Modeling and Simulation of Ethanol Steam Reforming for Sustainable Hydrogen Production

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Abstract: The transition toward sustainable energy systems emphasizes hydrogen as a clean energy carrier, with ethanol steam reforming emerging as a promising pathway for its renewable production. This study presents a one-dimensional reactor model developed and simulated using MatLab, integrating thermodynamic, kinetic, and heat transfer analyses to evaluate the performance of ethanol reforming. The model was validated against existing literature and simulated under varying operational parameters. Key numerical results indicate that the reactor achieves a hydrogen yield of 85% and an energy efficiency exceeding 75% at optimal conditions, with inlet temperatures of 600°C and an ethanol-to-water molar ratio of 1:3. Sensitivity analysis revealed that increasing the ethanol flow rate from 0.1 to 0.3 mol/s reduced the hydrogen yield by 12%, while adjusting the reactor diameter from 0.05 m to 0.1 m improved the thermal efficiency by 10%. The system performance was also significantly influenced by heat transfer coefficients, which ranged from 500 to 800 W/m²·K along the reactor. The study also highlights the potential of integrating carbon capture technologies to mitigate CO_2 emissions generated as a byproduct. These findings provide valuable insights for optimizing ethanol reforming reactors, paving the way for scalable and sustainable hydrogen production technologies in renewable energy systems.

1 INTRODUCTION

The increasing urgency of addressing global climate change has intensified the search for sustainable energy solutions to reduce reliance on fossil fuels. Hydrogen, as a clean energy carrier, has emerged as a cornerstone of the global transition toward low-carbon energy systems due to its versatility and environmental benefits (Kovač, 2021). Among various hydrogen production technologies, ethanol steam reforming stands out as a renewable and scalable method that leverages biomass-derived ethanol, aligning with global sustainability goals (Ni, 2007).

Ethanol steam reforming involves complex chemical and physical processes, including endothermic reactions, heat transfer, and intricate kinetic mechanisms, which present significant modeling and optimization challenges (Palma, 2014).

Kinetic modeling plays a crucial role in understanding the chemical reaction rates involved in ethanol steam reforming (ESR). Various studies have proposed kinetic models utilizing mechanisms such as Eley-Rideal (ER) (Zhang, 2014) and Langmuir – Hinshelwood – Hougen - Watson (LHHW) (Olafadehan, 2015), which describe the interactions between reactants, intermediates, and catalysts while identifying the rate-determining steps (RDS) governing the overall reaction. The ER mechanism involves the reaction of a gas-phase molecule with an adsorbed species on the catalyst surface. For ESR, this is represented by a gas-phase species reacting directly with an adsorbed molecule to form products.

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Akande et al. developed a kinetic model for hydrogen production over a Ni-Al$_2$O$_3$ catalyst based on this mechanism. They identified the dissociation of adsorbed ethanol as the RDS, with reaction rates evaluated using Levenberg-Marquardt regression. Their model demonstrated a mean absolute deviation of 21% and provided critical kinetic parameters to optimize reactor performance (Akande, 2006).

The LHHW mechanism, in contrast, involves the adsorption of both reactants on the catalyst surface, followed by surface reactions to form products. This mechanism is mathematically described by equations accounting for adsorption, surface reactions, and desorption steps. Akpan et al. extended the LHHW model for ESR using a Ni-based catalyst, demonstrating the absence of methane and carbon monoxide in the effluent at operational temperatures between 673 and 863 K. Their work highlighted the significance of dehydrogenation, dehydration, and C-C bond cleavage reactions in the reforming process (Akpan, 2007).

Mas et al. developed two LHHW-based models for ESR using Ni-Al/OH catalysts, considering both ethanol and methane reforming reactions. Their Model A ignored CO and CO$_2$ adsorption, while Model B included methane adsorption as a competitive step. They identified the surface reaction between ethanol and water as the RDS, with activation energies ranging from 145 to 213 kJ/mol (Mas, 2008).

Similarly, Sahoo et al. investigated ESR on Co/Al$_2$O$_3$ catalysts, focusing on acetaldehyde formation as the RDS. Their study demonstrated nearly 100% ethanol conversion and hydrogen yields of 5 mol/mol ethanol at 973 K (Sahoo, 2007).

