



Steam Reforming of Methanol and Reactor Optimization for Additional Hydrogen Production: Process Simulation

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ABSTRACT

Considering the escalating significance of hydrogen production as a high-energy-density fuel, coupled with the challenges associated with its transportation and storage, the necessity to generate hydrogen at the point of consumption has become more pronounced than ever before. Thus, this research endeavors to comprehensively investigate various hydrogen production processes and elucidate the merits and drawbacks of each technique. Additionally, the catalysts employed in these processes were examined, ultimately leading to the selection of methanol steam reforming using a Cu/ZnO/Al₂O₃ catalyst within a fixed bed reactor for hydrogen production. Subsequently, the process underwent initial simulation utilizing Aspen Plus software, enabling a close-to-reality assessment of the simulation's challenges. Following the validation of the simulation results, a comparative analysis was conducted between a reactor operating at a specified temperature (T=220°C) and a co-current reactor. Each reactor possessed distinct advantages and disadvantages. Through this comparison, it was observed that, in order to achieve the same conversion, the length of the co-current reactor could be reduced by 5.7 cm compared to the specified temperature reactor. Consequently, the construction cost was reduced; however, this modification resulted in an increased production of carbon monoxide, necessitating further investigation.

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INTRODUCTION

In recent years, the utilization of clean and alternative energy sources has garnered significant attention among researchers. Within this context, hydrogen production has emerged as a prominent area of interest for both researchers and industries as a viable alternative energy source. Among the various sources available for hydrogen production, methanol fuel has been recognized as an attractive feedstock due to its numerous advantages. However, the effluent stream from methanol steam reforming reactors contains carbon monoxide, which poses a challenge as it can cause catalyst poisoning in fuel cells.

Hydrogen holds a crucial position within the industrial sector, and its significance as an alternative energy carrier has witnessed substantial growth in recent years, driven by the depletion of fossil fuels and mounting

environmental concerns [1, 2]. Various processes exist for hydrogen production, including natural gas reforming, gasification, water electrolysis, photoelectrolysis, and biological processes [3]. Presently, large-scale hydrogen production is predominantly accomplished through two well-established processes: fossil fuel reforming and water electrolysis [4]. Reforming processes encompass steam reforming, partial oxidation, dry reforming, and autothermal reforming. Among these, steam methane reforming (SMR) is one of the oldest and most widely employed methods for hydrogen production from methane [5, 6]. Currently, natural gas steam reforming is more cost-effective and efficient compared to methanol steam reforming for hydrogen production. However, methane steam reforming is not a viable long-term solution for hydrogen production due to its high operating temperatures, which result in substantial carbon dioxide emissions [7, 8].

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Methanol, in general, possesses a high hydrogen-to-carbon ratio (approximately 3-4) and is devoid of sulfur compounds, unlike hydrocarbon fuels [9]. As a result, methanol does not require additional equipment for reforming. Moreover, methanol reforming processes are typically conducted at temperatures around 200-300°C [3]. The products of methanol steam reforming include methanol, water, carbon monoxide, carbon dioxide, and hydrogen [10]. When the purpose of hydrogen production is for use in fuel cells, the concentration of carbon monoxide in the product stream should be minimized (below 10 ppm) to prevent poisoning of the platinum anode catalyst. Various methods exist to reduce the carbon monoxide concentration, with preferential oxidation of carbon monoxide (PROX) being the simplest and most economical approach, considering the low concentration of CO in the effluent stream from methanol steam reforming (less than 1 mole percent) [12].

Ouzounidou et al. [13] designed and investigated an integrated system for hydrogen production via autothermal reforming of methanol in a polymer electrolyte membrane (PEM) fuel cell. The system comprised an autothermal reforming reactor, a preferential oxidation reactor (PROX), and a fuel cell. A CuO/CeO₂ catalyst was employed, and at a temperature of 200.5°C and an O₂/CO ratio of 1.5, approximately 98% of carbon monoxide was removed [13]. Numerous studies have been conducted to determine the optimal conditions for achieving high methanol conversion percentages and removing carbon monoxide from the system, focusing on operational parameters such as temperature and oxygen-to-carbon monoxide ratio [14, 15].

