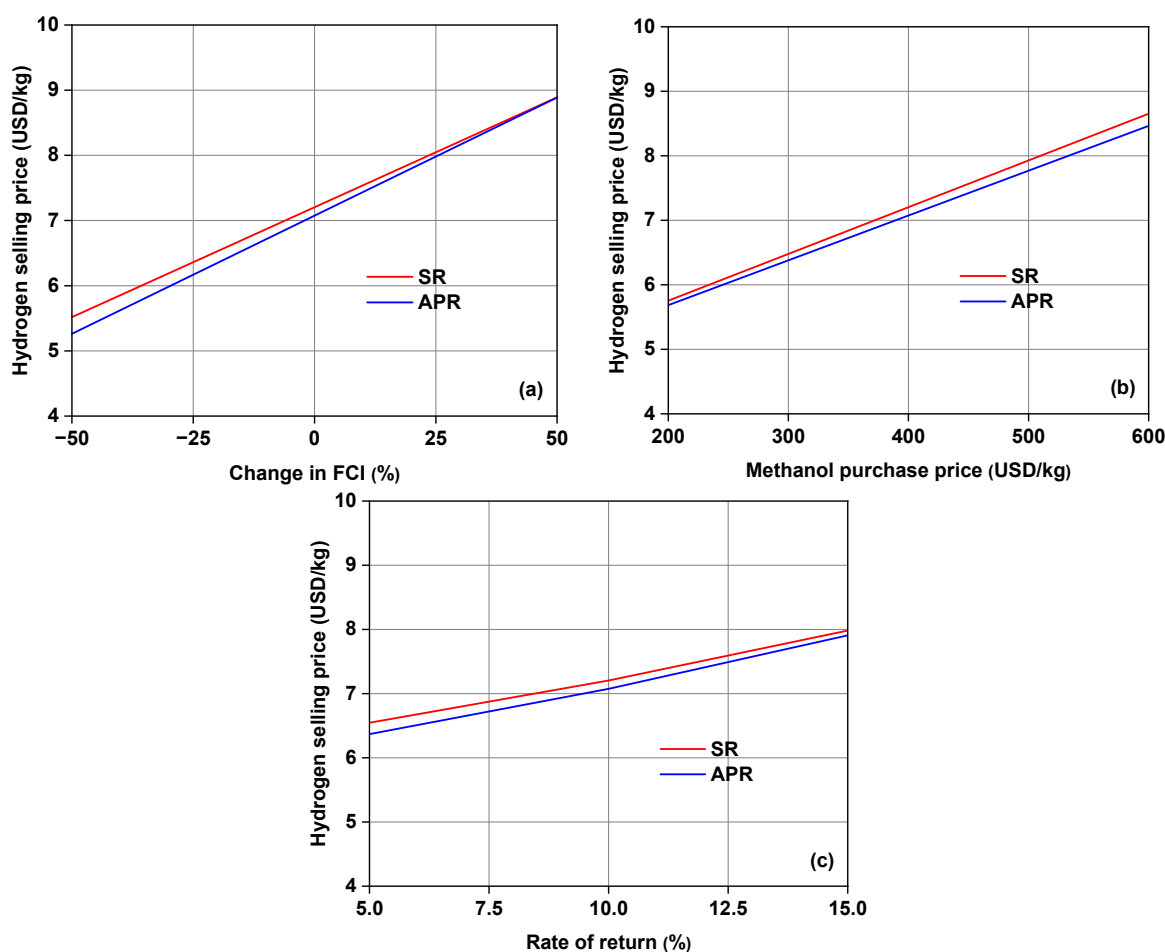


Figure 9. Sensitivity curves for the key economic parameters: (a) change in FCI; (b) methanol purchase; and (c) rate of return.

Based on the previous discussion, it can be concluded that the APR process exhibits a higher FCI, fixed operating costs, and annual capital charges compared to SR. However, it requires less reactant input, power, and cooling water, resulting in lower variable operating costs and a reduced minimum hydrogen selling price. Therefore, the APR process emerges as a more favorable option compared to the SR process.

