THERMODYNAMIC ANALYSIS OF THE STEAM-ETHANE PYROLYSIS PROCESS

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Abstract: Hydrogen is gaining recognition as a clean energy source, with numerous production methods available for its generation. This paper presents a detailed thermodynamic analysis of the steam-ethane pyrolysis reaction, focusing on optimizing the reaction enthalpy to maximize hydrogen output. A succinct review of the current hydrogen production technologies is provided, with a focus on ethane pyrolysis integrated with steam as the chosen methodology. The study employs a Lagrange multiplier method to minimize the reaction enthalpy under specific constraints, ensuring thermodynamic equilibrium. Simulation results demonstrate that the optimal operating conditions for maximum hydrogen production are achieved at a temperature of 840°C and a pressure of 3.8 bar, with a steam-to-ethane ratio of 3:1. The research offers the framework to design an efficient automation solution for the pyrolysis process, underscoring the significance of maintaining an ideal steam-to-ethane ratio of roughly 3:1, as well as the precise control of temperature and pressure. Simulation outcomes support the thermodynamic analysis's efficacy in boosting hydrogen production, highlighting its potential for large-scale applications with low-cost raw materials in the petrochemical industry.

Keywords: hydrogen production, ethane steam pyrolysis process, pyrolysis reaction thermodynamic equilibrium, thermodynamic analysis.

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1. INTRODUCTION

Hydrogen is gaining recognition as a crucial clean energy carrier, demonstrating expanding opportunities in fuel production and various industrial applications. To facilitate the shift towards hydrogen-based energy systems, efficient hydrogen production is vital, prompting research to prioritize catalytic processes such as steam reforming and the optimization of catalysts. Although considerable progress has been made, there is still no definitive agreement on the best production method [1].

Hydrogen production comprises several methods, each offering unique advantages and challenges. Notable processes include electrolysis, steam reforming of hydrocarbons, and ammonia decomposition, with continuous advancements aimed at improving catalyst efficiency. Given hydrogen's essential role in solar fusion, technologies such as photocatalysis and photovoltaics present promising avenues for capturing solar energy and promoting sustainable hydrogen production [2]. The main industrial techniques for hydrogen production can be divided into two categories: hydrocarbon-based processes and non-hydrocarbon-based processes. Hydrocarbon-based methods include steam-methane reforming (SMR), catalytic decomposition of natural gas, partial oxidation of heavy oil, and coal gasification. In contrast, non-hydrocarbon-based methods comprise water electrolysis, thermochemical water splitting, along with various photochemical, photoelectrochemical (PCE), and photobiological approaches [3].

Hydrogen is gaining recognition as a pivotal fuel for the future due to its environmental benefits. It can be produced through various methods, including thermochemical, electrochemical, and photocatalytic processes. Among these, pyrolysis, which integrates hydrocarbons and steam, is particularly notable for its cost-effectiveness and efficiency, fostering extensive industrial use. As demand for hydrogen rises in sectors such as transportation, chemistry, and energy, its importance is steadily increasing. Furthermore, advancements in hydrogen production technologies, combined with both traditional and renewable energy sources, are propelling the growth of fuel cell vehicles and the overall hydrogen economy [4].

Pyrolysis presents a viable alternative for producing hydrogen by subjecting hydrocarbons to heat in the absence of air, resulting in their breakdown into hydrogen and solid carbon. This method generates high-purity hydrogen and solid carbon, which offers advantages over gaseous CO2 in terms of handling. While this process is most effective with simple hydrocarbons, it can also yield by-products such as acetylene. Among the various options, the pyrolysis of ethane for hydrogen production is especially recommended due to its efficiency [5]. Additionally, Joung et al. advocate for the use of ethane in hydrogen generation due to its favorable characteristics and efficiency for this purpose [6].

This paper introduces an optimized control framework for ethane pyrolysis that harnesses the cost-effectiveness and hydrogen-rich attributes of ethane to enhance hydrogen production [7, 8]. The study adapts pyrolysis reactors traditionally employed for ethylene synthesis, proposing a sophisticated automated control system that manages critical operating parameters, including flow rates, temperature, and pressure [9, 10]. Simulation results substantiate the efficiency, robustness, and viability of this solution for large-scale hydrogen production within the petrochemical sector.