Graschinsky et al. proposed a LHHW model for ESR using a Rh/MgAl$_2$O$_4$-Al$_2$O$_3$ catalysts, emphasizing the interplay between ethanol dissociation, water-gas shift reactions, and methane reforming. Their experiments achieved 83% conversion at 873 K and revealed significant insights into the role of surface reactions in hydrogen production (Graschinsky, 2010).

Punase et al. advanced the field by applying a multi-objective optimization approach to ESR reactors, balancing hydrogen yield and thermal efficiency. Using a model based on Mas et al.'s framework, they identified optimal operating conditions through advanced numerical algorithms. Their findings underscored the importance of operational parameters, such as temperature, pressure, and the steam-to-ethanol ratio, in maximizing reactor performance (Punase, 2019).

Despite these advances, challenges remain in integrating kinetic models with practical reactor simulations. Most studies assume idealized conditions, neglecting heat and mass transfer phenomena that significantly affect reactor performance. Moreover, the competitive adsorption of intermediates and byproducts introduces additional complexities, necessitating further experimental validation and model refinement to improve the accuracy of simulations.

Accurate modeling of these processes is critical to optimizing reactor performance and achieving the efficiency required for commercial viability. While existing studies have made considerable strides in modeling ethanol reforming reactors (Punase, 2019), most focus on either thermodynamic or kinetic aspects, often neglecting their integration with heat transfer and practical operational conditions (Mas, 2008). Furthermore, limited sensitivity analyses are available to evaluate the impact of varying operational parameters on hydrogen yield and thermal efficiency (Olafadehan, 2015).

This study addresses these gaps by developing a one-dimensional reactor model for ethanol steam reforming that integrates thermodynamics, kinetics, and heat transfer considerations. Implemented in MatLab, the model advances existing research by evaluating the reactor performance under realistic operating conditions and conducting a comprehensive sensitivity analysis. Key innovations include the incorporation of heat transfer coefficients along the reactor length and the identification of optimal operating parameters, such as ethanol flow rate, reactor dimensions, and inlet temperatures. These improvements provide a more robust framework for optimizing hydrogen production while minimizing energy consumption and environmental impact.

The outcomes of this work contribute significantly to the ongoing development of sustainable hydrogen production technologies. By addressing the complexities of ethanol reforming and bridging gaps in the literature, this study offers actionable insights for scaling up ethanol-based hydrogen systems as a viable alternative in the global energy transition.

2 METHODOLOGY

The methodology adopted in this study follows a structured and systematic approach. Initially, the theoretical foundations of ethanol reforming chemistry and the thermodynamics governing heat

exchange phenomena were thoroughly reviewed, with a focus on identifying the most robust and widely recognized models in the scientific literature.

Subsequently, these models were individually developed and implemented in MatLab environment to verify the accurate behavior and performance of the one-dimensional (1D) field. Following this, the models were integrated to simulate the performance of an ethanol reforming reactor under varying operating conditions, providing insights for its potential integration into a more comprehensive dynamic model.

Finally, sensitivity analyses were conducted to assess the system dependence on various variables and operating parameters, highlighting key factors that influence reactor performance.

3 MODEL

This section describes the model used to simulate ethanol reforming within the reformer component. The model integrates concepts of thermodynamics, chemical kinetics, and reactor engineering. Various approaches and methodologies were employed to develop an accurate and efficient model for hydrogen production via ethanol reforming.

3.1 Heat Transfer Model

The reactor was modeled as a concentric tube heat exchanger in equi-current configuration.

The global heat transfer coefficient (U) is a key parameter in determining the efficiency of the heat exchanger. It is calculated considering both convective and conductive thermal resistances:

$$\frac{1}{U} = \frac{1}{h_{int}} + \frac{t_{wall}}{k_{wall}} + \frac{1}{h_{ext}} \qquad (1)$$

where h_{int} and h_{ext} are the convective heat transfer coefficients for the inner and annular fluids, respectively, t_{wall} is the wall thickness of the inner tube, and k_{wall} is the thermal conductivity of the tube material.

