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Research Article

Process Optimization of Hydrogen Production via the Water–Gas Shift Reaction Using CO Recycle and Exothermic Reactor Operation

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Abstract

Hydrogen production via the Water–Gas Shift Reaction (WGSR) is limited by thermodynamic equilibrium, restricting carbon monoxide (CO) conversion and process efficiency. The baseline process achieved 80.07% CO conversion, while the modified design incorporated CO recycle and controlled exothermic operation at 200 °C. These changes significantly improved CO conversion to approximately 98%, reducing raw material losses and enhancing hydrogen yield. The results demonstrate that integrating recycle streams and thermal management strategies effectively overcomes equilibrium constraints for sustainable hydrogen production.

Keywords: Hydrogen; Water–Gas Shift Reaction; equilibrium reactor; CO conversion; recycle; process simulation

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1. Introduction

The escalating global demand for energy, coupled with the urgent need to mitigate the impacts of climate change, has intensified the transition toward clean and sustainable energy sources [1]. Within this transition, hydrogen (H_2) has emerged as a pivotal energy carrier due to its versatility and critical role not only in the energy and transportation sectors but also in industrial applications, such as hydro-treating in petroleum refineries [2,3]. As the lightest and simplest element, hydrogen exists as a colorless and highly flammable gas, positioning it as an ideal candidate for future clean energy systems [4]. On a commercial scale, large-scale hydrogen production is predominantly achieved through steam reforming, followed by the Water-Gas Shift Reaction (WGSR) ($CO + H_2 \Leftrightarrow CO_2 + H_2$), which constitutes a key step in maximizing hydrogen yield [5].

To enhance the efficiency of largescale hydrogen production, process simulation has become an indispensable tool, with software such as Aspen HYSYS widely employed to model and optimize system performance. The process flow scheme of the Water–Gas Shift Reaction (WGSR), comprising unit operations including mixers, reactors, heat exchangers, and separators, has been reported to yield hydrogen of 100% purity with a carbon monoxide conversion of 80.07% [6]. However, reliance on equilibrium assumptions neglects the limitations of reaction kinetics and industrial reactor design parameters, leading to discrepancies between simulation results and actual plant performance [7]. These limitations underscore the need for more realistic modeling approaches that incorporate reaction rates, recycle strategies, and thermal effects [8].

In this study, the equilibrium reactor approach is retained but modified by introducing a carbon monoxide (CO) recycle stream. This modification reflects practical conditions in which CO is present in excess relative to steam, while the WGSR is inherently exothermic [9]. Lowering the

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reactor temperature in combination with recycle implementation is expected to enhance overall efficiency, even though single-pass conversion remains limited [10]. This approach highlights both the research gap and the novelty of the work, as previous studies have largely focused on equilibrium assumptions without considering more realistic operational conditions. Accordingly, the present study offers a systematic comparative framework to evaluate the performance of equilibrium reactors with recycle. The modification demonstrates a significant improvement, achieving a CO conversion of 98.40% compared to the previously reported 80.07% [6]. These findings emphasize the importance of developing processes that more closely reflect industrial reality.

The objective of this study is to conduct a quantitative evaluation of carbon monoxide (CO) conversion before and after process modification. All simulations were performed using Aspen HYSYS V11 with the Peng–Robinson Stryjek–Vera (PRSV) property package to ensure rigorous thermodynamic representation of the system. Overall, the study aims to identify the most accurate and energy-efficient modelling approach for hydrogen production via the Water–Gas Shift Reaction (WGSR).

2. Methods

2.1 Process Simulators Using Aspen HYSYS

Chemical Engineering (ChE) education and practice continue to evolve in response to increasingly complex industrial challenges, necessitating the integration of advanced computational methodologies. The adoption of process simulation software has exerted a profound influence on chemical engineering curricula and industrial workflows, establishing simulation as a critical instrument for the design, optimization, and operation of chemical plants [11]. Among the most widely utilized commercial simulators is Aspen HYSYS, which has become a cornerstone in process systems engineering by providing robust capabilities for steady state and dynamic modeling, rigorous thermodynamic property estimation, and optimization of highly integrated industrial processes. Its applications span diverse sectors, including power generation, petrochemicals, renewable fuels, and waste-heat recovery, with particular emphasis on the accurate resolution of mass and energy balances. Validated case studies have demonstrated that HYSYS enables engineers to quantitatively assess thermal efficiency, optimize mass flow distribution, and reduce environmental impacts [12].