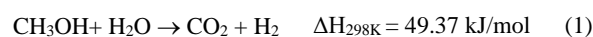
Several catalysts are utilized for the preferential CO oxidation process. Noble metal catalysts such as Pt, Pd, Ir, Ru, and Rh, primarily supported on alumina oxide, are commonly employed. When operating temperatures are below 100°C, a combination of gold catalyst with metal oxides like iron or magnesium oxide is highly suitable. The CuO/CeO₂ combination exhibits favorable catalytic activity and selectivity for operating temperatures between 170-190°C [16]. Noble metal catalysts such as Ru and Rh supported on Al₂O₃ demonstrate high activity and selectivity at temperatures around 100°C, while Pt-based catalysts on Al₂O₃ exhibit similar properties at temperatures around 200°C [16, 17].

To achieve high-purity hydrogen (above 99%), purification systems must be employed. Several methods for hydrogen purification exist, including cryogenic distillation, membrane separation, and pressure swing adsorption (PSA) [18, 19]. Among these methods, PSA has become the most prevalent separation process for hydrogen purification in the chemical and petrochemical industries [20]. Impurities, including CO₂, CO, and N₂, in the gas mixture, including hydrogen, are selectively adsorbed on mesoporous and microporous solid adsorbents such as zeolite, activated carbon, silica, and alumina gel at high partial pressures. The adsorbed

components are subsequently desorbed from the adsorbent by reducing the partial pressure of the gas phase, enabling the regeneration and reuse of the adsorbent. Ribeiro et al. [21] studied and simulated the purification of hydrogen from feed flow mixtures containing impurities using an activated carbon/zeolite adsorbent, resulting in hydrogen with a purity of 99.9994% in the simulated single bed column output stream.

Methanol steam reforming stands as one of the methods employed for hydrogen production. Methanol, being in liquid form under ambient conditions, enables compact storage and transportation prior to reformation [22]. The effluent of the methanol reformer reactor contains a small amount of carbon monoxide, which can be effectively reduced and converted into carbon dioxide through the utilization of a PROX reactor as the purification system. Finally, the PSA system is employed as one of the purification methods to obtain high-purity hydrogen.

CuO/ZnO/Al₂O₃ catalysts are typically employed in the methanol steam reforming process, operating within the temperature range of 473-573 K. The feed mixture in the simulated methanol steam reforming reactor comprises water and methanol with an S/C (stoichiometric) ratio ranging from 1 to 1.4 [23]. Under appropriate conditions, steam methanol reforming (SMR) is the most favorable stoichiometric reaction. The presence of methanol, steam, and the catalyst at elevated temperatures results in multiple parallel chemical reactions. Besides the SMR reaction, two other reactions commonly occur during the reforming process: water-gas shift (WGS) reaction and methanol decomposition (MD) reaction. The following equations represent the three main reactions in the methanol steam reformer [24].



The preferential oxidation of carbon monoxide (PROX) is a catalytic reaction that converts carbon monoxide to carbon dioxide. In this process, carbon monoxide competes with hydrogen for reaction with oxygen, leading to the consumption of oxygen. The catalyst employed in PROX plays a crucial role in enhancing carbon monoxide oxidation while minimizing hydrogen oxidation. Within the PROX reactor, two simultaneous reactions occur: the main reaction involving the oxidation of carbon monoxide and the side reaction involving the oxidation of hydrogen. It is imperative to carefully control the reaction conditions to ensure that the production of water and hydrogen oxidation remain negligible. The PROX reactions are represented by Equations (4) and (5) [25, 26].



Pressure swing adsorption (PSA) is a widely utilized technology in chemical engineering for the separation of different gases from gas mixtures, capitalizing on the varying adsorption tendencies of gases on solid surfaces. Adsorbent materials such as zeolites, activated carbon, and molecular sieves are commonly employed for the adsorption of specific gases with high affinity at elevated pressures [27]. The adsorbed components are subsequently desorbed by reducing the partial pressure of the gas phase, enabling the regeneration and reuse of the adsorbent. Among these materials, activated carbon is widely preferred worldwide as an adsorbent for carbon dioxide in off-gas streams generated in methane steam reformer units. To this end, an activated carbon layer is typically incorporated at the end of the adsorption column. Commercial activated carbon has demonstrated excellent performance in PSA systems, exhibiting effective adsorption capacity and selectivity for carbon dioxide [28]. In this study, we aimed to simulate the entire process of hydrogen production from steam methanol reforming using the Aspen Plus software. Subsequently, through reactor dimensions optimization, we strive to achieve the maximum hydrogen production efficiency. Additionally, we intend to reduce the operational costs and energy supply by conducting pinch analysis.