4. Conclusions

This study provides a comprehensive evaluation and comparison of the thermodynamic and techno-economic performance of hydrogen production via methanol APR and SR. The enthalpy and Gibbs free energy of reaction, as well as chemical and phase equilibrium based on the Gibbs free energy minimization method, were analyzed using Aspen Plus software. The findings reveal that, when accounting for the heat of evaporation of the reactants, the energy demands of both APR and SR are remarkably similar. However, the APR process demonstrates superior overall energy efficiency by avoiding the energy losses associated with evaporation and compression (from atmospheric to reaction pressure). A specific threshold temperature is required for APR to proceed spontaneously, while SR is expected to be more thermodynamically efficient than APR at the same temperature owing to a more negative Gibbs free energy. While APR typically operates at higher pressures and lower temperatures compared to SR, leading to a higher molar fraction of H₂ and a lower molar fraction of CO in gas products, this also results in a reduced single-pass conversion rate of methanol. A techno-economic comparison of APR and SR processes was conducted for a distributed hydrogen production system with a pure hydrogen output capacity of 50 kg/h. The results show that the APR process incurs higher fixed operating costs and annual capital charges compared to the SR process, owing to the greater FCI required. However, APR benefits from lower reactant consumption, reduced power demand, and lower cooling water usage, leading to reduced variable operating costs. This, in turn, results in a lower total annual cost compared to SR. The minimum hydrogen selling price for APR, calculated using the discounted cash flow method with a NPV of zero, was found to be 7.07 USD/kg, which is more competitive than SR's minimum price of 7.20 USD/kg. These findings suggest that the APR process is a more economically viable alternative compared to SR.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/en18010081/s1>, Table S1: Summary of the costs of raw materials and utilities; Table S2: Calculated bubble and dew point data for methanol–water mixture. References [53,54] are cited in the supplementary materials.