Process simulators function as advanced computational platforms that automate complex engineering calculations. Their core functionalities encompass mass and energy balance computations, estimation of thermophysical properties for pure substances and multicomponent mixtures, and implementation of mathematical models for a wide range of unit operations and reactor configurations. Furthermore, these simulators support process design, techno-economic evaluation, and optimization by employing numerical algorithms to solve large systems of nonlinear algebraic and differential equations [13].

In the present study, Aspen HYSYS V11 is employed to simulate hydrogen production via the Water–Gas Shift Reaction (WGSR). The software's interactive process flow diagram environment is utilized to construct and navigate large-scale simulations, enabling systematic evaluation of process performance under varying reactor modeling assumptions [6].

2.2 Property Package

Aspen HYSYS is equipped with a wide range of thermodynamic equations of state, enabling rigorous analysis of phase equilibria and enthalpy behavior in multicomponent mixtures. The appropriate selection of a property package is essential to ensure accurate representation of thermodynamic conditions and reliable simulation outcomes. In the present hydrogen production study, the Peng–Robinson Stryjek–Vera (PRSV) property package is employed, as it provides enhanced accuracy in predicting vapor–liquid equilibrium and enthalpic properties for systems involving light gases and hydrocarbons.

2.3 Water Gas Shift Reactions (WGSR)

Hydrogen production in petrochemical and energy industries frequently incorporates the Water–Gas Shift Reaction (WGSR), which remains one of the most established processes for enhancing hydrogen yield [6]. The WGSR is typically integrated into steam reforming operations and serves as a critical step for adjusting the relative concentrations of hydrogen and carbon monoxide in synthesis gas streams. In this reaction, steam reacts with carbon monoxide to produce hydrogen and carbon dioxide, thereby facilitating downstream CO_2 separation and enabling the recovery of high-purity hydrogen [14]. The overall reaction is expressed as [15]:

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad \Delta H_{298K} = -41.1\ \text{kJ/mol} \quad (1)$$

2.4 Process Stages in Hydrogen Production via Water–Gas Shift Reaction

Reactant Mixing (Mixer): Hydrogen production begins with the mixing of feed streams in a dedicated mixer unit. Carbon monoxide (CO) is introduced at ambient conditions (25 °C, 101.3 kPa), while steam is supplied at its boiling point (100 °C, 101.3 kPa). The mixing process ensures homogeneity of the reactants, producing a combined stream (Reactor In) with a thermodynamically balanced temperature.

Chemical Reaction (Reactor): The mixed stream enters the reactor, where the Water-Gas Shift Reaction occurs: $CO + H_2 \leftrightarrow CO_2 + H_2$. This reaction reduces the carbon monoxide fraction while simultaneously increasing hydrogen yield. The process is exothermic, releasing heat the elevates the temperature of the reactor effluent. The extent of conversion is governed by equilibrium thermodynamics, reactor design, and operating conditions.

Initial Cooling and Condensation (Heat Exchanger 1): The hot effluent is directed to the first heat exchanger (HE-1). This unit facilitates heat removal, lowering the stream temperature and inducing partial condensation of steam. The primary objective is to prepare the stream for efficient phase separation. No material transfer occurs in this step; thus, molar composition and mass flow remain constant, while enthalpy decreases due to heat exchange.

Product Separation (Separator): The cooled and partially condensed stream (Separator In) is introduced into a separation unit. This device divides the mixture into two distinct streams: the top stream (Separator Top), consisting of pure hydrogen (100% mole fraction), and the bottom stream (Separator Bottom), containing non-hydrogen components. The separation efficiency is critical for achieving high-purity hydrogen suitable for downstream applications.

