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Thermal Decomposition Pathways for Hydrogen Production: Selection and Efficiency Enhancement

Chengyan Sun*

School of Resources and Environmental Engineering, East China University of Science and Technology, Energy and Power Engineering, Shanghai 201424, China

**Corresponding author: Chengyan Sun.*

Abstract

The dual-carbon target has driven the low-carbon transformation of hydrogen energy. Thermal decomposition for hydrogen production, which can be coupled with high-temperature heat sources such as solar energy, nuclear energy, and industrial waste heat, has emerged as an important direction for green hydrogen production. This paper systematically reviews four core pathways: direct hydrothermal decomposition of water, pyrolysis of hydrocarbons, ammonia thermal decomposition, and thermochemical cycle water splitting. It compares their reaction mechanisms, process conditions, technical advantages and disadvantages, as well as applicable scenarios. Direct hydrothermal decomposition uses clean raw materials but requires ultra-high temperatures and remains at the fundamental research stage. Hydrocarbon pyrolysis technology is mature and serves as a transitional solution for the shift from fossil energy to hydrogen energy. Ammonia thermal decomposition features mild reaction conditions and is well-suited for distributed hydrogen supply scenarios. Thermochemical cycle water splitting reduces the required reaction temperature and represents the core technology for future large-scale zero-carbon hydrogen production. The study indicates that pathway selection must comprehensively consider factors including raw materials, heat sources, carbon emissions, application scenarios, and economic viability. In the future, thermal decomposition for hydrogen production will develop toward low-temperature and high-efficiency processes, coupling with clean energy sources, and system integration. These advancements will provide strong support for the industrialization of hydrogen energy and the low-carbon transformation of the energy sector.

Keywords

thermal decomposition for hydrogen production, efficiency, pathways

1. Introduction

The global energy transition is currently entering a critical phase from policy consensus to large-scale implementation. More than 140 countries worldwide have set explicit carbon neutrality targets, and the focus of energy transition has shifted from “emission reduction priority” to equal emphasis on decarbonization and energy security. China has become a core driving force in the global development of clean hydrogen energy. Under the “dual-carbon” target, the demand for low-carbon hydrogen production technologies has made the advancement of hydrogen production techniques particularly important. At present, mainstream hydrogen production technologies are still dominated by fossil fuel-based routes such as natural gas reforming and coal

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gasification. However, these processes generate substantial carbon emissions, which conflict with green development goals. Although water electrolysis can achieve zero-carbon hydrogen production, its large-scale industrial deployment still faces numerous bottlenecks due to the high cost of clean electricity and constraints related to power grid load.

Thermal decomposition for hydrogen production is driven by high-temperature thermal energy and can be coupled with high-grade heat sources such as solar thermal energy, nuclear energy, and industrial waste heat. It requires no large-scale electricity input and offers advantages in low-carbon environmental protection and energy compatibility. As a result, it serves as a key technology bridging traditional energy systems and renewable hydrogen systems and represents an important research direction in the field of green hydrogen production.

Thermal decomposition for hydrogen production encompasses multiple technical pathways, including direct thermal decomposition of water, thermochemical cycle water splitting, methane pyrolysis, and biomass pyrolysis. These pathways differ significantly in reaction mechanisms, process conditions, energy consumption levels, and application scenarios. Direct thermal decomposition of water produces hydrogen with high purity but requires ultra-high reaction temperatures, making engineering implementation extremely difficult. Thermochemical cycle water splitting effectively reduces the required reaction temperature, yet it faces challenges such as loss of cycling media and difficulties in separation and purification. Methane pyrolysis enables the resourceful utilization of carbon resources, but it suffers from high reaction energy consumption and easy deactivation of catalysts. Biomass pyrolysis for hydrogen production aligns with the concept of renewable recycling, yet it encounters issues including low hydrogen purity, difficult impurity treatment, and unstable conversion efficiency. Each hydrogen production method has its own advantages and disadvantages. Currently, the industry lacks a systematic pathway selection and evaluation system. The suitable scenarios and comprehensive benefits of different technical routes have not yet formed unified standards. Moreover, the optimization of core process parameters and the mechanisms for efficiency improvement remain unclear, which severely constrains the engineering implementation of thermal decomposition hydrogen production technologies.

