Research on Energy and Mass Integration of Green Electricity Hydrogen Production and Ammonia Synthesis

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Abstract. As we strive to attain "dual carbon goals," the chemical industry faces an immediate imperative to diminish its carbon emissions. Leveraging renewable energy to generate green hydrogen via water electrolysis for ammonia synthesis has emerged as a significant pathway towards the industry's green transformation—this not only effectively utilizes new energy but also promotes sustainable development. However, such an interconnected system encompasses a multitude of intricate processes, ranging from thermochemistry and electrochemistry to power cycles, each with varying energy input and output grades. The study seeks to elucidate the synergistic interplay of energy conversion and energy-mass exchange across these diverse processes within the integrated system. It necessitates solving optimization issues related to energy usage and heat exchange. By delving into the intricacies of the coupled system, we aim to uncover the fundamental principles and performance evaluation methodologies pertinent to system design. These insights can provide valuable guidance for the real-world application of new energy power-driven hydrogen production and green ammonia synthesis systems. Ultimately, widespread application of these renewable energy practices within the chemical industry will not only contribute to sustainable development but also help in further mitigating carbon emissions.

Keywords: Green electricity hydrogen production, ammonia synthesis, heat and mass transfer, energy and quality.

1. Introduction

In pursuit of goals such as achieving carbon peak by 2030 and carbon neutrality by 2060, the Chinese government has enacted numerous policies [1]-[4]. These policies aim to transition energy consumption from a heavy reliance on fossil fuels to a balanced utilization of green energy. However, the large-scale integration of new energy introduces uncertainty in power supply, potentially hindering its incorporation into the grid and user consumption. This could lead to significant waste of wind and photovoltaic power generation.

Hydrogen, as a clean energy medium with high energy density, is easy to store and transmit. Converting wind and photovoltaic power to produce hydrogen through water electrolysis can transform hard-to-store electrical energy into easily storable hydrogen energy. However, the economics of hydrogen storage present challenges, and meeting hydrogen demand remains problematic.

Traditional hydrogen production largely depends on carbon-based fossil energy sources such as coal and natural gas, resulting in substantial carbon emissions. Consequently, in the race to achieve the "dual carbon goal," producing green hydrogen through water electrolysis using renewable energy has emerged as a critical solution. This approach not only effectively utilizes new energy but also facilitates the green transformation of the chemical industry, significantly reducing carbon emissions and offering vast potential for scale.

Several domestic [5] [6] and international scholars, as well as institutions like the University of Cambridge and the University of Minnesota [7] [8], have made progress in studying foundational aspects, production technology, and economic operation models of producing green hydrogen and green ammonia from renewable energy.

The green hydrogen coupling system, comprised of multiple complex thermochemical, electrochemical, and power cycle processes, involves a variety of energy inputs and outputs of different grades. The system experiences complex energy conversions, mass exchanges, and intricate energy flows. Consequently, it's crucial to investigate the interaction characteristics between various processes within the system, as well as the synergistic effects of diverse energy conversions and energy-mass exchanges.

From a systems engineering perspective, Professor Ji Xu's team [9] at Sichuan University and scholars like H. Ishaq have used simulation software among other tools to research green hydrogen ammonia synthesis systems, aiming to enhance system efficiency and achieve efficient zero-carbon emissions.

In the process industry, to reduce production costs and use resources efficiently, process integration technology has evolved from optimizing single device operations to optimizing entire systems. Of these, the Pinch Point Design Method, developed by Linnhoff and others in the 1970s, is the most successful process integration technology. Starting from device heat flow analysis and based on thermodynamics principles, pinch technology analyzes energy flow distribution along temperature in the system from a macro perspective to identify the system's energy consumption "bottleneck."

Scholars worldwide have used pinch technology to optimize heat transfer in integrated systems. For instance, Dong Qiwu [10] and colleagues simulated the ammonia synthesis section of a large-scale ammonia synthesis plant using chemical engineering simulation software. They identified issues like large heat transfer temperature differences and unoptimized energy use and suggested improvements. Similarly, Xie Dongsheng [11] used Aspen Energy Analyzer software and pinch technology for energy-saving optimization of large-scale methanol synthesis processes..