Final Liquefaction (Heat Exchanger 2): The hydrogen vapor obtained from the separator top is subsequently passed through a second heat exchanger (HE-2). The purpose of this stage is to liquefy the hydrogen, enabling its collection as the final product. Cooling reduces the vapor fraction to zero, yielding high-purity liquid hydrogen. This step ensures the hydrogen product is in a storable and transportable form, suitable for industrial utilization.

2.5 Method to Improve Yield and Conversion in Hydrogen Production via Water–Gas Shift Reaction

The application of reactor models in hydrogen production is fundamentally governed by thermodynamic principles and heat transfer phenomena [16]. Advances in reactor design aim to overcome equilibrium limitations by enhancing conversion efficiency, optimizing mass transfer, and mitigating constraints imposed by thermodynamic boundaries [17].

In this study, two modeling approaches were systematically employed for comparative evaluation. First, the reactor was implemented following the methodology reported by Olateju [6], using process data consistent with the referenced study. Second, the simulation was carried out under exothermic operating conditions with the application of a recycle stream. In chemical engineering, the use of recycle streams is a fundamental strategy to enhance process efficiency. Theoretically, recycling allows unreacted species to re-enter the reaction zone, thereby driving the system toward a higher overall conversion, even when the single-pass conversion remains relatively low [18]. However, the simulation results indicated that the application of recycle alone did not yield optimal conversion. Consequently, an additional modification was introduced in the reactor by considering the exothermic nature of the reaction. This step was undertaken to improve the efficiency of hydrogen production. According to Le Chatelier's principle, lowering the temperature in the exothermic water-gas shift reaction shifts the equilibrium toward the products. As a result, the conversion of CO to H_2 and CO_2 is higher at lower temperatures compared to higher temperatures, thereby enhancing the equilibrium conversion of CO [19]. In this simulation, the modification was implemented by reducing the operating temperature from 466 °C to 200 °C.

Based on this approach, the recycle stream in the simulation was focused on carbon monoxide (CO) that remained unconverted after passing through the reactor. The residual CO was separated in the downstream separation unit and returned to the reactor inlet via a controlled recycle loop. This strategy was designed to increase the effective residence time of CO within the reaction system and enhance the likelihood of CO molecules undergoing the water-gas shift reaction in subsequent passes. The recycle rate was regulated with careful consideration of operational stability and the potential accumulation of inert components, necessitating the implementation of a small purge stream. Through this mechanism, the overall CO conversion can be improved beyond the single-pass conversion limit, without increasing fresh feed consumption, thereby significantly enhancing hydrogen production efficiency.

This comparative framework provides the basis for a quantitative assessment of hydrogen production under both simulation conditions,

prior to and following modification. To ensure methodological consistency, all simulations were conducted using Aspen HYSYS V11, with the Peng–Robinson Stryjek–Vera (PRSV) property package selected to guarantee a rigorous and accurate thermodynamic representation of the system.

3. Results and Discussion

3.1 Comparison of the Basic Process and the Modified Process

The hydrogen production process via the Water–Gas Shift Reaction (WGSR) was simulated for both the basic configuration and the modified configuration using Aspen HYSYS with the Peng–Robinson Stryjek–Vera (PRSV) property package. The process flow diagram (PFD) of basic process simulation (unmodified) is presented in Figure 1, while the corresponding process simulation using Aspen HYSYS is shown in Figure 2. In the basic configuration, the system consists solely of a reactant mixing unit, an equilibrium reactor, a cooler, and a separator, without any recycle stream or specific heat management. In contrast, process flow diagram of the modified process is presented in Figure 3, while the process simulation using Aspen HYSYS of the modified process is depicted in Figure 4. In the modified configuration, a recycle stream was introduced for unreacted CO, and the reactor operating conditions were adjusted to achieve a more controlled exothermic state. The key differences between the two process configurations lie in the presence of the recycle stream and the management of reaction heat, both of which aim to enhance CO conversion and improve overall hydrogen production efficiency, as summarized in Table 1.