This study focuses on the selection of thermal decomposition pathways for hydrogen production and the enhancement of efficiency. It employs a research approach consisting of literature review, pathway classification, parameter comparison, efficiency analysis, and improvement strategies. The study systematically compares the advantages, disadvantages, and applicable scenarios of various technical pathways. By comparing key parameters such as reaction temperature, catalyst ratio, and reaction residence time, it explores the influence patterns and enhancement mechanisms of hydrogen production efficiency. The research aims to clarify the optimal technical pathways and the best process parameters, thereby addressing the core challenges of relatively low conversion efficiency and insufficient selection basis in thermal decomposition hydrogen production. It seeks to provide theoretical support and technical references for the industrial application of thermal decomposition hydrogen production technologies. This study will not only improve the theoretical system of thermochemical hydrogen production but also contribute to cost reduction and efficiency improvement in green hydrogen energy. It holds significant theoretical value and practical importance for promoting low-carbon energy transition and safeguarding national energy security.

2. Classification and Fundamental Principles of Hydrogen Production via Thermal Decomposition

Hydrogen production through thermal decomposition is a technical route that relies on thermal energy to directly or indirectly break the chemical bonds of hydrogen-containing feedstocks (such as water, hydrocarbons, ammonia, methanol, etc.), thereby achieving the separation and preparation of hydrogen gas. It differs from water electrolysis, which is driven by electrical energy, and from fossil fuel reforming, which involves coupled oxidation-reduction reactions. Its core characteristic is the purely thermally driven cleavage and recombination of chemical bonds. This approach represents an important technological direction for achieving zero-carbon or low-carbon hydrogen production and for adapting to high-temperature heat sources [1, 2].

According to feedstock type, reaction mechanism, heat supply method, and relevant standards and specifications, thermal decomposition for hydrogen production is primarily classified into four core pathways:

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direct thermal decomposition of water, thermal pyrolysis of hydrocarbons, thermal decomposition of ammonia, and thermochemical cyclic water splitting. These technologies exhibit significant differences in reaction principles, operating conditions, and key characteristics, which form the fundamental basis for pathway selection [3, 4].

Direct thermal decomposition of water uses pure water as the feedstock and breaks the H-O covalent bonds through high-temperature thermal energy. This reaction can hardly proceed spontaneously under ambient temperature and pressure. Thermodynamic equilibrium constraints require reaction temperatures above 2500 °C to achieve a noticeable decomposition rate. It is theoretically the cleanest pathway with the most accessible feedstock among thermal decomposition routes. However, the extreme high-temperature conditions constitute the primary bottleneck for its industrial application [5].

Thermal pyrolysis of hydrocarbons employs hydrocarbon feedstocks such as natural gas, methane, biomass, and heavy oil. It achieves C-H bond cleavage through anaerobic or oxygen-lean pyrolysis, simultaneously producing hydrogen and solid carbon. A typical reaction is methane pyrolysis, with operating temperatures generally ranging from 800 to 1400 °C. This technology has relatively high maturity and enables carbon capture and resource utilization. It serves as a transitional technology for the shift from the current fossil energy system toward a hydrogen energy economy [6, 7].

Thermal decomposition of ammonia utilizes liquid ammonia as a hydrogen storage carrier. Under the action of catalysts, it releases hydrogen through thermal decomposition at reaction temperatures of 400–600 °C. This pathway offers advantages including high hydrogen storage density, ease of feedstock storage and transportation, and simple product separation. It is well suited for distributed hydrogen production and hydrogen supply scenarios for fuel cells [8, 9].

Thermochemical cyclic water splitting divides the single-step high-temperature decomposition of water into multiple sequential thermochemical reactions at moderate to low temperatures, thereby circumventing the need for extreme high temperatures. The overall reaction remains the decomposition of water into hydrogen and oxygen. The temperature of individual steps can be reduced to 800–1500 °C. This method represents the core improved pathway to overcome the bottlenecks of direct thermal water decomposition and is currently a research hotspot in thermal decomposition-based hydrogen production [10].

3. Mainstream Technical Pathways for Hydrogen Production via Thermal Decomposition

3.1 Direct Thermal Decomposition of Water

The core advantages of direct thermal decomposition of water lie in its zero-carbon feedstock, pure products, and absence of by-products. Throughout its life cycle, it consumes only water and thermal energy. This pathway is compatible with high-temperature clean energy sources such as concentrated solar energy, nuclear energy, and industrial waste heat, making it the ultimate low-carbon thermal decomposition route for hydrogen production [2, 5].