METHODS

Investigating the kinetics of reactions

Reformer reactor

The steam reforming process is characterized by its endothermic nature, necessitating a controlled oxidation of methanol to supply the required heat for the reaction mixture. Autothermal reforming of methanol relies on carefully selecting the reactant ratios to achieve thermal equilibrium within the reactor. The reactions involved in the reformer can be attributed to the combination of water-gas shift and methanol decomposition reactions [7, 8, 29].

Steam reforming of methanol (SRM):

$$R_r = -K_r \times C_{\text{CH}_3\text{OH}} \quad (6)$$

$$K_r = C_r [A_1 + B_1 \cdot \ln(\sigma)] e^{(-E_1/RT)} \quad (7)$$

where, SRM reaction correction factor is equal to $C_r = 5.5$, SRM reaction rate constant (A_1) is $1.15 \times 10^6 \text{ m}^3/\text{kg.s}$, SR reaction rate constant (B_1) is $9.41 \times 10^5 \text{ m}^3/\text{kg.s}$, S/C ratio of the methanol-water mixture at the inlet (σ) is equal to 1.4 and SR reaction activation energy (E_1) is $8.41 \times 10^4 \text{ J/mol}$.

Methanol decomposition (MD):

$$R_d = K_d \quad (8)$$

$$K_d = C_d \times A_2 \times e^{(-E_2/RT)} \quad (9)$$

MD reaction correction factor: $C_d = 35$

MD reaction rate constant: $A_2 = 7.09 \times 10^7 \text{ mol/kg.s} = 7.09 \times 10^4 \text{ kmol/kg.s}$

MD reaction activation energy: $E_2 = 1.112 \times 10^5 \text{ J/mol}$

Water-Gas shift (WGS):

$$R_{\text{WGS}} = 11.2 \times K_{\text{WGS}} \left[P_{\text{CO}} \times P_{\text{H}_2\text{O}} - \left(\frac{P_{\text{CO}_2} \times P_{\text{H}_2}}{K_{\text{eq}}} \right) \right] \quad (10)$$

$$K_{\text{WGS}} = C_{\text{WGS}} [1 + A_3 \delta + B_3 \delta^2] T^\alpha \times e^{(-E_3/RT)} \quad (11)$$

LT-WGS reaction correction factor: $C_{\text{WGS}} = 1.74 \times 10^{17}$

LT-WGS reaction rate constant: $A_3 = -0.154$

LT-WGS reaction rate constant: $B_3 = 0.008$

LT-WGS reaction rate constant: $\alpha = -8.5$

LT-WGS reaction activation energy: $E_3 = 35 \text{ J/mol}$

Water to CO molar ratio: $\delta = 6.25$

PROX reactor

The kinetics of the preferential CO oxidation (PROX) reactions are as follows:

Carbon monoxide oxidation reaction [8]:

$$-R_{\text{CO}} = k e^{(-E/R_g T)} P_{\text{CO}}^\alpha P_{\text{O}_2}^\beta \quad (12)$$

$$E = 81 \left(\frac{\text{kJ}}{\text{mol}} \right)$$

$$\alpha = -0.5$$

$$\beta = 0.81$$

Hydrogen oxidation reaction[8]:

$$-R_{\text{H}_2} = k e^{(-E/R_g T)} P_{\text{O}_2}^\alpha \quad (13)$$

$$k = 2.053 \times 10 \left(\frac{\text{m}^3}{\text{Kg}_{\text{cat}} \cdot \text{s}} \right)$$

$$E = 18.742 \left(\frac{\text{kJ}}{\text{mol}} \right)$$

$$\alpha = 0.5$$

Process simulation

In this simulation, three main cycles were considered for the process:

1. The main cycle: This cycle involves the entry of pure methanol feed. The methanol feed is split into two streams using a splitter. A small portion of the feed enters a burner where combustion takes place. The heat generated from methanol combustion is utilized

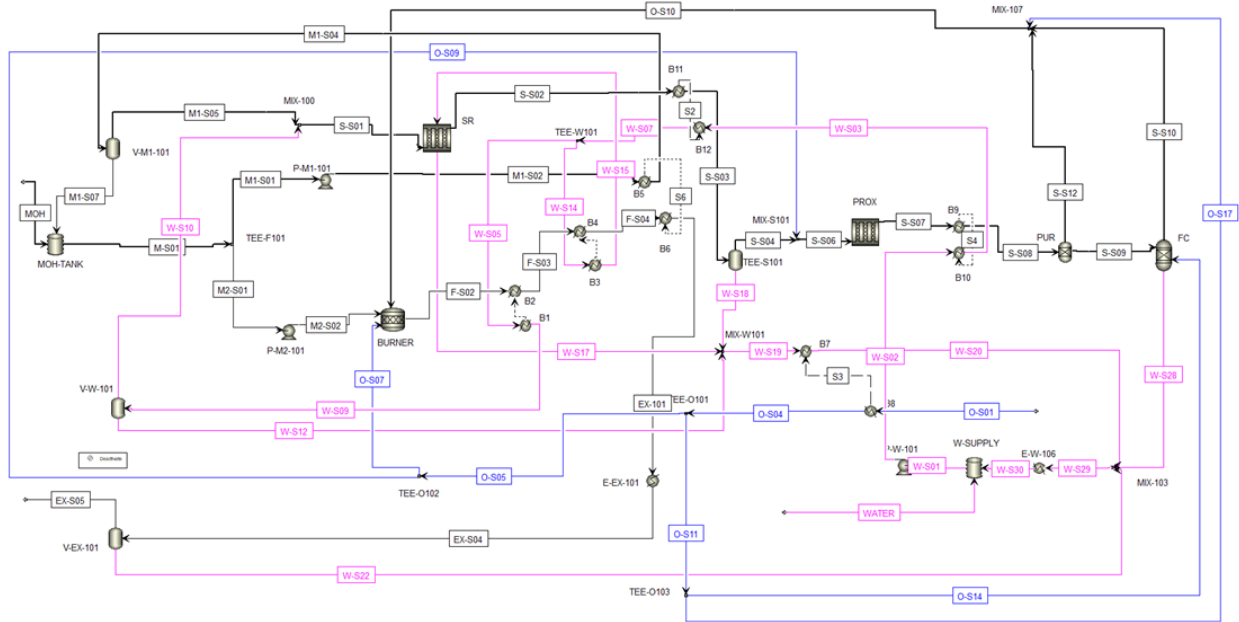


Figure 1. Main flowsheet of simulation

to provide heat for the reaction and to preheat the feed entering the reforming reactor. This eliminates the need for an external heat source, resulting in lower energy supply costs. A pinch operation is implemented in this process. The output flow from the burner is then directed to the carbon capture unit after multiple stages of heat exchange.

2. The water cycle: This cycle's purpose is to supply heat for the reaction and to mix with methanol. The incoming water flow to the shell part is at a temperature of 290°C, which provides heat for the reaction.
3. The oxygen cycle: This cycle is responsible for supplying the required oxygen for the process. The oxygen flow is mixed with the output stream from the reforming reactor with an O/C ratio of 1.25 to achieve the minimum possible concentration of carbon monoxide (CO). The PROX reactor, simulated as an adiabatic Rplug reactor, is employed for this purpose. The kinetics for the reactions are defined using the Power law. The inlet temperature for this reactor is set at 200.5°C, and other inlet parameters are specified in Table 1.