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References

1. Faye, O.; Szpunar, J.; Eduok, U. A critical review on the current technologies for the generation, storage, and transportation of hydrogen. *Int. J. Hydrogen Energy* **2022**, *47*, 13771–13802. [\[CrossRef\]](#)
2. Rasul, M.G.; Hazrat, M.A.; Sattar, M.A.; Jahirul, M.I.; Shearer, M.J. The future of hydrogen: Challenges on production, storage and applications. *Energy Convers. Manag.* **2022**, *272*, 116326. [\[CrossRef\]](#)
3. Zhao, J.; Shi, R.; Li, Z.; Zhou, C.; Zhang, T. How to make use of methanol in green catalytic hydrogen production? *Nano Sel.* **2020**, *1*, 12–29. [\[CrossRef\]](#)
4. Garcia, G.; Arriola, E.; Chen, W.H.; De Luna, M.D. A comprehensive review of hydrogen production from methanol thermochemical conversion for sustainability. *Energy* **2021**, *217*, 119384. [\[CrossRef\]](#)
5. Deka, T.J.; Osman, A.I.; Baruah, D.C.; Rooney, D.W. Methanol fuel production, utilization, and techno-economy: A review. *Environ. Chem. Lett.* **2022**, *20*, 3525–3554. [\[CrossRef\]](#)
6. Joshi, A.N.; Vaidya, P.D. Recent studies on aqueous-phase reforming: Catalysts, reactors, hybrid processes and techno-economic analysis. *Int. J. Hydrogen Energy* **2024**, *49*, 117–137. [\[CrossRef\]](#)
7. Cortright, R.D.; Davda, R.R.; Dumesic, J.A. Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water. *Nature* **2002**, *418*, 964–967. [\[CrossRef\]](#) [\[PubMed\]](#)
8. Roy, B.; Sullivan, H.; Leclerc, C.A. Effect of variable conditions on steam reforming and aqueous phase reforming of n-butanol over Ni/CeO₂ and Ni/Al₂O₃ catalysts. *J. Power Sources* **2014**, *267*, 280–287. [\[CrossRef\]](#)
9. Cheng, X.; Shi, Z.; Glass, N.; Zhang, L.; Zhang, J.; Song, D.; Liu, Z.; Wang, H.; Shen, J. A review of PEM hydrogen fuel cell contamination: Impacts, mechanisms, and mitigation. *J. Power Sources* **2007**, *165*, 739–756. [\[CrossRef\]](#)
10. Valdés-López, V.F.; Mason, T.; Shearing, P.R.; Brett, D.J.L. Carbon monoxide poisoning and mitigation strategies for polymer electrolyte membrane fuel cells: A review. *Prog. Energy Combust. Sci.* **2020**, *79*, 100842. [\[CrossRef\]](#)
11. Alamiery, A. Advancements in materials for hydrogen production: A review of cutting-edge technologies. *ChemPhysMater* **2024**, *3*, 64–73. [\[CrossRef\]](#)
12. Shchegolkov, A.V.; Shchegolkov, A.V.; Zemtsova, N.V.; Stanishvskiy, Y.M.; Vetcher, A.A. Recent advantages on waste management in hydrogen industry. *Polymers* **2022**, *14*, 4992. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Hossain, M.A.; Islam, M.R.; Hossain, M.A.; Hossain, M. Control strategy review for hydrogen-renewable energy power system. *J. Energy Storage* **2023**, *72*, 108170. [\[CrossRef\]](#)
14. Jeje, S.O.; Marazani, T.; Obiko, J.O.; Shongwe, M.B. Advancing the hydrogen production economy: A comprehensive review of technologies, sustainability, and future prospects. *Int. J. Hydrogen Energy* **2024**, *78*, 642–661. [\[CrossRef\]](#)
15. Pipitone, G.; Zoppi, G.; Pirone, R.; Bensaid, S. A critical review on catalyst design for aqueous phase reforming. *Int. J. Hydrogen Energy* **2022**, *47*, 151–180. [\[CrossRef\]](#)
16. Lin, L.; Zhou, W.; Gao, R.; Yao, S.; Zhang, X.; Xu, W.; Zheng, S.; Jiang, Z.; Yu, Q.; Li, Y.W.; et al. Low-temperature hydrogen production from water and methanol using Pt/alpha-MoC catalysts. *Nature* **2017**, *544*, 80–83. [\[CrossRef\]](#)
17. Lin, L.; Yu, Q.; Peng, M.; Li, A.; Yao, S.; Tian, S.; Liu, X.; Li, A.; Jiang, Z.; Gao, R.; et al. Atomically dispersed Ni/α-MoC catalyst for hydrogen production from methanol/water. *J. Am. Chem. Soc.* **2021**, *143*, 309–317. [\[CrossRef\]](#)
18. Li, D.; Li, Y.; Liu, X.; Guo, Y.; Pao, C.W.; Chen, J.L.; Hu, Y.; Wang, Y. NiAl₂O₄ spinel supported Pt catalyst: High performance and origin in aqueous-phase reforming of methanol. *ACS Catal.* **2019**, *9*, 9671–9682. [\[CrossRef\]](#)
19. Zhang, S.; Liu, Y.; Zhang, M.; Ma, Y.; Hu, J.; Qu, Y. Sustainable production of hydrogen with high purity from methanol and water at low temperatures. *Nat. Commun.* **2022**, *13*, 5527. [\[CrossRef\]](#)
20. Lu, M.; Liu, S.; Zhu, H.; Huang, H.; Lin, C.; Li, J.; Zhang, B.; Zheng, Z.; Hu, C.; Wu, X.; et al. Highly efficient releasing of hydrogen from aqueous-phase reforming of methanol over Cu-SP/Al₂O₃-ZnO catalyst by carbon layer encapsulated hierarchical porous microsphere strategy. *Int. J. Hydrogen Energy* **2024**, *52*, 125–139. [\[CrossRef\]](#)
21. Li, J.; Lu, M.; Ge, Y.; Lu, W.; Liu, Z.; Xu, H.; Zhang, Y.; Li, Z.; Zheng, Z.; Gao, P.; et al. Efficient and sustainable H₂ production from aqueous-phase reforming of methanol over Cu@CA-Val catalyst at low temperatures. *Int. J. Hydrogen Energy* **2024**, *71*, 775–784. [\[CrossRef\]](#)
22. Chen, B.; Zheng, Z.; Hu, C.; Zengcai, Z.; Liu, Z.; Lu, M.; Meng, Q.; Wang, T. High-content graphitized N-doped carbon encapsulated Cu catalyst in aqueous phase reforming of methanol for efficient hydrogen production. *Fuel* **2024**, *371*, 131888. [\[CrossRef\]](#)
23. Zheng, Z.; Fang, Y.; Ma, L.; Wu, X.; Meng, Q.; Wang, T. High-loaded sub-6 nm Cu catalyst with superior hydrothermal-stability and efficiency for aqueous phase reforming of methanol to hydrogen. *Int. J. Hydrogen Energy* **2022**, *47*, 22752–22762. [\[CrossRef\]](#)
24. Pi, Y.; Wu, X.; Zheng, Z.; Ma, L.; Wang, T. Chitosan-lignin carbon framework-encapsulated Cu catalyst facilitates base-free hydrogen evolution from methanol/water. *Catal. Sci. Technol.* **2022**, *12*, 1941–1949. [\[CrossRef\]](#)
25. Xie, J.; Su, D.; Yin, X.; Wu, C.; Zhu, J. Thermodynamic analysis of aqueous phase reforming of three model compounds in bio-oil for hydrogen production. *Int. J. Hydrogen Energy* **2011**, *36*, 15561–15572. [\[CrossRef\]](#)

