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A review of hydrogen generation methods via aluminum-water reactions

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ABSTRACT

This article presents a comparison of the various methodologies reported in the literature to generate hydrogen through the reaction between aluminum powders and water. This reaction, however, is hindered by the surface oxide layer, which prevents direct contact between pure aluminum and water. The low cost of aluminum, its infinite recyclability, and the potential to carry out the reaction in an environmentally sustainable manner make it a promising material for hydrogen production. Given the critical need to address the limitations of hydrogen storage and transportation, as well as to accelerate the adoption of hydrogen as an energy carrier for the energy transition, this comparison focuses on the two most environmentally promising methodologies: ball milling and steam oxidation methodologies.

1. Introduction

The global demand for energy is increasing at an unprecedented rate, driven in large part by continuous population growth and rapid industrialization. As the world's population approaches 9 billion by 2050, the pressure on existing energy infrastructures will only intensify. Historically, this demand has been met predominantly through the use of fossil fuels—coal, oil, and natural gas—which have powered industrial economies for over a century and now cover the 80 % of the energetic global need with petrol and gas that cover the 53–55 % [1–3]. However, the heavy reliance on these non-renewable sources has led to serious environmental concerns, including greenhouse gas emissions, climate change, and air pollution.

The transition to renewable energy sources such as solar, wind, and hydropower is now widely recognized as a critical step to mitigate these environmental impacts. Renewable energy offers a cleaner, more sustainable alternative to fossil fuels, with the potential to drastically reduce carbon emissions and promote long-term energy security. Yet, despite the growing awareness of these benefits, the pace of transition remains slow, hindered by technological, economic, and political challenges.

Actually, although hydrogen is the most abundant element on Earth, it is rarely found in its free state, as it is almost always bonded to other atoms, such as oxygen in water or carbon in hydrocarbons. This makes hydrogen difficult to access directly in its pure form. Nevertheless, hydrogen is a highly promising energy carrier because it burns without releasing greenhouse gases, producing only water as a byproduct. This makes it an attractive alternative for clean energy applications, particularly in the context of reducing carbon emissions [4–6].

To utilize hydrogen as an energy source, it must first be liberated from its compounds, which requires specific methods and technologies. Hydrogen can be produced through various processes, including water electrolysis, steam methane reforming, and biomass gasification [7,8].

The challenges associated with hydrogen is the storage and transportation due to hydrogen's high explosiveness (with an explosive range of 4.0–75.6 % in air), which complicates its safe handling and limits the broader adoption of hydrogen as an energy source. Hydrogen can be stored in three main ways: compressed gas, cryogenic liquid, and cryo-compression. Compressing hydrogen to high pressures (up to 700 bar) demands significant energy and strong materials, along with regular safety checks. In liquid storage, hydrogen is cooled below its boiling point (−252.87 °C), requiring tanks with advanced thermal insulation and durable materials; moreover, the liquefaction process consumes about 30 % of hydrogen's total energy. Cryo-compression combines gaseous and cryogenic methods, cooling hydrogen to cryogenic temperatures and compressing it to pressures between 250 and 350 bar, offering a balanced solution to the limitations of the other two techniques [9].

Considering all these critical aspects, it is essential to explore complementary solutions alongside renewable energy, such as the use of

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aluminum powders to produce hydrogen. These powders, which can be derived from industrial waste or commercially available materials, offer a promising avenue for energy production, further diversifying the options for a sustainable future.

Aluminum powder is identified as an ideal material for portable hydrogen generation because of its cost-effectiveness, environmental friendliness, high hydrogen yield when reacting with water, and minimal pollution in its reaction products [10]. This quality makes aluminum-based materials particularly useful for mobile applications, where conventional propulsion systems may be replaced with hydrogen-fueled engines or fuel cells [10–14] or in scenarios like field engineering and operations in isolated or extreme environments, where conventional hydrogen storage or transport is challenging [6,15–18].

Several studies have investigated how to react aluminum powder with water, following the reaction that results in the production of heat, aluminum oxide/hydroxide and hydrogen.

Unfortunately, to initiate the reaction between aluminum and water, it is necessary to break the aluminum oxide layer that forms upon contact with air. The destabilization of the alumina layer, having a melting point of 2072 °C, requires either a chemical action involving the use of corrosive substances, or a mechanical action, or the application of high temperatures and pressures.