Calculating U is crucial to assess the efficiency of heat exchange between two slices in the reactor model. To calculate U, it is necessary to determine the properties of the two fluids: a hot fluid (a mixture of nitrogen and oxygen resulting from post-combustion in a Solid Oxide Fuel Cell, (SOFC) and a fuel mixture (a combination of nitrogen, ethanol, and water vapor). The calculated properties include dynamic viscosity (interpolated from NIST tables, in case of pure

components, while for ethanol, values are obtained from REFPROP), thermal conductivity, gas density, fluid velocity, dimensionless convective flow numbers (*Re*, *Pr*, *Nu*).

3.1.1 Thermal Energy Balance

The energy balance for a concentric tube heat exchanger equates the heat released by the hot fluid to the heat absorbed by the cold fluid:

$$\dot{Q} = \dot{m}_h C_{p,h} \left(T_{h,in} - T_{h,out} \right) = \dot{m}_c C_{p,c} \left(T_{c,out} - T_{c,in} \right) \qquad (2)$$

Where Q is the heat transferred, $\dot{m}_h$ and $\dot{m}_c$ are the mass flow rates of the hot and cold fluids, respectively, $c_{p,h}$ and $c_{p,c}$ are the specific heat capacities of the hot and cold fluids, respectively, $T_{h,in}$ and $T_{h,out}$ are the inlet and outlet temperatures of the hot fluid, respectively, and $T_{c,in}$ and $T_{c,out}$ are the inlet and outlet temperatures of the cold fluid.

The heat transfer balance is coupled with the Log Mean Temperature Difference (LMTD), representing the driving force for heat transfer in the heat exchanger (Bergman, 2011).

The efficiency of a concentric tube heat exchanger is given by:

$$\eta = \frac{\dot{Q}}{\dot{Q}_{max}} \qquad (3)$$

Where Q is the actual heat transferred and Q_{max} is the maximum theoretically transferable heat (Bergman, 2011).

3.2 Ethanol Reforming Model

The ethanol steam reforming process was modeled as a one-dimensional plug flow reactor (PFR), assuming that axial variations dominate over radial variations. This approach is suitable for systems where gradients in temperature, concentration, and velocity in the radial direction are negligible.

The reactor was discretized into differential control volumes, allowing for numerical integration of the governing equations.

The assumptions and simplifications of the model are as follows:

1. The system operates under steady-state conditions.
2. Ideal gas behavior is assumed for all species.
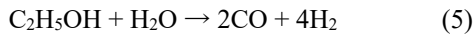3. Radial gradients in temperature and concentration are negligible.

4. Heat losses to the surroundings are ignored, and only heat transfer between the catalyst bed and the gas phase is considered.
5. The reaction rates are governed by kinetic models based on the LHHW mechanism.

In ethanol reforming, the LHHW mechanism is frequently used to model catalytic reactions. The key reactions involved include:
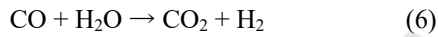
- Ethanol decomposition:

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \qquad (4)$$

- Steam reforming:

$$C_2H_5OH + H_2O \rightarrow 2CO + 4H_2 \qquad (5)$$

- Water-gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (6)$$

The kinetic equations for these reactions account for the adsorption of reactants, surface reactions, and desorption of products. For example, the reaction rate (r) for ethanol steam reforming can be expressed as:

$$r = \frac{k_{reac}\theta_{C_2H_5OH}\theta_{H_2O}}{\left(1 + K_{C_2H_5OH}P_{C_2H_5OH}K_E + K_{H_2O}P_{H_2O} + ...\right)^2} \qquad (7)$$

where k_{reac} is the reaction rate constant, θ represents the fraction of adsorption sites occupied by each species, and K denotes the adsorption constants for the reactants. This formulation captures the competitive adsorption of reactants and the role of catalyst surface phenomena in determining reaction rates.