The output stream from the PROX reactor undergoes heat exchange before entering the PSA (Pressure Swing Adsorption) unit to increase the purity of hydrogen. In the simulation, a SEP (Selective Expansion Process) was used instead of the PSA unit to transfer 90% of hydrogen to the output stream, resulting in a stream with 99.997% hydrogen purity for entry into the fuel cell. This stage

Table 1. Input parameters in reactors

Reforming reactor	
Catalyst	Cu/ZnO/Al ₂ O ₃
Reactor type	Reactor with co-current thermal fluid
Number of tubes	50
Length	23.5 cm
Diameter	0.6 cm
Process stream	Vapor-Only
Thermal fluid stream	Vapor-Liquid
Bed voidage	0.4
Particle density	1235.4 kg/cum
Pressure drop	0
S/C	1.4
PROX reactor	
Catalyst	Pt/AL ₂ O ₃
Reactor type	Adiabatic reactor
Number of tubes	50
Length	48 cm
Diameter	0.6 cm
Process stream	Vapor-Only
Bed voidage	0.46
Particle density	1240 kg/cum
Pressure drop	0
O/C	1.25

involves the release of energy, which is the desired outcome of the process.

The overall process flow diagram (PFD) is depicted in Figure 1. The kinetics, reactor type, and inlet parameters are summarized in Table 1.

Validation of simulation results

In order to validate the simulation results, the research data from Chougule and Sonde [23] were utilized. The study considered a constant temperature of 220°C in the reforming reactor. Figures 2 to 6 present a comparison of the conversion process of reactants and by-products along the reactor length. The graphs demonstrate a decrease in methanol and water concentrations as the reaction progresses, while the concentrations of hydrogen, carbon dioxide, and carbon monoxide increase.

The observed changes in the molar percentages of the components throughout the reactor in our study align with the findings of Chougule and Sonde [23]. This successful validation is illustrated in the graphs. Figure 7 illustrates the molar percentage changes of the components in the

current research, specifically for the reactor operating at a constant temperature of 220°C [31].

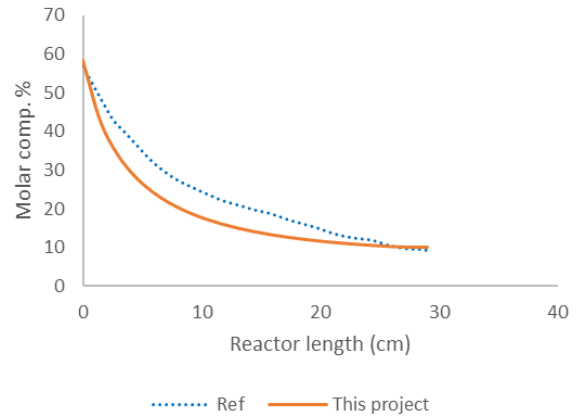


Figure 4. The process of changing the molar composition of water during reactor length with specified temperature 220°C

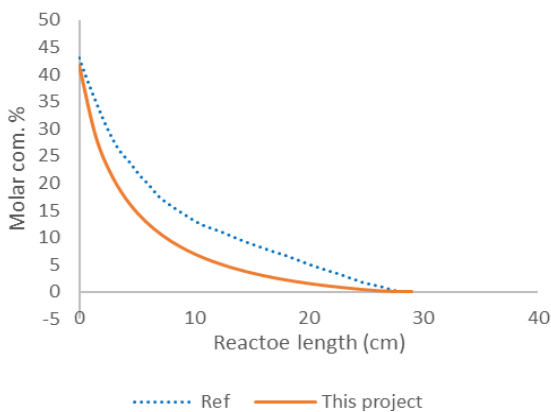


Figure 2. The process of changing the molar composition of methanol during reactor length with specified temperature 220°C

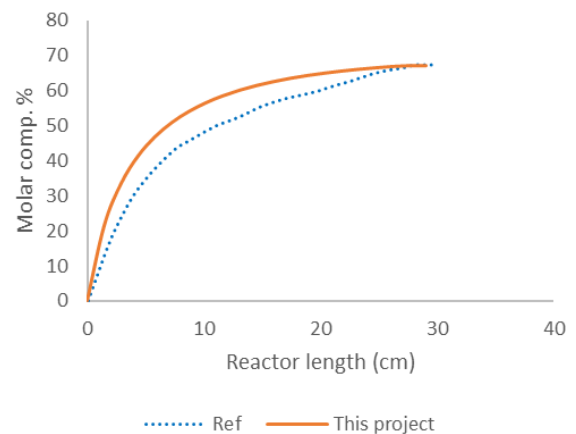


Figure 5. The process of changing the molar composition of H₂ during reactor length with specified temperature 220°C