26. Seretis, A.; Tsiakaras, P. A thermodynamic analysis of hydrogen production via aqueous phase reforming of glycerol. *Fuel Process. Technol.* **2015**, *134*, 107–115. [\[CrossRef\]](#)
27. Özcan, O.; Akın, A.N. Thermodynamic analysis of methanol steam reforming to produce hydrogen for HT-PEMFC: An optimization study. *Int. J. Hydrogen Energy* **2019**, *44*, 14117–14126. [\[CrossRef\]](#)
28. Kuo, J.K.; Wei, H.C. Numerical investigation into hydrogen content of reformat gas produced by methanol-water fuel mixtures in reforming. *Int. J. Energy Res.* **2019**, *43*, 4417–4426. [\[CrossRef\]](#)
29. Palo, D.R.; Dagle, R.A.; Holladay, J.D. Methanol steam reforming for hydrogen production. *Chem. Rev.* **2007**, *107*, 3992–4021. [\[CrossRef\]](#) [\[PubMed\]](#)
30. Fajín, J.L.C.; Cordeiro, M.N.D.S. Insights into the mechanism of methanol steam reforming for hydrogen production over Ni-Cu-based catalysts. *ACS Catal.* **2022**, *12*, 512–526. [\[CrossRef\]](#)
31. Kappis, K.; Papavasiliou, J.; Avgouropoulos, G. Methanol reforming processes for fuel cell applications. *Energies* **2021**, *14*, 8442. [\[CrossRef\]](#)
32. Xing, S.; Zhao, C.; Ban, S.; Liu, Y.; Wang, H. Thermodynamic performance analysis of the influence of multi-factor coupling on the methanol steam reforming reaction. *Int. J. Hydrogen Energy* **2020**, *45*, 7015–7024. [\[CrossRef\]](#)
33. Wu, Z.; Xu, G.; Zhang, W.; Xue, X.; Chen, H. Thermodynamic and economic analysis of a new methanol steam reforming system integrated with CO₂ heat pump and cryogenic separation system. *Energy* **2023**, *283*, 128501. [\[CrossRef\]](#)
34. Peppley, B.A.; Amphlett, J.C.; Kearns, L.M.; Mann, R.F. Methanol-steam reforming on Cu/ZnO/Al₂O₃. Part 1: The reaction network. *Appl. Catal. A Gen.* **1999**, *179*, 21–29. [\[CrossRef\]](#)
35. Li, D.; Xu, F.; Tang, X.; Dai, S.; Pu, T.; Liu, X.; Tian, P.; Xuan, F.; Xu, Z.; Wachs, I.E.; et al. Induced activation of the commercial Cu/ZnO/Al₂O₃ catalyst for the steam reforming of methanol. *Nat. Catal.* **2022**, *5*, 99–108. [\[CrossRef\]](#)
36. Faungnawakij, K.; Kikuchi, R.; Eguchi, K. Thermodynamic evaluation of methanol steam reforming for hydrogen production. *J. Power Sources* **2006**, *161*, 87–94. [\[CrossRef\]](#)
37. Yang, W.; Ma, X.; Tang, X.; Dou, P.; Yang, Y.; He, Y. Review on developments of catalytic system for methanol steam reforming from the perspective of energy-mass conversion. *Fuel* **2023**, *345*, 128234. [\[CrossRef\]](#)
38. Latsky, C.; Cordeiro, B.; Schwarz, C.E. High pressure bubble- and dew-point data for systems containing CO₂ with 1-decanol and n-hexadecane. *Fluid Phase Equilibria* **2020**, *521*, 112702. [\[CrossRef\]](#)
39. Latsky, C.; Schwarz, C.E. Measurement and modelling of high pressure bubble- and dew-point data for the CO₂ + 1-decanol + 3,7-dimethyl-1-octanol system. *Fluid Phase Equilibria* **2019**, *488*, 87–98. [\[CrossRef\]](#)
40. Mosayebi, A.; Eghbal Ahmadi, M.H. Combined steam and dry reforming of methanol process to syngas formation: Kinetic modeling and thermodynamic equilibrium analysis. *Energy* **2022**, *261*, 125254. [\[CrossRef\]](#)