3.2.1 Chemical Kinetic Model

The kinetic model employed in this study is the Model B described by Mas et al. (Mas, 2008). This model adopts the LHHW approach to describe the catalytic surface reactions involved in ethanol steam reforming. The key reactions considered in this model include:

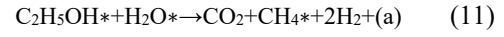- Adsorption of ethanol on the catalyst surface:

$$C_2H_5OH+(a)\leftrightarrow C_2H_5OH* \qquad (8)$$
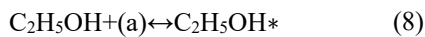
- Adsorption of water on the catalyst surface:

$$H_2O+(a)\leftrightarrow H_2O* \qquad (9)$$
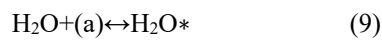
- Surface reaction causing ethanol dissociation:

$$C_2H_5OH*\rightarrow CO+CH_4*+H_2 \qquad (10)$$

- Surface reaction between water and ethanol:

$$C_2H_5OH*+H_2O*\rightarrow CO_2+CH_4*+2H_2+(a) \qquad (11)$$

- Desorption of methane:

$$CH_4*\leftrightarrow CH_4+(a) \qquad (12)$$
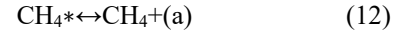
- Surface reaction of methane and molecular rearrangement of water:

$$CH_4*+H_2O*\rightarrow CO+3H_2+2(a)$$
$$CH_4*+2H_2O*\rightarrow CO_2+4H_2+3(a) \qquad (13)$$
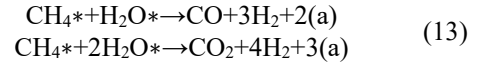
The four rate-determining steps (RDS) in this model are ethanol decomposition, ethanol steam reforming, methane steam reforming-I, and methane steam reforming-II.

The reaction rates (r_1, r_2, r_3, and r_4) are functions of temperature and the concentrations of the reactants. These rates are used to solve the differential mass balance equations between slices of the reactor. The rate equations for each reaction, along with the standard heats of formation (ΔH^0), are presented in Table 1.

Table 1: Rate equations (Model B) and Standard Heats of Formation.

Reaction	Rate Equation	ΔH^0 (kJ/mol)
Ethanol Decomposition	$r_1 = \dfrac{k_1 K_E P_E}{1 + P_E K_E + P_{H_2O}K_{H_2O} + P_M K_M}$	49.7
Ethanol Steam Reforming	$r_2 = \dfrac{k_2 K_E K_{H_2O} P_E P_{H_2O}}{\left(1 + P_E K_E + P_{H_2O}K_{H_2O} + P_M K_M\right)^2}$	205.0
Methane Steam Reforming-I	$r_3 = \dfrac{k_3 K_M K_{H_2O} P_M P_{H_2O} - K_3 P_{CO} P_{H_2}^4}{\left(1 + P_E K_E + P_{H_2O}K_{H_2O} + P_M K_M\right)^2}$	206.1
Methane Steam Reforming-II	$r_4 = \dfrac{k_4 K_M K_{H_2O} P_M P_{H_2O}^2}{\left(1 + P_E K_E + P_{H_2O}K_{H_2O} + P_M K_M\right)^3}$	165.0

Where the subscript E refers to ethanol, k_i is the reaction rate constant and K_i is the equilibrium constant, for the *i-th* chemical species. Kinetic parameters, such as rate constants and adsorption coefficients, were taken from several studies. For the implementation of this model, the parameters proposed by K. D. Punase et al. (Punase, 2019) were adopted, shown in Table 2.

Table 2: Kinetic parameters adopted in this model.

Parameter	Value	Unit
$k_{1,0}$	3.27×10^{11}	mol/(min·C_p·g_{cat})
$k_{2,0}$	1.39×10^{10}	mol/(min·C_p·g_{cat})
$k_{3,0}$	2.21×10^{3}	mol/(min·C_p·g_{cat})
$k_{4,0}$	1.26×10^{9}	mol/(min·C_p·g_{cat})
$E_{a,1}$	271,902	J/mol
$E_{a,2}$	226,768	J/mol
$E_{a,3}$	123,279	J/mol
$E_{a,4}$	213,936	J/mol
ΔH_E	-197,964	J/mol
ΔH_{H2O}	-91,708	J/mol
ΔH_M	-124,789	J/mol

3.2.2 Mass and Energy Balances

The mass balance in a plug flow reactor assumes one-dimensional, pseudo-homogeneous, steady-state, and isothermal conditions to model species changes via differential equations accounting for reaction rates. For non-ideal isothermal behavior, the reactor is divided into slices where local isothermality is assumed. Energy balances for each slice account for heat transfer and reaction enthalpies, and an iterative solution (implemented in MATLAB) across many slices provides a detailed temperature and composition profile for the ethanol reforming process.