2. Math Model

Water electrolysis hydrogen production technology uses electricity derived from renewable energy sources to split water into hydrogen and oxygen. Several variants of this technology exist, including the mature yet improvable alkaline water electrolysis technology, emerging proton exchange membrane (PEM) water electrolysis technology, solid oxide electrolytic cell (SOEC) technology, and anion exchange membrane water electrolysis technology.

Ammonia synthesis, or the Haber-Bosch process, involves the production of NH3 in a synthesis loop. During this process, hydrogen and nitrogen react at a 3:1 molar ratio under high temperature and pressure conditions, typically catalyzed by iron, to generate ammonia. The method employed to obtain hydrogen directly influences the NH3 production process.

These are some fundamental concepts and technologies related to green hydrogen and ammonia synthesis. By using renewable energy to electrolyze water, green hydrogen - a raw material for ammonia synthesis — can be produced. This not only enables the effective utilization of new energy but also serves as a crucial path for the green transformation of the chemical industry, significantly reducing its carbon emissions.

The ongoing development and refinement of water electrolysis hydrogen production technology, coupled with innovations in the ammonia synthesis process, are critical for achieving the carbon emission reduction goals in the sustainable energy and chemical industries.

$$\mathrm{N_2} + 3\mathrm{H_2} \leftrightarrow 2\mathrm{NH_3} \Delta H_{298\mathrm{K}} = -92.44 \frac{\mathrm{kJ}}{\mathrm{mol}} \tag{1}$$

The Haber-Bosch reaction is an important industrial process that uses an iron catalyst to react hydrogen and nitrogen to produce ammonia. According to the stoichiometric relationship of the Haber−Bosch reaction, the reactor rate equation for the reactants can be determined as follows:

$$r_{\mathrm{NH_3}} = -2r_{\mathrm{N_2}} = -\frac{2}{3} r_{\mathrm{H_2}} \tag{2}$$

The general equilibrium equation for thermodynamic analysis, the expression can be articulated as follows:

$$\sum\dot{m}_{\mathrm{in}} = \sum\dot{m}_{\mathrm{out}} \tag{3}$$

$$\begin{gathered}\dot{Q}_i + \dot{W}_i + \sum_i \dot{m}_i \left(h_i + \frac{V_i^2}{2} + gZ_i\right) = \\ \dot{Q}_e + \dot{W}_e + \sum_e \dot{m}_e \left(h_e + \frac{V_e^2}{2} + gZ_e\right)\end{gathered} \tag{4}$$

$$\sum_i \dot{m}_i s_i + \sum_i \left(\frac{\dot{Q}_k}{T_k}\right) + \dot{S}_{gen} = \sum_e \dot{m}_e S_e + \sum_e \left(\frac{\dot{Q}_k}{T_k}\right) \tag{5}$$

$$\begin{gathered}\sum_i \dot{m}_i ex_i + \dot{Q}_i \left(1 - \frac{T_0}{T}\right) + \dot{E}x_{Win} = \\ \sum_e \dot{m}_e ex_e + \dot{E}x_{Wo} + \dot{Q}_e \left(1 - \frac{T_0}{T}\right) + \dot{E}x_{dest}\end{gathered} \tag{6}$$

Among them, m represents the mass flow rate, i means the inlet, e represents the outlet, CV represents the control volume, Q is the heat transfer rate, W is the power, h is the specific enthalpy, V is the velocity, Z is the elevation angle, g is the gravity acceleration, and Sgen is Entropy is produced, T is the temperature, and Exdest represents the exergy destruction rate.

$$E\dot{x}^Q = \dot{Q}_i \left(1 - \frac{T_0}{T_s}\right) \tag{7}$$

Here, the factor ExQ are the heat transfer exergy, Ts is the boundary temperature and T0 is the ambient temperature. The correlation of calculating total workload, physical workload and chemical workload can be expressed below:

$$ex = ex_{ch} + ex_{ph} \tag{8}$$

$$ex_{ph} = h - h_0 - T_0(s - s_0) \tag{9}$$

$$ex_{ch} = \sum x_j ex_{ch}^0 + RT_0 \sum x_j \ln\left(x_j\right) \tag{10}$$

Among them, exch means chemical exergy, exph means physical exergy, h means specific enthalpy, s means specific entropy, R means the universal gas constant, excg 0 means standard chemical exergy, T0 means the reference temperature, and xj means the mole fraction.