However, the technology faces three major technical barriers. First, the thermodynamic constraints are extremely stringent. The required reaction temperature exceeding 2500 °C far surpasses the limits of conventional industrial heat sources and can only be achieved through concentrated solar power, high-temperature nuclear reactors, or plasma heat sources. The cost and stability of heat supply remain insufficient [4]. Second, the reaction kinetics are slow. At high temperatures, the reverse recombination reaction of hydrogen and oxygen is intense, necessitating rapid product separation to suppress the reverse reaction. This imposes extremely high requirements on reactor structure and separation technology [5]. Third, material durability is inadequate. Under ultra-high temperatures and strongly oxidizing atmospheres, reactor materials are prone to corrosion, creep, and failure. Industrial breakthroughs in high-temperature oxidation-resistant material systems have not yet been achieved [4].

At present, this technology remains at the laboratory basic research stage. Trace hydrogen production has only been realized in small-scale test devices using plasma assistance or solar concentrator coupling. There remains a significant gap to large-scale industrial application [4].

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3.2 Thermal Pyrolysis of Hydrocarbons for Hydrogen Production

Thermal pyrolysis of hydrocarbons is currently the most technologically mature and widely industrially applied pathway among thermal decomposition routes. Methane (natural gas) pyrolysis and biomass pyrolysis constitute the core research directions [6, 7].

Methane pyrolysis for hydrogen production operates at moderate temperatures (800–1200 °C). The technical route has achieved pilot-scale demonstration. Hydrogen purity can exceed 95 %, and the co-produced solid carbon can be applied in carbon materials, metallurgy, soil improvement, and other fields, enabling a closed-loop carbon resource utilization. Compared with conventional natural gas steam reforming, it can reduce carbon dioxide emissions by more than 90 % [6].

Biomass pyrolysis for hydrogen production uses agricultural and forestry residues as well as organic waste as feedstocks. It falls within the category of renewable energy-based hydrogen production. The reaction temperature ranges from 500 to 900 °C. This pathway combines carbon cycle neutrality with waste resource utilization and is suitable for distributed applications in rural areas and industrial parks. However, it faces challenges such as high moisture content in the feedstock, complex composition, large fluctuations in hydrogen yield, and tar by-products that easily clog the reactor [7].

The core shortcomings of this pathway lie in its strong dependence on feedstock. Fossil-based hydrocarbon pyrolysis still entails implicit carbon emissions, while biomass feedstock is limited by regional availability, seasonal variations, and collection costs, restricting large-scale deployment. In addition, catalyst deactivation due to carbon deposition at high temperatures and low efficiency in solid carbon separation and collection are key issues constraining hydrogen production efficiency and continuous operation [7].

3.3 Thermal Decomposition of Ammonia for Hydrogen Production

Ammonia, as a zero-carbon hydrogen storage carrier, offers the advantages of high volumetric hydrogen storage density (approximately 17.6 wt% for liquid ammonia), easy liquefaction and transportation under ambient temperature and pressure, and well-established infrastructure. The reaction conditions for ammonia thermal decomposition are mild (400–600 °C), significantly lower than those of water thermal decomposition and hydrocarbon pyrolysis. It can be driven by industrial waste heat or low-grade thermal energy, resulting in high energy utilization efficiency and strong system integration. Consequently, it has become the preferred thermal decomposition pathway for distributed hydrogen supply, onboard hydrogen supply for fuel cell vehicles, and hydrogen production in remote areas [8].

The core of ammonia decomposition technology lies in the development of high-efficiency catalysts. Traditional iron-based catalysts exhibit low activity and require high reaction temperatures. Ruthenium- and platinum-based noble metal catalysts demonstrate excellent activity but are prohibitively expensive. Non-noble metal-based catalysts (nickel-, cobalt-, and molybdenum-based) have therefore become a research focus. Through support modification, elemental doping, and structural regulation, their low-temperature catalytic activity and stability can be significantly enhanced [8]. In addition, incomplete ammonia decomposition leads to trace ammonia residues in the produced hydrogen, necessitating efficient purification systems. This is a critical issue affecting applications in precision equipment such as fuel cells. Furthermore, ammonia production still relies on conventional Haber-Bosch processes; achieving a closed-loop zero-carbon life cycle requires the synthesis of green ammonia using green electricity and green heat [9].