3.2 Description of the Basic Process (without Modification)

In the base process configuration, hydrogen production begins with the mixing of carbon

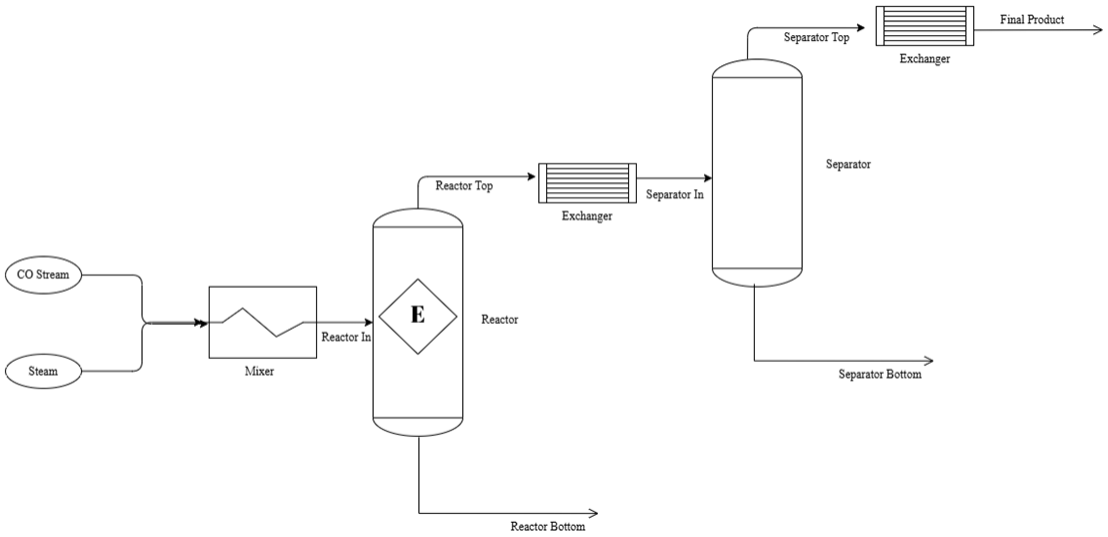

Figure 1. Process flow diagram (PFD) of hydrogen production before modification.

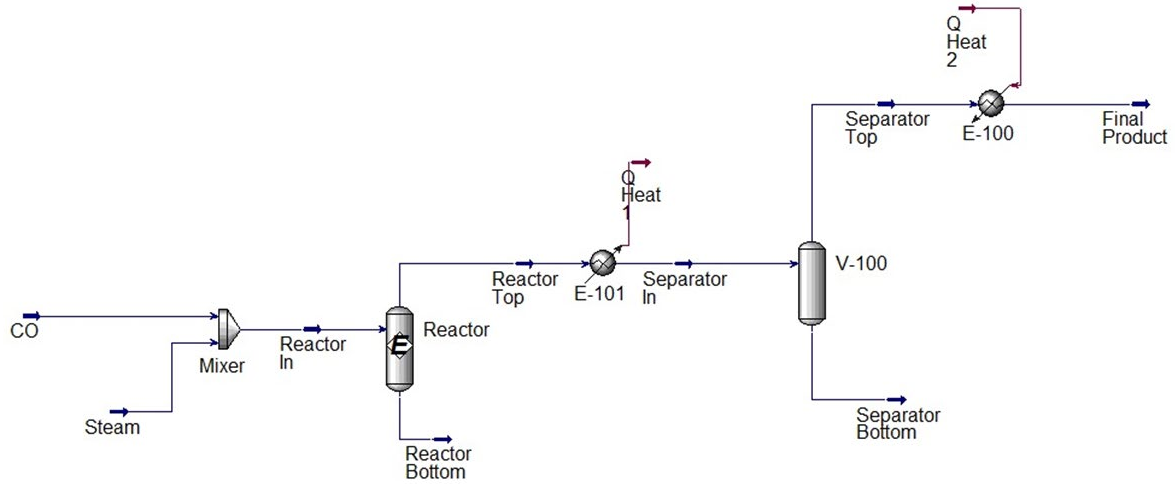

Figure 2. Process simulation (HYSYS) for the production process of hydrogen before modification.

monoxide (CO) and steam (H_2O) in the mixer unit. Carbon monoxide is introduced under ambient conditions, at a temperature of 25 °C and a pressure of 101.3 kPa, while steam is supplied at 100°C under the same pressure. The resulting reactant mixture is then directed into the equilibrium reactor to carry out the Water–Gas Shift Reaction (WGSR).