Section 2 examines the technological and thermodynamic considerations associated with ethane pyrolysis, elaborating on the mechanisms of hydrogen production via steam ethane pyrolysis, by emphasizing the thermodynamic equilibrium pertinent to the pyrolysis reaction, to produce substantial amounts of hydrogen. Section 3 is dedicated to the design of automation control systems specifically for steam-ethane pyrolysis. Section 4 showcases simulation results that validate the effectiveness of the proposed optimal control solution. Section 5 addresses the conclusions, presents the results, and outlines future perspectives [11].

2. STUDY OF THERMODYNAMIC EQUILIBRIUM IN ETHANE-STEAM PYROLYSIS REACTIONS

Hydrogen is crucial in numerous industrial applications, especially in refining, where it facilitates catalytic reactions like hydrodesulfurization, hydrogenation, and hydrocracking. In chemical plants, hydrogen can be obtained from refining processes, specialized production units, or from external sources. Steam reforming is a prominent method for hydrogen production, typically yielding purities of 95% to 98%, and up to 99.9% (when utilizing selective absorption techniques). Accurately assessing the composition at thermodynamic equilibrium is vital for optimizing these processes [12].

Grasping equilibrium conversion is vital for the design and operation of chemical processes. To optimize reactions such as steam reforming, it is essential to understand the equilibrium composition and how it depends on critical parameters. Steam reforming, a significant method for producing synthesis gas, entails the reaction of light hydrocarbons with steam over a nickel catalyst, resulting in a mixture of H_2, CO, CO_2, CH_4, and H_2O [5].

In systems featuring a single chemical reaction, the equilibrium composition is usually established using the equilibrium constant. However, in processes that involve multiple simultaneous reactions, it necessitates the use of numerical methods grounded in a thermodynamic equilibrium criterion. For steam ethane pyrolysis, this criterion is characterized by the reaction enthalpy, which is minimized through an optimization process. Therefore, this study concentrates on the thermodynamic regime of ethane pyrolysis with steam injection, with the objective of maximizing hydrogen production close to equilibrium conditions.

To study the reaction enthalpy, we must first comprehend the process of the chemical reaction involving a general hydrocarbon, represented as C_nH_m [5]:

$$C_nH_m + nH_2O \rightarrow nCO + \left(\frac{m}{2} + n\right) H_2 \qquad (1)$$

Regarding steam ethane pyrolysis, equation (1) is customized as follows:

$$C_2H_6 + 2H_2O \rightarrow 2CO + 5H_2 \qquad (2)$$

The optimization of hydrogen pyrolysis focuses on maximizing hydrogen output by reaching thermodynamic equilibrium, characterized by the minimization of enthalpy. The equilibrium composition is established through numerical methods, considering variables such as temperature, pressure, and the composition of reactants. By utilizing ethane and steam as feedstocks, the process relies on reducing enthalpy under constant temperature and pressure, to determine the ideal conditions for achieving the highest hydrogen yield. The system of simultaneous chemical reactions examined in this study, which encompasses N components, can be characterized by the thermodynamic function of free enthalpy (H), expressed as follows [13]:

$$H = n^T \mu = \sum_1^N n_i \mu_i \qquad (3)$$

The vector n^T represents the molar quantities of each component 'i,' while μ^T denotes the vector of chemical potentials corresponding to the respective components involved in the reaction (Table 1).

Table 1 – Standard chemical potentials for Steam-Ethane pyrolysis

Component	μ_i/RT
CH_4	3.425
C_2H_4	13.743
C_2H_2	17.707
CO_2	-42.948
H_2	0
CO	-22.812
O_2	0
H_2O	-20.100
C_2H_6	14.458

In chemical processes, energy transfer is facilitated by work and heat, both of which are contingent upon the specific conditions of the process. As a state function, enthalpy remains invariant to the reaction pathway, allowing for the establishment of standardized enthalpy data across diverse reactions. In the pyrolysis of ethane in the presence of steam, the reaction is classified as endothermic, necessitating considerable energy input to attain thermodynamic equilibrium essential for optimal hydrogen production. This requirement arises from the fact that the products possess a higher enthalpy than the reactants, thereby necessitating the addition of heat to propel the reaction forward [14].