41. Byun, M.; Lee, B.; Lee, H.; Jung, S.; Ji, H.; Lim, H. Techno-economic and environmental assessment of methanol steam reforming for H₂ production at various scales. *Int. J. Hydrogen Energy* **2020**, *45*, 24146–24158. [\[CrossRef\]](#)
42. Khodabandehloo, M.; Larimi, A.; Khorasheh, F. Comparative process modeling and techno-economic evaluation of renewable hydrogen production by glycerol reforming in aqueous and gaseous phases. *Energy Convers. Manag.* **2020**, *225*, 113483. [\[CrossRef\]](#)
43. Sladkovskiy, D.A.; Godina, L.I.; Semikin, K.V.; Sladkovskaya, E.V.; Smirnova, D.A.; Murzin, D.Y. Process design and techno-economical analysis of hydrogen production by aqueous phase reforming of sorbitol. *Chem. Eng. Res. Des.* **2018**, *134*, 104–116. [\[CrossRef\]](#)
44. Murzin, D.Y.; Garcia, S.; Russo, V.; Kilpio, T.; Godina, L.I.; Tokarev, A.V.; Kirilin, A.V.; Simakova, I.L.; Poulston, S.; Sladkovskiy, D.A. Kinetics, modeling, and process design of hydrogen production by aqueous phase reforming of xylitol. *Ind. Eng. Chem. Res.* **2017**, *56*, 13240–13253. [\[CrossRef\]](#)
45. Lee, J.K.; Lee, I.B.; Han, J. Techno-economic analysis of methanol production from joint feedstock of coke oven gas and basic oxygen furnace gas from steel-making. *J. Ind. Eng. Chem.* **2019**, *75*, 77–85. [\[CrossRef\]](#)
46. Turton, R.; Bailie, R.C.; Whiting, W.B.; Shaeiwitz, J.A. *Analysis, Synthesis and Design of Chemical Processes*; Pearson Education: London, UK, 2008.
47. Galera, S.; Ortiz, F.G. Techno-economic assessment of hydrogen and power production from supercritical water reforming of glycerol. *Fuel* **2015**, *144*, 307–316. [\[CrossRef\]](#)
48. Ripken, R.M.; Meuldijk, J.; Gardeniers, J.G.E.; Le Gac, S. Influence of the water phase state on the thermodynamics of aqueous-phase reforming for hydrogen production. *ChemSusChem* **2017**, *10*, 4909–4913.
49. Thattarathody, R.; Artoul, M.; Digilov, R.M.; Sheintuch, M. Pressure, diffusion, and S/M ratio effects in methanol steam reforming kinetics. *Ind. Eng. Chem. Res.* **2018**, *57*, 3175–3186. [\[CrossRef\]](#)
50. Nilsson, T.; Niedderer, H. Undergraduate students' conceptions of enthalpy, enthalpy change and related concepts. *Chem. Educ. Res. Pract.* **2014**, *15*, 336–353. [\[CrossRef\]](#)
51. Dilmac, O.F.; Ozkan, S.K. Energy and exergy analyses of a steam reforming process for hydrogen production. *Int. J. Exergy* **2008**, *5*, 241. [\[CrossRef\]](#)

52. Luberti, M.; Ahn, H. Review of Polybed pressure swing adsorption for hydrogen purification. *Int. J. Hydrogen Energy* **2022**, *47*, 10911–10933. [[CrossRef](#)]
53. Slavin, B.; Wang, R.; Roy, D.; Ling-Chin, J.; Roskilly, A.P. Techno-economic analysis of direct air carbon capture and hydrogen production integrated with a small modular reactor. *Appl. Energy* **2024**, *356*, 122407. [[CrossRef](#)]
54. Dickson, R.; Fasahati, P.; Liu, J. Optimal design for integrated macroalgae-based biorefinery via mixed alcohol synthesis. *Comput. Aided Chem. Eng.* **2019**, *46*, 253–258.

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