The main reaction (Equation (1)) is exothermic, resulting in heat release during the process. According to the simulation results, the stream temperature increased from approximately 83.95 °C at the reactor inlet to 466°C at the reactor outlet. This temperature rise indicates that the reaction heat was not actively controlled and entirely contributed to the increase in the outlet stream temperature. Under these conditions, the CO conversion achieved was 80.07%. This conversion value demonstrates that a portion of CO remained unreacted and exited along with the reactor product stream. The reactor effluent was subsequently cooled using a heat exchanger before entering the separation unit. In the separator, hydrogen was separated from other components such as CO_2 and residual CO. However, since unreacted CO still escaped from the reactor, the overall process efficiency remained limited.

3.3 Effect of Process Modification on Conversion Improvement

The process modification was carried out to enhance carbon monoxide (CO) conversion as well as hydrogen production efficiency. The primary

Table 1. Comparison of CO conversion before and after process modification.

Process	CO Conversion (%)
Modified	98.40%
Unmodified	80.07%

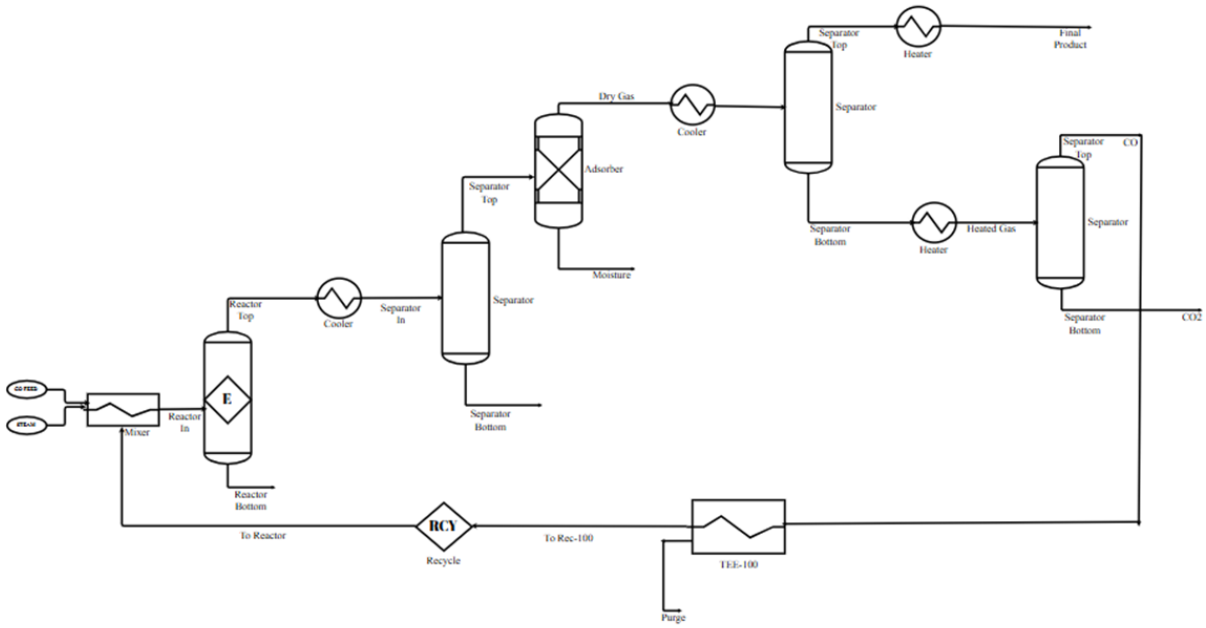

Figure 3. Process flow diagram (PFD) of the modified hydrogen production process.