For this study, enthalpy H of steam-ethane pyrolysis reactions is given by next equation:

$$H = \sum_{i=1}^{N} n_i \left[\mu_i^0(T) + RTln\, p + RTln \frac{n_i}{\sum_{i=1}^{N} n_i}\right] \quad (4)$$

where $\mu_i^0(T)$ represents the standard chemical potential of component i and R denotes the gas constant [16].

To attain thermodynamic equilibrium, the enthalpy of the reaction must be minimized while adhering to the principles of atomic mass conservation.

3. FORMULATION OF THE OPTIMIZATION PROBLEM FOR MINIMIZING THE REACTION ENTHALPY

To achieve thermodynamic equilibrium, the enthalpy of the reaction needs to be minimized, all while following the laws of atomic mass conservation. This condition facilitates maximum hydrogen production, as the system stabilizes at an optimal energy state where the conversion of reactants to products occurs with maximum efficiency. Thus, we formulate the following nonlinear optimization problem with constraints, where H is the reaction enthalpy [15]:

$$min\{H = \sum_1^N n_i \mu_i | \sum_1^N a_{ji} n_i = b_j\,, j = 1, 2, \dots, m\} \quad (5)$$

The mathematical model used to describe the process enthalpy function presents several limitations that arise from its simplifying assumptions. The enthalpy has a linear behavior being a direct result of the fact that simulation was made considering an equilibrium point defined by certain temperature and pressure conditions.

In mathematical terms, solving the optimization problem described in the following chapter involves identifying a saddle point by minimizing the enthalpy within the concentration space. From a process perspective, this corresponds to determining the equilibrium operating point, as the minimization is performed under fixed process conditions—constant temperature and pressure. Through this study, we will demonstrate that temperature and pressure significantly influence hydrogen production

Next, this paper focuses on enhancing theoretical hydrogen production by leveraging technological parameters and key chemical data, including reaction products, atomic matrices, standard chemical potentials, and atomic abundances. The theoretical hydrogen yields achievable at equilibrium during pyrolysis reactions will be predicted through simulation. Additionally, the optimization of the process will be approached using the Lagrange multiplier method, which will facilitate the maximization of hydrogen production while maintaining compliance with the constraints of atomic conservation.

Considering equations (1), (2), (3), (4), and (5), the optimization problem for minimizing the reaction enthalpy function criterion is formulated as follows:

$$\min_{n_1, n_2, \dots, n_N} H = \sum_{i=1}^{N} n_i \left[\mu_i^0(T) + RTln\, p + RTln \frac{n_i}{\sum_{i=1}^{N} n_i}\right] \quad (6)$$

with next constraints

$$\sum_1^N a_{ji} n_i = b_j\,, j = 1, 2, \dots, m \quad (7)$$

As there can be no negative numbers of moles, then the condition $n_i \geq 0$ is self-evident.

In this context:

- a_{ji} refers to the elements of the atomic matrix, indicating the quantity of atoms of element 'j' within component 'i' of the system. For detailed information regarding the values of the elements involved, please refer to Table 2
- The term b_j denotes the atomic abundance of the chemical element 'j', representing the initial number of atoms of element 'j' introduced into the system.
- Additionally, 'm' signifies the total number of chemical elements present within the reaction system.

Table 2 - Atomic Matrix for Steam Ethane pyrolysis

Component	C (Carbon)	H (Hydrogen)	O (Oxygen)
CH_4	1	4	0
C_2H_4	2	4	0
C_2H_2	2	2	0
CO_2	1	0	2
H_2	0	2	0
CO	1	0	1
O_2	0	0	2
H_2O	0	2	1
C_2H_6	2	6	0

For this process, atomic matrix, containing a_{ji} elements is presented in Appendix A, while standard chemical potentials table is shown in Appendix B.