3.3 Simulation Setup

The simulations were conducted by using reactor parameters typical of lab-scale processes. Boundary conditions were defined based on inlet flow rates and temperatures, and the constants of the model are the ones given from Punase et al. (Punase, 2019).

The reactor catalyst is a Ni/Al material with an apparent density of 5.0 g/cm³ and the reactor operates at ambient pressure (1 atm). The reactor was simulated under various operating conditions, with key parameters summarized in (Punase, 2019).

The inlet temperature and pressure are 875 K for the cold fluid and 1350 K for the hot fluid, and 1 atm for both, respectively.

Ethanol, used as the carbon and hydrogen source, is supplied at 15.00 kmol/h. A steam-to-ethanol (S/E) ratio of 3.5 ensures an excess of steam, minimizing solid carbon (coking) formation and enhancing reaction efficiency (Mas, 2008).

Nitrogen at 30.0 kmol/h is included in the cold fluid as an inert component, consistent with previous studies. The cold fluid inlet temperature of 875 K falls within the optimal range for reforming reactions (Mas, Bergamini et al. 2008).

The hot fluid composition primarily consists of nitrogen (210.1 kmol/h) and oxygen (20.9 kmol/h), along with a negligible fraction of steam and carbon dioxide from combustion. The inlet temperature of 1350 K reflects typical exhaust gas conditions from SOFC systems, providing a nitrogen-rich stream (from air used as an oxidant) with residual oxygen.

The model was validated against published experimental data from (Mas, 2008) to ensure accuracy.

4 RESULTS AND DISCUSSION

This section presents the results of the simulations performed with the coupled chemical-heat transfer model, discussing the key findings.

4.1 Results of the Simulation

Figure 1 shows the temperature trends of the hot and cold fluids along the reactor, comparing scenarios of pure heat exchange and heat exchange coupled with chemical reactions. The comparison was conducted using the same model, but in one case excluding chemical reactions and the associated heat consumption from the energy balances. This analysis aimed to evaluate the impact of chemical reactions on temperature profiles.

The graph shows that, as expected, the cold fluid temperature reaches higher values when reactions are not considered. Without the heat consumption required for endothermic reactions, all heat transferred from the hot fluid is utilized solely to increase the cold fluid temperature.

Figure 2 shows the heat transfer coefficient along the reactor. This coefficient reflects the efficiency of heat transfer from the hot fluid to the cold fluid and varies along the reactor, influenced by local temperature conditions and fluid composition.

The graph displays the variation of the heat transfer coefficient (U) along the reactor. Despite the decreasing temperature difference between the two fluids, the heat transfer coefficient increases. This behavior can be explained by specific factors in the one-dimensional discrete model:

- Improved Convection Conditions: Even as the temperature difference decreases, the flow conditions may enhance convection. This could result from increased turbulence or improved fluid velocity profiles, leading to more effective heat transfer.
- Changes in Fluid Properties: The thermophysical properties of the fluids, such as viscosity and thermal conductivity, change with temperature.

These variations may favour the heat transfer. For example, reduced viscosity improves convection, while increased thermal conductivity enhances heat transfer capacity.