The total energy efficiency of the system is defined by Equation 11, where ηNH3 is the number of moles of liquid NH3 in mol/s, LHVNH3 is the lower heating value of NH3, corresponding to 318 kJ/mol, and Pel, total refers to the total power requirement of the system., unit is kW:

$$\eta_{\mathrm{NH}_3} = \frac{\dot{n}_{\mathrm{NH3}} \times \mathrm{LHV}_{\mathrm{NH}_3}}{P_{\mathrm{el,total}}} \times 100 \tag{11}$$

In the formula, LHV_{NH_2} represents the low calorific value of 1""mol ammonia; $\dot{n}_{\mathrm{NH}_2}$ represents the ammonia synthesis rate.

The following diagram is a simulation diagram of an Aspen Plus project (Fig.1)

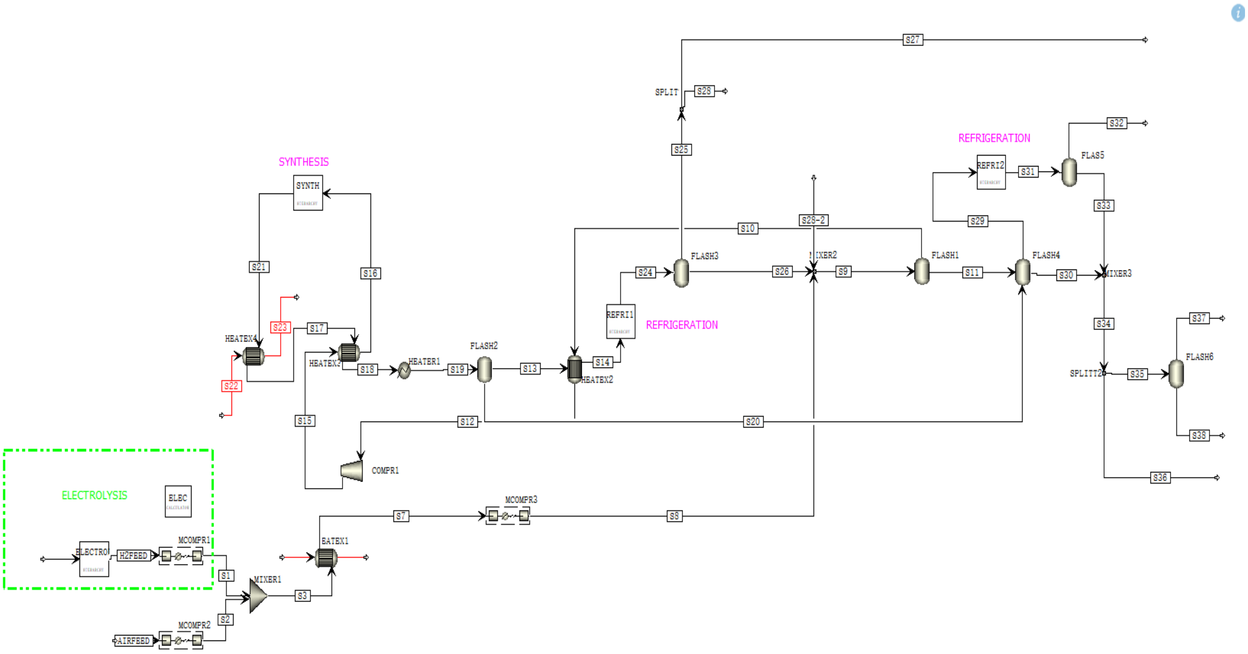

Figure 1. Simulation diagram of Aspen Plus for a certain project

3. Pinch Technology

Pinch technology is a method used for designing heat exchanger networks (HENs). The basic concept revolves around creating an initial network starting from the maximum heat recovery energy and then modifying that network based on the balance of equipment costs and energy costs to obtain an optimal heat exchange network structure.