Reaction products for this pyrolysis are H_2, CO, CO_2, CH_4, C_2H_4, O_2, H_2O and C_2H_6, resulting in an N value of N = 9.

The atomic abundance vector in the right-hand side of the equality constraints is derived from the atomic matrix of components:

$$b^T = (2, 12, 3) \quad (8)$$

which are calculated as follows:

$$\begin{cases} b_1 = 0 \times 3 + 2 \times 1 = 2 \\ b_2 = 3 \times 3 + 6 \times 1 = 12 \\ b_3 = 1 \times 3 + 0 \times 1 = 3 \end{cases} \quad (9)$$

4. EXTREMAL ENTHALPY BY LAGRANGE MULTIPLIER METHOD

The model, as initially formulated, does not incorporate temperature and pressure variations during the process, which significantly impacts its accuracy in real-world applications where thermal and pressure gradients are present. Given that the chemical potential is inherently temperature-dependent, it directly influences equilibrium states, phase transitions, and reaction kinetics. Neglecting this dependency oversimplifies the thermodynamic behavior of the system. Additionally, the assumption of constant heat capacities disregards their typical variation with temperature, potentially leading to deviations in calculated enthalpy values. Entropy, a fundamental thermodynamic state function, is also omitted, despite its critical role in determining reaction spontaneity and energy distribution.

To enhance the model's predictive capability and applicability to real-world processes, it is necessary to account for the influence of temperature and pressure. By applying the Lagrange multiplier method at various equilibrium points—each defined by a (T, p) pair—it becomes possible to identify the optimal thermodynamic conditions under which enthalpy minimization ensures maximum hydrogen production.

In the following section, we will address the optimization problem outlined in (6), subject to the constraints specified in (7). Our goal is to compute the minimum enthalpy by employing the Lagrange multiplier method. So, we define the Lagrangian function as follows:

$$\mathcal{L} = H - \sum_{j=1}^{m} \lambda_j \left(\sum_{1}^{n} a_{ji} n_i - b_j \right) \qquad (10)$$

To ascertain the enthalpy optimum, we derive the system of equations based on the null gradient conditions. This involves computing the Lagrangian with respect to each variable n_i and each Lagrange multiplier λ_j [19]. The derived equations establish the foundational framework for determining the equilibrium composition corresponding to the minimum reaction enthalpy:

$$\frac{\partial \mathcal{L}}{\partial n_i} = \mu_i^0(T) + RTln\, p + RT + RTln\left(\frac{n_i}{\sum_1^N n_i}\right) - n_i RT \frac{1}{\sum_1^N n_i} - \sum_1^M \lambda_j a_{ij} = 0 \qquad (11)$$

$$\frac{\partial \mathcal{L}}{\partial \lambda_j} = \sum_1^N a_{ij} n_i - b_j = 0 \qquad (12)$$

Representing all components from (11) and (12) in matrix form, we arrive at the following (13):

$$\frac{\partial \mathcal{L}}{\partial n} = \mu + RTln\, p + RT\mathbf{1} + RTln\left(\frac{n}{1^T n}\right) - RT\frac{n}{1^T n} - A^T \lambda = 0$$

$$An = b \qquad (14)$$

where,

n = $[n_1, n_2, \ldots, n_N]^T$ is the vector of the quantities of moles

$\lambda = [\lambda_1, \lambda_2, \ldots, \lambda_m]^T$ is the vector of the Lagrange multiplicators

A=$[a_{ij}]$ is the atom matrix (Table 2).

5. RESULTS AND SIMULATIONS

Enthalpy optimization problem (6) withs constraints (7) was solved utilizing Lagrange multiplicators as optimization method, by implementing (11), (12), (13), (14) in Matlab.

The MATLAB implementation was designed to account for the previously mentioned conditions: defining the reaction enthalpy function and minimizing it using the Lagrange multiplier method. This process was performed around an operating point defined by the temperature-pressure pair (T, p).