3.4 Thermochemical Cyclic Water Splitting for Hydrogen Production

Thermochemical cyclic water splitting introduces intermediate media (such as metal oxides, halides, and sulfides) to divide the single-step high-temperature decomposition of water into 2–5 sequential medium- to low-temperature thermochemical reactions. The temperature of individual steps is controlled between 800 and 1500 °C. This approach enables direct coupling with high-temperature gas-cooled reactors, concentrated solar power, and industrial high-temperature waste heat, thereby avoiding the demand for extreme high temperatures, substantially improving thermal energy utilization efficiency, and serving as an engineering-oriented improvement pathway for direct thermal water decomposition. It represents a core direction for future large-scale zero-carbon thermal decomposition hydrogen production [10].

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More than one hundred thermochemical cycles have been reported to date. Mainstream pathways include the sulfur-iodine cycle (S-I), manganese-iron cycle (Mn-Fe), zinc oxide cycle (ZnO), perovskite-type oxide cycles, and others. Among them, the sulfur-iodine cycle has the highest technological maturity, with a reaction temperature of approximately 850 °C and a theoretical hydrogen production efficiency exceeding 50 %. It has already completed kilowatt-scale pilot demonstrations [10, 11]. Metal oxide cycles (such as those based on \ce{CeO2} and \ce{Fe3O4/FeO}) rely on redox reactions to achieve water splitting. These pathways feature simple reaction routes and minimal by-products, making them particularly suitable for coupling with concentrated solar thermal sources, and have become a research hotspot in recent years [12].

The core challenges of this pathway include insufficient cyclic stability, as intermediate media are prone to loss and deactivation. The multiplicity of reaction steps leads to complex system integration, significant heat losses, and high investment in separation and purification equipment. The economic viability and operational reliability of large-scale implementation still require further optimization [10, 12].

3.5 Comprehensive Comparison of the Four Core Pathways and Influencing Factors

In terms of technological maturity, the ranking is as follows: thermal pyrolysis of hydrocarbons > thermal decomposition of ammonia > thermochemical cyclic water splitting > direct thermal decomposition of water. Regarding feedstock cleanliness, direct thermal decomposition of water and thermochemical cyclic water splitting (using water as feedstock) rank highest, followed by ammonia thermal decomposition (using green ammonia), biomass pyrolysis, and fossil-based hydrocarbon pyrolysis. In terms of reaction temperature requirements, ammonia thermal decomposition (400–600 °C) < hydrocarbon pyrolysis (500–1400 °C) < thermochemical cyclic water splitting (800–1500 °C) < direct thermal decomposition of water (> 2500 °C). With respect to compatible heat sources, ammonia thermal decomposition and hydrocarbon pyrolysis are suitable for low- to medium-grade waste heat, thermochemical cyclic water splitting is compatible with medium- to high-temperature nuclear heat and solar energy, while direct thermal decomposition of water can only be coupled with ultra-high-temperature specialized heat sources. In terms of application scenarios, ammonia thermal decomposition is suitable for distributed hydrogen supply, hydrocarbon pyrolysis for large-scale industrial hydrogen production, thermochemical cyclic water splitting for large-scale zero-carbon hydrogen production bases, and direct thermal decomposition of water remains at the basic research stage [4, 8]. Pathway selection requires multi-dimensional trade-offs based on feedstock availability, heat source conditions, application scenarios, carbon emission requirements, and economic viability [3].

The selection of a thermal decomposition pathway for hydrogen production is not a choice based solely on the superiority of a single technology, but rather a systematic decision involving the coupling of multiple factors, including technical feasibility, feedstock supply, heat source conditions, carbon emission constraints, application scenarios, and economic performance. Different regions, industries, and scales of application require matching with differentiated technical routes [3].

The availability and cost of feedstock supply constitute the fundamental constraints. In regions with abundant water resources and sufficient clean energy, priority should be given to the deployment of direct thermal water decomposition and thermochemical cyclic hydrogen production [2, 10]. In natural gas-producing areas and fossil energy bases, fossil-based hydrocarbon pyrolysis can be prioritized, with simultaneous integration of carbon resource utilization [6]. In agricultural and forestry regions rich in biomass resources, biomass pyrolysis for hydrogen production is appropriate [7]. In scenarios with well-developed liquid ammonia storage and transportation infrastructure and urgent demand for distributed hydrogen supply, ammonia thermal decomposition is the preferred choice [9].