In a process stream, the characteristic curve can be represented by a temperature-enthalpy diagram. On this diagram, the y-axis represents temperature (T), and the x-axis represents heat enthalpy (H). All hot streams in the process are continuously plotted on the temperature-enthalpy diagram according to the temperature change interval and the corresponding enthalpy change value, forming a hot stream composite curve from high to low temperature. Similarly, a cold stream composite curve can be drawn from low to high temperature. The heat change amount of the streams is represented by the enthalpy difference ΔH between two points on the x-axis.

When designing a heat exchange network in pinch technology, a minimum heat transfer temperature difference (ΔTmin) should be provided. This is the smallest allowable heat transfer temperature difference throughout the entire heat exchange network. On the temperature-enthalpy diagram, the hot stream composite curve is positioned at the upper left and the cold stream composite curve at the lower right. The cold composite curve is translated along the H axis, getting as close as possible to the hot composite curve. Throughout this process, the heat transfer temperature difference (ΔT) of each part gradually decreases, until the heat transfer temperature difference (ΔT) of a certain part finally equals ΔTmin. This point is known as the "pinch point," that the heat flux is zero.

The upper right corner of the diagram indicates that at least QH, min of heat must be provided by the hot utility to raise the cold stream to the target temperature. Conversely, the lower left corner indicates that at least QC, min of cooling must be provided by the cold utility to cool the hot stream to the target temperature. The maximum recoverable heat is QR, max.

There are two main methods for determining the location of the pinch point: T-H diagram method and problem table method.

(a) T-H Diagram Method

The T-H diagram method provides a simple, vivid, and intuitive representation of the pinch position within a process system. To pinpoint the process system's pinch point, the following information is required: composition, mass flow, pressure, initial and target temperatures of all process streams, and the corresponding heat exchange between selected hot and cold streams. Additionally, the minimum allowable heat transfer temperature difference (ΔT min) is essential. The steps to locate the pinch point on the T-H diagram are as follows:

Utilize the provided data on cold and hot logistics to plot the respective composite curves on the T-H diagram.

Overlay the hot composite curve above the cold one and gradually move them horizontally towards each other. The point where the vertical gap between the two curves precisely equals ΔT min identifies the pinch point.

(b) Question Form Method

This method becomes advantageous when dealing with numerous logistics, as using composite temperature and enthalpy lines can be cumbersome and less accurate. The question form method involves precise calculations and follows these steps:

Divide the temperature range based on the average temperatures of the cold and hot fluids. The average temperature for the hot fluid should be decreased by ΔTmin2 relative to the heat fluid, and increased by ΔT min2 relative to the cold fluid, ensuring the hot flow's average temperature in each zone surpasses that of the cold flow.

Calculate the heat balance in each temperature zone to ascertain the necessary heating and cooling.

Conduct a thermal cascade analysis without external heat input, evaluating the heat flux between each temperature zone under these conditions. Heat flux should descend from top to bottom between zones, without any reverse flow.

To ensure non-negative heat flux between zones, based on step 3 results, identify the minimum external heat required, indicating the least heating utility consumption.

Calculate the thermal cascade with the minimum heating utility input from outside. The heat exiting the final temperature zone represents the minimum cooling utility consumption.

The pinch point is located where the heat flux between temperature zones is zero.

Composite curves(Fig.2), hot-cold composite curves (Fig.3), and heat exchange network diagrams (Fig.4) for a large-scale water electrolysis hydrogen production and ammonia synthesis project can help in designing a suitable heat exchange network to maximize energy recovery and optimize energy consumption.

Please note that as a text-based AI, I'm unable to create or display diagrams or graphics. You'll need to use appropriate software tools to visualize this process based on the process data.