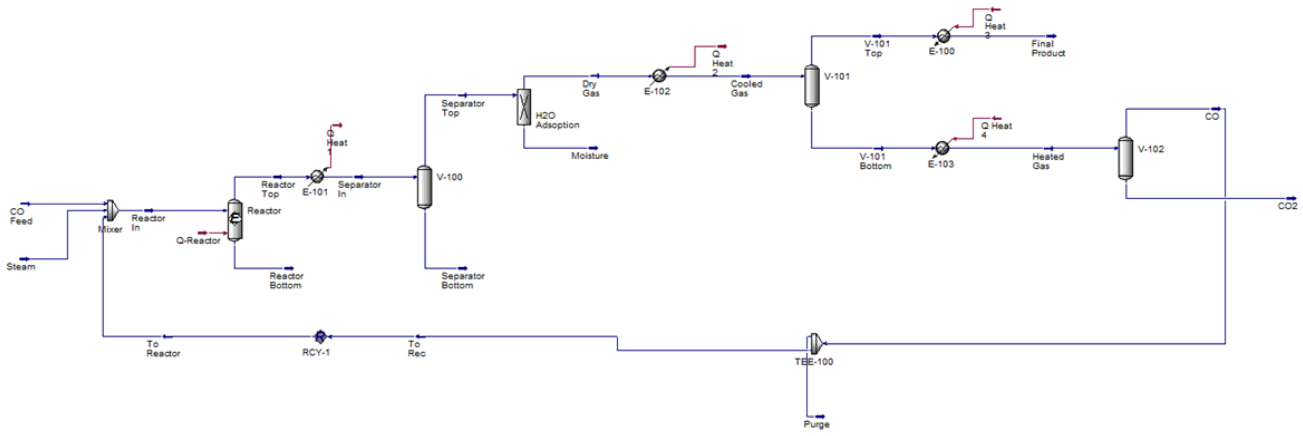

Figure 4. Process simulation using Aspen HYSYS of the modified hydrogen production process.

modifications included the introduction of a CO recycle stream and the adjustment of reactor exothermic operating conditions. In the modified configuration, a portion of the stream still containing CO from the separation unit was redirected to the reactor inlet through the recycle loop. This recycle stream was then mixed with the fresh feed of CO and H_2O before entering the reactor. The addition of the recycle stream aimed to extend the effective residence time of the reactants within the system, allowing unreacted CO from one pass to re-enter the reaction zone and undergo conversion in subsequent passes.

Based on the simulation results, the reactor outlet temperature in the modified process was approximately 200 °C, which is lower than that observed in the base process. This reduction in temperature indicates that the reaction heat did not entirely raise the stream temperature but was instead controlled to maintain conditions favorable for shifting the equilibrium of the Water–Gas Shift reaction. With the implementation of both modifications, carbon monoxide (CO) conversion increased significantly from 80.07% in the base process to 98.40% in the modified process. This improvement indicates that the majority of CO was successfully converted into hydrogen and carbon dioxide. Furthermore, the amount of CO leaving the system was substantially reduced, directly contributing to enhanced feedstock utilization efficiency and a higher hydrogen production rate.

The CO conversion values for both the base process and the modified process are presented in Table 1. CO conversion was calculated as the ratio of the amount of CO reacted to the amount of CO fed into the system, expressed by the following equation [20]:

$$\text{CO Conversion (\%)} = \frac{\text{CO reactor}}{\text{CO feed}} \times 100\% \quad (2)$$

The conversion calculations confirm that implementing CO recycle and controlling the reactor's exothermic conditions are effective strategies for enhancing overall conversion in hydrogen production via the Water–Gas Shift Reaction.

CRedit Author Statement

Author Contributions: Dias Fitriana: Writing, Visualization, Simulation, Methodology; Nova Christiana: Writing, Methodology, Simulation, Formatter, Review; Olivia Refa Kusumawati: Writing, Simulation, Formatter, Editing; Salsadila Nur Fatima Azzahra: Writing, Simulation, Data Curation. All authors have read and agreed to the published version of the manuscript.

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