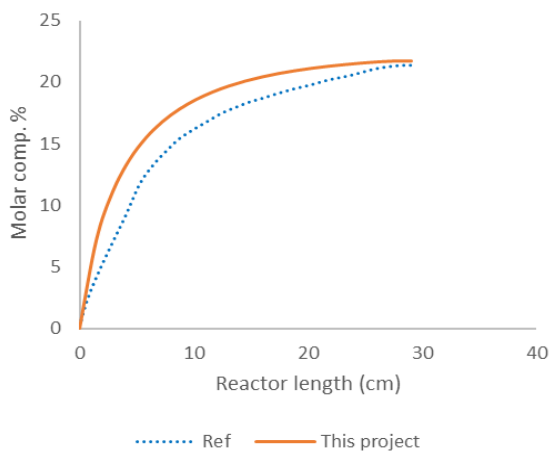


Figure 3. The process of changing the molar composition of CO₂ during reactor length with specified temperature 220°C

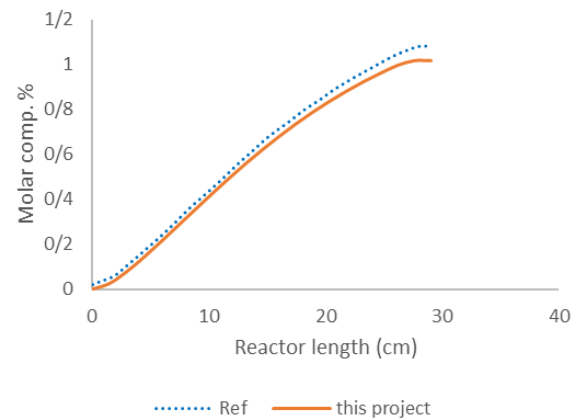


Figure 6. The process of changing the molar composition of CO during reactor length with specified temperature 220°C

RESULTS AND DISCUSSION

One of the key aspects addressed in the present study was the comparison between a reactor with co-current flow and a reactor with specified temperature, which is discussed below.

Comparison of the reactor with specified temperature and the co-current reactor

In the preceding section, the outcomes of the reformer reactor operating at a specific temperature were examined. In this study, an alternative approach was explored for supplying heat to the reformer. Zhu et al. [24] conducted a comparison between co-current and counter-current reactors. Their findings revealed that the conversion levels at the same reactor length were nearly identical for both modes, but the co-current configuration exhibited a preferable outcome due to reduced carbon monoxide production. Consequently, a co-current reactor configuration was also adopted in our investigation. The subsequent graphs present a comparison between the concurrent reactor and the reactor operating at the specified temperature ($T = 220^{\circ}\text{C}$).

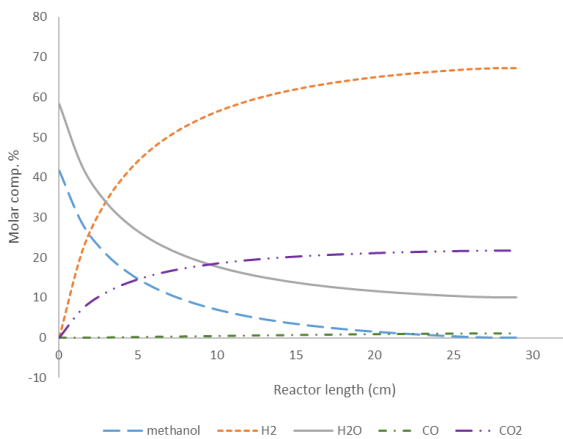


Figure 7. Changing molar composition of materials in this project ($T=220^{\circ}\text{C}$)