Initially, we set the operating conditions at T=840°C and p=3.8 bar and executed the MATLAB designed routine, resulting in the following outcomes:

- hydrogen percentage:

  n_{H2} = 39.93%

- Lagrange solutions:

  $\lambda = [\lambda_1, \lambda_2, \lambda_3]^T = [-22\,605, 2456, -5466]^T$

- Components percentages:

  n_{CH4} = 10.46%
  n_{C2H4} = 2.01%
  n_{C2H2} = 1.38%
  n_{CO2} = 1.50%
  n_{H2} = 39.93%
  n_{CO} = 3.39%
  n_{O2} = 11.99%
  n_{H2O} = 25.59%
  n_{C2H6} = 2.93%

- Enthalpy value:

  H = 15294 J/mol

Figure 1 illustrates how the calculation of the objective function evolves.

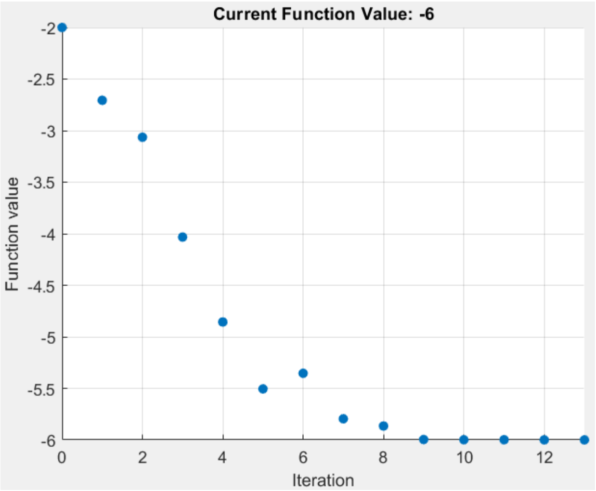

Figure 1. Optimization plot for starting point $x_0 = 2$

The optimization algorithm demonstrates robust convergence but is highly sensitive to initial conditions. Initializing far from the optimal region (e.g., near zero) significantly increases the number of iterations and the magnitude of Lagrange multipliers, reflecting greater computational effort to enforce feasibility. Conversely, starting from values closer to the expected solution (e.g., 2) improves efficiency by reducing iteration count. While less efficient, low initial values allow for broader solution space exploration, potentially avoiding local minima and capturing global optima.

The enthalpy minimization process exhibits stable convergence, with a consistent decline in both the objective function and first-order optimality, alongside progressive step-size reduction—typical of trust-region methods. Although the iteration count is high, the algorithm maintains robustness and convergence stability. Optimization efficiency could be further enhanced through advanced step-size control or convergence acceleration techniques.

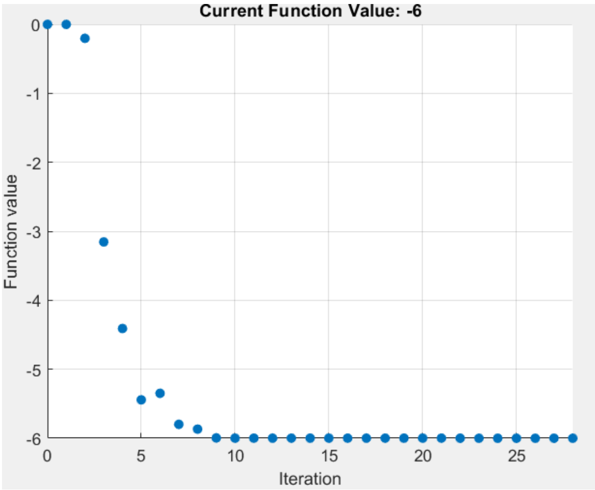

Figure 2. Optimization plot for starting point $x_0 = 0.001$

Considering this sensitivity and the fact that ethane steam pyrolysis occurs at high temperatures and relatively low pressures, we conducted the optimization at three different operating points: (T=850°C, p=4 bar), (T=840°C, p=3.8 bar, outcomes previously shown) and (T=870°C, p=4.2 bar). Effectively, this approach involved minimizing the enthalpy function at three distinct equilibrium conditions, with a continuous focus on maximizing hydrogen production.