The reaction can occur in three different forms depending on the operating temperature. Specifically, under atmospheric pressure and without any additives, bayerite ($Al(OH)_3$) or gibbsite (γ-$Al(OH)_3$) forms within the temperature range of 20 °C to 280 °C. Conversely boehmite (AlOOH) tends to form at temperatures below 20 °C, while alumina (Al_2O_3) is preferentially produced at temperatures exceeding 480 °C [19,20]:

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \quad \Delta H = -16.3\ kJ/g\ of\ Al\ (20 - 280^\circ C) \tag{1}$$

$$2Al + 4H_2O \rightarrow 2AlOOH + 3H_2 \quad \Delta H = -15.5\ kJ/g\ of\ Al\ (280 - 480^\circ C) \tag{2}$$

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2 \quad \Delta H = -15.1\ kJ/g\ of\ Al\ (> \ 480^\circ C) \tag{3}$$

The stoichiometry of the H_2O-Al reaction demonstrates significant yield for hydrogen production. Specifically, reacting 1 g of aluminum with 2 g of water generates 0.112 g of H_2, corresponding to 1.2 NL (Normal Liters) of hydrogen. Considering the high calorific value of hydrogen (120 MJ/kg), 0.112 g of H_2 equates to an energy of 13.4 kJ. Moreover, the reaction is highly exothermic, releasing an additional 16.3 kJ of thermal energy. Consequently, the total energy output from 1 g of aluminum is 29.7 kJ.

The literature presents other reviews on hydrogen generation through the reaction between aluminum and water. However, this review paper stands out from previous studies for some reasons.

Firstly, this study differs from other review papers in the literature because, in addition to examining the activation methods of aluminum powders in water, it also considers the use of steam as a conversion medium. This latter technique, which has not been discussed in previous reviews, represents a direct approach to hydrogen production, as it does not require a preliminary activation phase of the powders.

Secondly, the existing review papers primarily analyzed studies where aluminum is used in various shapes, including sheets, powders, chips, and pellets. In contrast, this work focuses almost exclusively on aluminum in form of powder, providing a comprehensive and systematic overview of the state of the art in this specific domain. The aim is to promote the recycling and reuse of waste aluminum powder, which would otherwise be disposed of in landfills with significant environmental impact. While other forms of aluminum are relatively easier to recycle, waste aluminum powder, composed of micrometric and nanometric particles that is highly reactive and hazardous, pose significant challenges for recovery, particularly for industries that generate this kind of waste powder.

2. Methodologies

The current literature offers various methods to dissolve or break the oxide layer that inhibits the reaction.

The methodologies can be classified into activation methods and conversion methods. Activation methods involve a preliminary treatment that makes aluminum powders reactive upon contact with water. Consequently, these methods consist of two sequential phases: the activation treatment followed by the aluminum-water reaction. Conversely, conversion methods do not require a preliminary activation step and involve a single reaction phase, specifically the aluminum-steam oxidation.

Activation methods

1. Ball milling: mechanical ball milling enhances aluminum reactivity by reducing particle size, increasing surface area, and creating defects that interrupt the natural Al_2O_3 passivation layer. Conducted in an inert atmosphere, this process produces micro or nano-scale powders with high reactivity, especially in Al-water reactions. Additives like salts or metals further boost activity by forming reactive composites, while the milling action introduces microcracks and imperfections critical for sustained reactions. Nevertheless, it is necessary to assess whether the energy expended on grinding is recovered through the H_2 production [21,19,22,23].
2. Atomization (high-pressure gas jet in an atomization chamber): this approach offers several advantages, most notably the ability to produce powders with a uniform distribution of alloying elements like bismuth and tin, while also enabling precise control over microstructure and specialized morphologies. Atomization also facilitates rapid removal of the oxide layer and ensures complete powder reactivity, leaving no unreacted material. However, the technique has drawbacks, as it requires specialized equipment and stringent process control [24–26].
3. Low melting point alloys: the activation of aluminum for hydrogen generation via hydrolysis is significantly enhanced by the addition of low melting point metals such as gallium (Ga), indium (In) and tin (Sn). The Ga-In-Sn phase forms a liquid coating on aluminum grains. This coating provides diffusion channels, enabling aluminum to access reaction sites and maintain a high hydrogen production rate. However, it's important to note that Ga and In are expensive elements [27,28]. Since this review focuses on hydrogen generation methods through the reaction between aluminum powder and water, this method will not be examined, as it is primarily applied to foils, ingots or other aluminum-based material forms rather than powders.

Conversion methods

1. Alkaline or acidic solutions such as caustic soda (NaOH), potassium hydroxide (KOH), hydrochloric acid (HCl): they can react rapidly with aluminum, dissolving the surface layer. However, these are toxic and hazardous substances. They can also easily corrode the equipment used. Variables such as temperature, aluminum size and porosity, pH, and solution concentration strongly influence reaction kinetics [12,29].
2. Steam oxidation: this approach holds significant promise as it leverages high temperatures or pressures to initiate and sustain the reaction, eliminating the need for catalysts or additives that could generate undesirable by-products, particularly from a circular economy perspective. Steam efficiently infiltrates the porous oxide, ensuring the reaction progresses effectively. Even in this case, it is crucial to evaluate the energy balance, as the system expends energy in generating and superheating the steam necessary for the reaction with the aluminum [30–33].