Heat source conditions determine technical compatibility. Low-grade waste heat (< 600 °C) is only suitable for ammonia thermal decomposition and low-temperature biomass pyrolysis [8]. Medium- to high-temperature heat sources (800–1500 °C) are compatible with hydrocarbon pyrolysis and thermochemical cyclic water splitting [11]. Ultra-high-temperature specialized heat sources (> 2500 °C) can only support laboratory research on direct thermal water decomposition [4]. The availability of clean energy heat sources directly determines the carbon intensity of hydrogen production. Thermal decomposition pathways coupled with nuclear heat, solar energy, or industrial waste heat represent the core options for achieving zero-carbon or low-carbon hydrogen production [10].

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Carbon emission constraints and policy orientation serve as key guiding factors. Under the “dual carbon” targets, fossil-based hydrocarbon pyrolysis should only be used as a transitional technology and must be strictly integrated with carbon capture, utilization, and storage (CCUS). Green ammonia thermal decomposition, biomass pyrolysis, thermochemical cyclic water splitting, and direct thermal water decomposition constitute the long-term mainstream directions. Policy subsidies and carbon trading mechanisms will further promote the large-scale application of low-carbon pathways [3].

Application scenarios and scale determine technology selection. Large-scale industrial hydrogen production bases (at the level of ten thousand tons per year) should prioritize thermochemical cyclic water splitting and natural gas pyrolysis to meet the requirements of scale and low cost [11]. Distributed small-scale hydrogen production units (at the level of hundreds of tons per year or below) should prioritize ammonia thermal decomposition and biomass pyrolysis, which are suitable for modular design, easy operation and maintenance, and utilization of low-grade waste heat [8]. Onboard and portable hydrogen supply scenarios are only compatible with low-temperature, miniaturized pathways such as ammonia thermal decomposition.

Economic viability and technological maturity are prerequisites for practical implementation. At present, the hydrogen production costs of hydrocarbon pyrolysis and ammonia thermal decomposition have achieved market competitiveness. Thermochemical cyclic water splitting remains in the pilot stage with relatively high costs, while direct thermal water decomposition has not yet achieved industrialization. Pathway selection must balance short-term deployability with long-term technological iteration [3].

4. Development Trends and Future Outlook

In response to the demand for zero-carbon and large-scale development of hydrogen energy, hydrogen production via thermal decomposition will form a layered and progressive technological structure:

Thermochemical cyclic water splitting will become the core direction for medium- to long-term zero-carbon hydrogen production, with emphasis on coupling with high-temperature nuclear heat and concentrated solar power. Efforts will focus on simplifying processes and improving cyclic stability [10, 12]. Ammonia thermal decomposition, leveraging its advantages in low-temperature operation, high efficiency, and storage-transportation, will primarily target distributed hydrogen supply scenarios and advance toward low-cost catalysts and closed-loop green ammonia systems [8, 9]. Hydrocarbon pyrolysis, with a focus on biomass, will serve as a low-carbon transitional technology while simultaneously achieving carbon resource utilization [7]. Direct thermal decomposition of water will continue to emphasize basic research and gradually explore decomposition pathways under milder conditions [4].

In the future, thermal decomposition for hydrogen production will deeply integrate with high-temperature industry, nuclear power, and solar energy. Through innovations in materials, catalysts, and system integration, costs will be reduced, standard systems will be improved, and the technology will progressively transition from laboratory scale to industrialization, and from transitional technology to a mainstream zero-carbon solution [3].

5. Conclusions

This paper provides a review of hydrogen production technologies based on thermal decomposition. It systematically examines the fundamental principles, technical characteristics, and applicable scenarios of the four mainstream pathways: direct thermal decomposition of water, thermal pyrolysis of hydrocarbons, thermal decomposition of ammonia, and thermochemical cyclic water splitting. These pathways exhibit significant differences in reaction temperature, feedstock dependence, technological maturity, and cleanliness. In practical applications, reasonable selection must be made through comprehensive consideration of feedstock supply, heat source conditions, carbon emission requirements, and economic factors. Overall, ammonia thermal decomposition is suitable for distributed hydrogen supply, hydrocarbon pyrolysis is technologically mature and can serve as a transitional solution, thermochemical cyclic water splitting represents the key direction for future large-scale zero-carbon hydrogen production, and direct thermal decomposition of water remains at the basic research stage. In the future, hydrogen production via thermal decomposition will develop toward low-temperature and high-efficiency operation, coupling with clean energy sources, and system integration.

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Through continuous innovation in materials and processes, energy efficiency will be improved and costs reduced, gradually realizing industrialization and low-carbon applications.

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Conflicts of Interest

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