Simulation outcomes for (T=850°C, p=4 bar) are as follows:

- Hydrogen percentage:

  $n_{H2} = 39.44\%$

- Lagrange solutions:

  $\lambda = [\lambda_1, \lambda_2, \lambda_3]^T = [-22\,605, 2456, -5466]^T$

- Components percentages:

  $n_{\mathrm{CH4}} = 10.60\%$
  $n_{\mathrm{C2H4}} = 2.01\%$
  $n_{\mathrm{C2H2}} = 1.33\%$
  $n_{\mathrm{CO2}} = 2.30\%$
  $n_{\mathrm{H2}} = 39.44\%$
  $n_{\mathrm{CO}} = 3.26\%$
  $n_{\mathrm{O2}} = 12.03\%$
  $n_{\mathrm{H2O}} = 25.97\%$
  $n_{\mathrm{C2H6}} = 3.05\%$

- Enthalpy value:

  $H = 12977$ J/mol

Simulation outcomes for (T=870°C, p=4.2 bar) are as follows:

- hydrogen percentage:

  $n_{H2} = 38.96\%$

- Lagrange solutions:

  $\lambda = [\lambda_1, \lambda_2, \lambda_3]^T = [-22\,605, 2456, -5466]^T$

- Components percentages:

  $n_{\mathrm{CH4}} = 10.74\%$
  $n_{\mathrm{C2H4}} = 2.01\%$
  $n_{\mathrm{C2H2}} = 1.28\%$
  $n_{\mathrm{CO2}} = 2.28\%$
  $n_{\mathrm{H2}} = 38.96\%$
  $n_{\mathrm{CO}} = 3.15\%$
  $n_{\mathrm{O2}} = 12.06\%$
  $n_{\mathrm{H2O}} = 26.35\%$
  $n_{\mathrm{C2H6}} = 3.16\%$

- Enthalpy value:

  $H = 70940$ J/mol

Also, to obtain the maximum hydrogen quantity, the optimum to steam/ethane ratio is $\frac{n_{H_2O}}{n_{C_2H_6}} = 3$.

The simulation results indicate the pair (T, p) that maximizes hydrogen production is (T=840°C, p= 3.8 bar).

The conducted thermodynamic analysis confirmed minimizing reaction enthalpy achieves thermodynamic equilibrium. The equilibrium thermodynamic of the steam-ethane pyrolysis reaction for hydrogen production is crucial, as it provides an efficient automation strategy for the pyrolysis process. This automation solution ensures the proper proportioning of the two reactants and maintains the reaction environment parameters—high temperature and low pressure—at values close to T=840°C and p=3.8 bar.

6. CONCLUSIONS

This study addressed the thermodynamic analysis of the ethane-steam pyrolysis reactions for hydrogen production, aiming to minimize the reaction enthalpy for maximizing hydrogen yield.

To achieve equilibrium in the process reaction, the optimization problem was addressed alongside equality constraints by employing the Lagrange multiplier method. As a result, an optimal operating point for the ethane pyrolysis process was identified, with the goal of maximizing hydrogen quantity

Optimal operating point was identified with a steam-to-ethane ratio of 3:1, which maximizes hydrogen production.

Simulations showed that the algorithm is sensitive to the starting point: smaller values led to a larger number of iterations and higher Lagrange multipliers.

Although robust, the convergence rate could be improved through refined step-size control or acceleration strategies.

While both pressure and temperature significantly influence hydrogen production, their impact becomes marginal near the thermodynamic equilibrium point. Close to T = 840°C and p = 3.8 bar, variations in operating conditions yield only minor changes in hydrogen output, indicating a region of process stability and robustness.

The simulation results identify the optimal thermodynamic conditions for hydrogen production via steam-ethane pyrolysis as T = 840°C and p = 3.8 bar.

The thermodynamic analysis confirms that enthalpy minimization leads to equilibrium, providing a reliable foundation for process control. Maintaining this temperature-pressure pair ensures efficient reactant proportioning and supports automation of the reactor under conditions favoring maximum hydrogen yield.

Based on the findings, we propose an automation solution that is economically viable, as it relies on low-cost raw materials—steam and ethane—which are both affordable and readily available in industrial contexts.

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