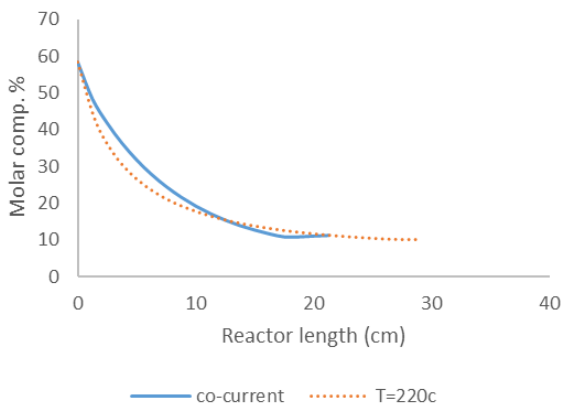


Figure 8. Comparison of water molar composition changes in specified temperature reactors and co-current reactor

The comparison between the co-current reactor and the reactor operating at the specified temperature mode reveals both advantages and disadvantages of utilizing the co-current configuration. One notable advantage is the

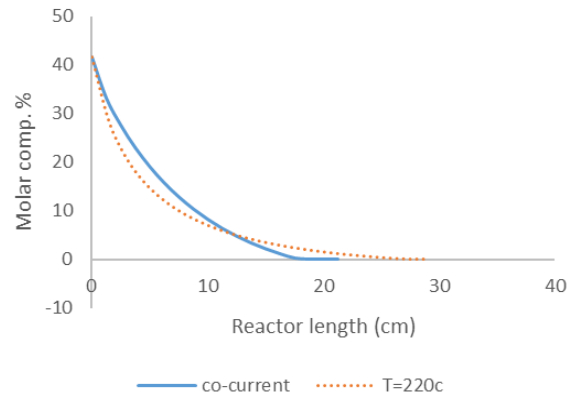


Figure 9. Comparison of methanol molar composition changes in specified temperature reactors and co-current reactor

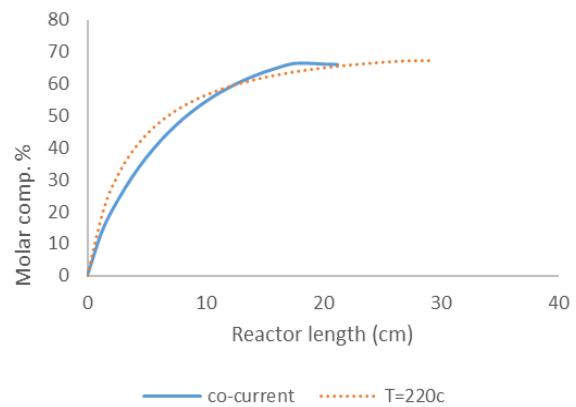


Figure 10. Comparison of H₂ molar composition changes in specified temperature reactors and co-current reactor

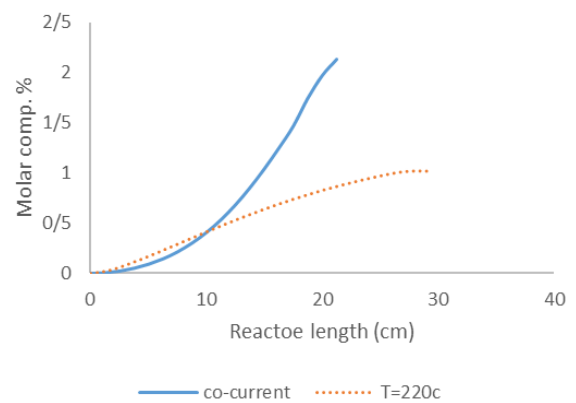


Figure 11. Comparison of CO molar composition changes in specified temperature reactors and co-current reactor