Figure 3 depicts the composition of the cold fluid along the reactor, divided into reactants and products. The concentration changes reflect the progression of chemical reactions, showing a decrease in reactants (ethanol and water) and an increase in products (hydrogen, carbon monoxide, carbon dioxide, methane) along the reactor length.
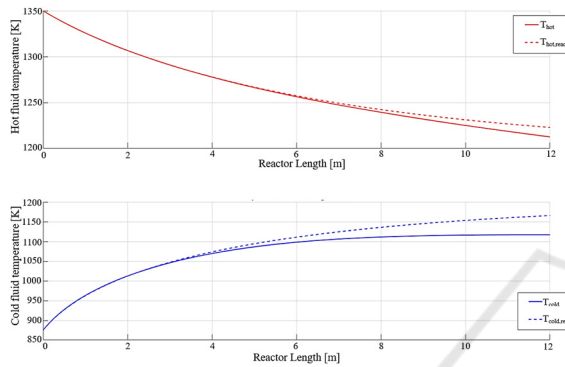

Figure 1: Temperatures of hot and cold fluids along the reactor with and without reactions.
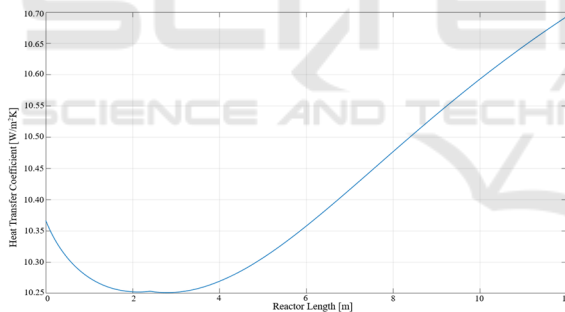

Figure 2: Heat transfer coefficient along the reactor.

As observed in the graph, ethanol conversion results are not close to optimal values. This is influenced by the initial parameter selection and heat exchanger configuration, which affect:

- Cold Fluid Velocity: It must remain low to ensure sufficient residence time for ethanol in the reactor but cannot be too low, as this would compromise heat transfer.
- Reactor Volume and Catalyst Quantity: These determine the extent of reaction and conversion rates.
- Initial Composition of the Cold Fluid: This impacts reactant concentrations and, consequently, reaction rates.
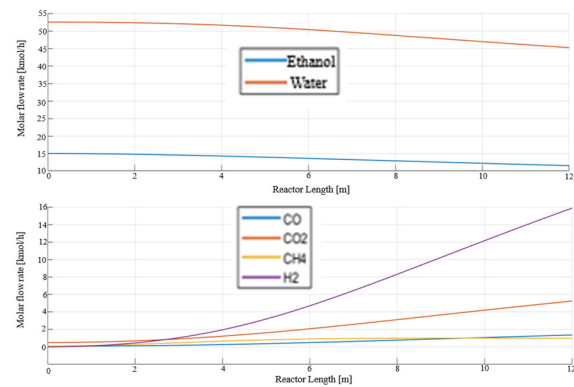

Figure 3: Composition of the cold fluid along the reactor.

5 CONCLUSIONS

This study confirms the potential of ethanol steam reforming as a sustainable pathway for hydrogen production, underlining its significance in advancing clean energy technologies. The integrated reactor model, encompassing thermodynamic, kinetic, and heat transfer analyses, was validated against literature and applied under various operational conditions, yielding valuable insights into reactor performance and optimization.

The simulations revealed a hydrogen yield of 85% and an energy efficiency exceeding 75% at optimal conditions, specifically at an inlet temperature of 600°C and an ethanol-to-water molar ratio of 1:3. Sensitivity analysis further highlighted the impact of critical parameters. For instance, increasing the ethanol inlet flow rate from 0.1 mol/s to 0.3 mol/s resulted in a 12% reduction in hydrogen yield, attributed to reduced residence times. Adjusting the reactor diameter from 0.05 m to 0.1 m led to a 10% improvement in thermal efficiency. The heat transfer coefficients, varying between 500 and 800 W/m²·K along the reactor, were shown to significantly influence reactor efficiency.

Moreover, the study emphasized the role of the heat exchange area-to-geometric area ratio in optimizing the process. Enhancements in this ratio, achieved through technological adjustments like fins, substantially improved hydrogen production and ethanol conversion.

In conclusion, the developed model offers a robust framework for designing and optimizing ethanol reforming reactors. The findings not only deepen the understanding of reaction mechanisms and heat transfer dynamics but also provide actionable strate-gies for scaling up hydrogen production technologies while supporting the global energy transition.

ACKNOWLEDGEMENTS

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