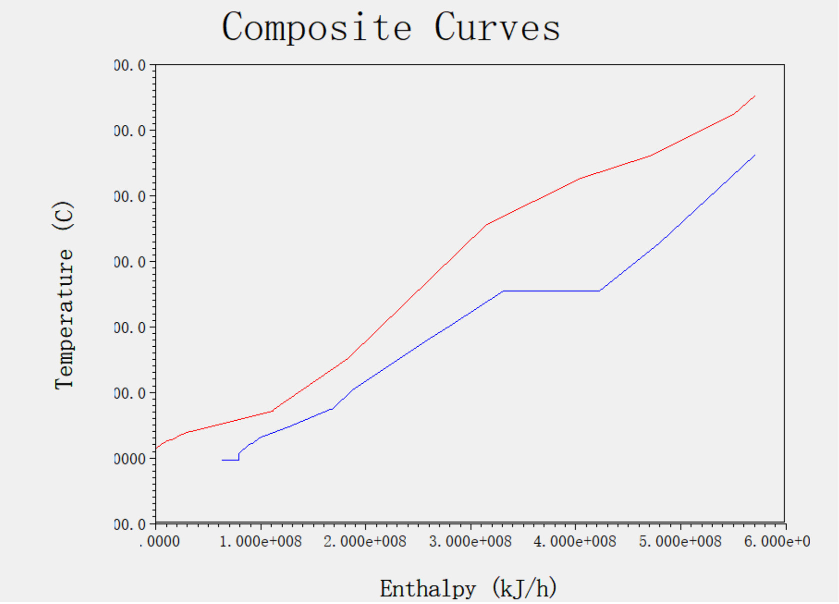

Figure 2. Combination Curve of a Certain Project

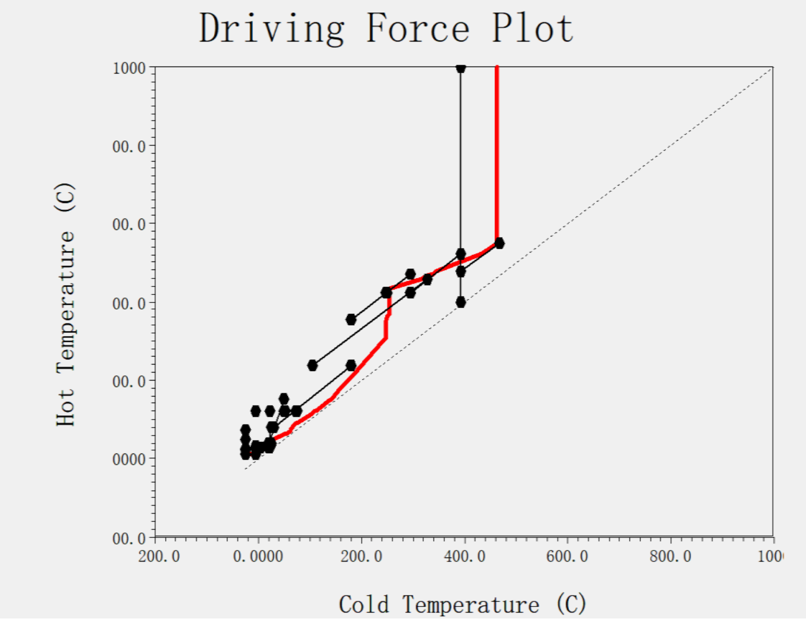

Figure 3. Cold and hot combination curve of a certain project

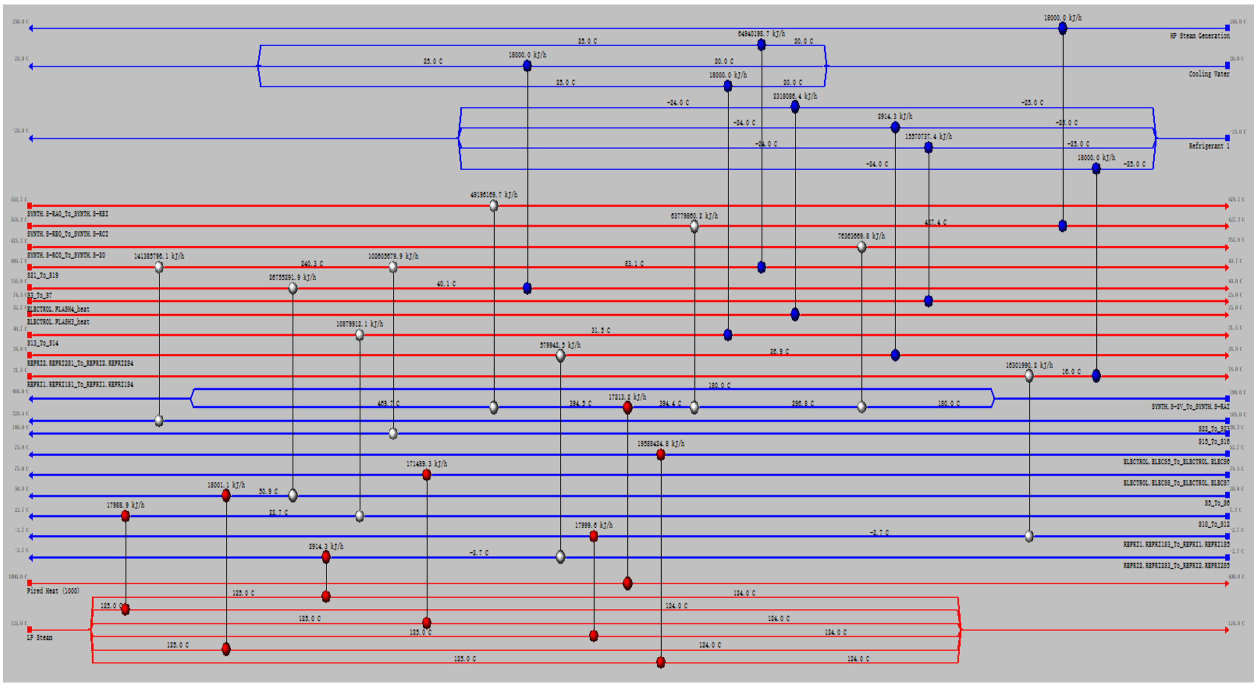

Figure 4. Heat exchange network diagram of a certain project

4. Conclusion

Achieving "dual carbon goals" in the context of the chemical industry involves reducing carbon emissions. One significant way of accomplishing this is by producing green hydrogen through the electrolysis of water using renewable energy. Despite its immense potential for scaling, most projects using renewable energy to produce hydrogen for ammonia/alcohol production are currently small-scale or in the startup phase, with no large-scale operational cases of green hydrogen ammonia production (green ammonia). Consequently, there are significant challenges in designing and operating large-scale renewable energy electrolysis systems for water to produce hydrogen and ammonia.

Such a coupled system consists of multiple complex processes, including thermochemistry, electrochemistry, and power cycles, and involves various grades of energy input and output. The energy conversion and mass exchange within this system are highly complex, with numerous material flows and even more complicated energy flows. Therefore, researchers need to explore the coupling and interaction characteristics of multiple processes within the system, understand the synergistic effects between different processes, and reveal the integration rules and essential characteristics of the coupled system. Through such research, the fundamental issues of system design can be unveiled, the system performance potential can be evaluated, and an engineering foundation and theoretical guidance for the development of high-efficiency, zero-carbon emission systems for hydrogen production and green ammonia synthesis powered by new energy can be provided.

In research, it is necessary to explore the synergistic effects of energy conversion and energy-mass exchange between various processes within the coupled system. This exploration may involve issues such as optimized energy use, thermal management, and catalyst design. Simultaneously, the material flow within the system needs to be studied, including raw material supply, product separation, and waste treatment, to ensure the system's efficient operation and environmental friendliness.

By conducting in-depth research on the coupling system, the basic principles and performance evaluation methods of system design can be revealed, providing guidance for the engineering implementation of new energy power-driven hydrogen production and green ammonia synthesis systems. This research will promote the widespread application of renewable energy in the chemical industry, further sustainable development, and reduce carbon emissions even more.

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