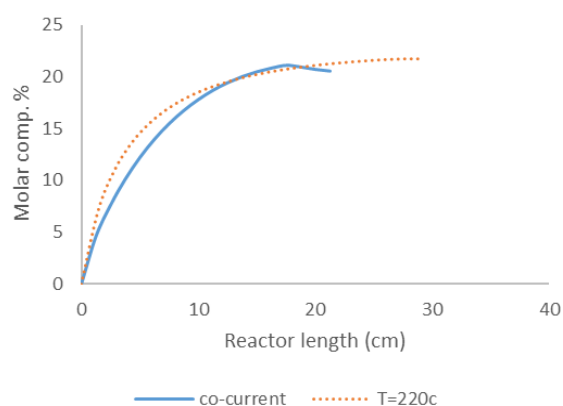


Figure 12. Comparison of CO₂ molar composition changes in specified temperature reactors and co-current reactor

reduction in reactor length required to achieve the same conversion percentage, resulting in lower construction costs. This reduction in length can be attributed to the temperature-dependent kinetics of the water-gas shift reaction, which alters the reaction rate along the reactor length. Thus, based on the provided reaction kinetics, the optimal temperature conditions need to be determined in order to minimize the production of carbon monoxide under the same conditions. This way, the subsequent purification costs are reduced. Another advantage is the cost reduction in providing the necessary thermal energy, as it can be obtained from the heat released by the burner. However, a disadvantage of the co-current reactor is the higher production of carbon monoxide, which is an undesirable by-product and poses challenges in its removal within the PROX reactor.

In the case of the co-current reactor, the operating temperature range spans from 247°C to 207°C, and the required reactor length is reduced to 17.8224 cm to achieve the same conversion. Additionally, the heating water is introduced into the reactor at a temperature of 290°C.

CONCLUSION

In this study, a comprehensive investigation was conducted to explore various methods of hydrogen production. Ultimately, the steam reforming of methanol was selected as the preferred method. The research involved a thorough examination of previous studies in the field to identify the influential parameters affecting the conversion rate and extract the process kinetics. Subsequently, a preliminary simulation of the process was performed. After validating the simulation and obtaining satisfactory results, a comparative analysis was conducted to evaluate the differences between a reactor operated at a specified temperature of 220°C and a co-current reactor.

The findings revealed that the co-current reactor achieved the same conversion rate in a shorter time (with a reduction of approximately 5.7 cm in reactor length), resulting in lower construction costs. Furthermore, the utilization of the burner's heat eliminated the need for an external heat source, employing a pinch operation. However, this approach exhibited a drawback in the form of increased carbon monoxide production compared to the specified temperature method. This higher carbon monoxide production poses challenges during separation processes and may lead to increased purification costs. The temperature-dependent kinetics of the water-gas shift reaction were identified as the probable cause for the elevated carbon monoxide levels in the co-current reactor, as the temperature variations in this mode are more significant compared to the other mode.

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Persian Abstract

چکیده

با توجه به اهمیت روزافزون تولید هیدروژن به عنوان سوخت با دانسیته انرژی بالا و در عین حال مشکلات حمل و نقل و ذخیره‌سازی آن، نیاز به تولید هیدروژن در محل مصرف آن بیش از پیش حس می‌گردد. از این رو، در این پژوهش ابتدا فرآیندهای تولید هیدروژن به طور کامل بررسی گردید و مزایا و معایب هر روش بیان شد. کاتالیست‌های مورد استفاده در این فرآیندها بررسی شدند و در نهایت روش ریفرمینگ با بخار متانول برای تولید هیدروژن در راکتور بستر ثابت با کاتالیست $\text{Cu/ZnO/Al}_2\text{O}_3$ انتخاب شد. در مرحله بعد شبیه‌سازی اولیه فرآیند با نرم‌افزار Aspen Plus انجام شد و چالش‌ها و گلوگاه‌های شبیه‌سازی نزدیک به واقعیت بررسی شد و در نهایت پس از اعتبارسنجی نتایج شبیه‌سازی، به مقایسه‌ی راکتور با دمای ثابت و راکتور با جریان همسو و در نهایت به بهینه‌سازی ابعاد راکتور ریفرمینگ پرداخته شد. هرکدام از راکتورها مزایا و معایب خاصی داشتند که در نهایت راکتور با جریان همسو انتخاب شد. مشاهده شد که طول راکتور با جریان همسو نسبت به راکتور با دمای ثابت برای رسیدن به همان درصد تبدیل ۶۶/۷ درصد حدود ۵/۷ سانتی‌متر کمتر شده و در نتیجه هزینه‌ی ساخت آن کاهش می‌یابد ولی میزان CO تولیدی بیشتر شده که باید چاره‌ای برای آن اندیشید.