The objective of this paper is to provide an overview and comparison of all the methodologies which enable the reaction of aluminum powders with H_2O to generate hydrogen with a focus on the two most promising from the environment perspective: the ball milling and the high-temperature and high-pressure reaction. As already mentioned, onsite hydrogen production from aluminum powders represents a potential solution to the challenges associated with hydrogen transportation and storage. Furthermore, utilizing waste aluminum powders could serve as an effective means of recycling industrial waste while simultaneously producing a sustainable energy carrier.

3. Activation methods

3.1. Ball milling

Mechanical ball milling is an extensively studied and effective method for activating aluminum particles to enhance their reactivity, particularly in the aluminum-water reaction [22]. Conducted in an inert atmosphere, ball milling both reduces the particle size of aluminum and increases its surface area, facilitating shorter induction times and higher hydrogen production rates [34]. This high-speed operation impacts, grinds, and compresses aluminum particles, causing them to break and generating defects and dislocations within the lattice structure [35,36].

The ball milling process is unique in that it combines mechanical alloying with milling [37]. Large aluminum particles are reduced to fine powders, potentially even nano-powders, creating Al-based composites with high reactivity. Milling with different additives, such as salts, metals [38,39], metal oxides, metal hydrides, further enhances aluminum's hydrolytic activity by forming composites, like Al-chloride or Al-oxide, with increased reactivity [36]. The milling balls fracture deformed aluminum particles, thereby introducing microcracks, defects, and surface imperfections, which disrupt the natural Al_2O_3 passivation layer that would otherwise inhibit the aluminum-water reaction [40,41].

Additives used in the milling process adhere to or penetrate aluminum particles, enhancing reactivity by creating new pathways for water penetration. These pathways open local gates in the oxide layer, enabling better contact between aluminum and water [42].

Thus, ball-milled aluminum composites exhibit irregular shapes, cracks, and rough surfaces that significantly expand their reaction area. The result is a highly reactive material with improved kinetics for hydrogen generation via hydrolysis, as the structural imperfections and increased grain boundaries enable more efficient and sustained hydrogen production.

Procedure

The procedure generally proceeds as follows: aluminum powder and additives are mixed with a planetary ball mill or hand-milled using a glass mortar. Eventually, after milling, the solid fuel mixture can be pressed into a pellet using a pellet press machine. In this case the reaction then takes place by immersing the pellet in water [43,21].

The experimental setup typically includes three main components: the reactor vessel, the tank vessel, and the collection vessel. The reactor vessel is pre-loaded with aluminum powder (or pellets) mixed with additives, which have been prepared using a ball mill. Water is stored in the tank vessel and supplied to the reactor vessel as needed. The hydrogen gas generated during the reaction is first cooled to room temperature using a heat exchanger, then passed through a drying or condensation system to eliminate moisture from the gas stream. The condensed water vapor is collected in the collection vessel. The rate of hydrogen production is monitored using either a mass flowmeter or a gas analyzer.

3.1.1. Ball milling with salt

Milling aluminum with salt enhances its activation. The local gates opened during milling are temporarily blocked by salts, preventing the reoxidation of the surface oxide layer when exposed to ambient air. When these powders are subsequently immersed in water, the salts dissolve, allowing the reaction between water and the pure aluminum core of the particles to occur. For this reason, powders milled with salts can be stored in air without undergoing reoxidation, thereby maintaining their reactivity with water. This process also creates defects in the aluminum oxide layer, reduces particle agglomeration, increases the specific surface area, improving the powder's reactivity [23,44,45].

This technique is particularly advantageous compared to others because it requires only salt and aluminum, without the need for high water temperatures or corrosive agents.

Hydrogen production phases

After the ball milling, when the powder is immersed in water, hydrogen production occurs in three main phases, characterized by a specific reaction progression [22,23,46].

Induction phase: during this initial period, the reaction is limited as the aluminum-water system stabilizes. The duration of this phase depends on water temperature, salt type and milling time, ranging from a few seconds to several minutes. At this stage, salts begin to dissolve, locally opening the oxide surface and initiating particle surface hydration.

High-kinetics phase: hydrogen production accelerates rapidly due to the increased specific surface area of aluminum and the dissolution of salts, allowing more efficient water access to the metal. With a significant salt concentration (at least a 0.5 % molar ratio), numerous local openings form on the surface increasing the reactive surface area and enhancing reaction kinetics.

Low-Rate phase: as the reaction progresses, hydrogen production slows down due to the buildup of solid byproducts, mainly aluminum hydroxide, which block active surfaces and limit water access. This accumulation occurs alongside the reaction between aluminum and water, generating H_2 and depositing aluminum hydroxide within the pores, progressively decelerating the reaction.

Reaction products and byproducts

The byproducts of the reaction consist of solid aluminum oxides that remain as residue.

According to Swamy and Shafirovich [23], the nature of the byproduct depends on the reaction temperature. At lower temperatures, around 35 °C, the reaction produces a mixture of bayerite ($Al(OH)_3$) and boehmite (AlOOH). As the temperature increases to a range between 50 °C and 80 °C, boehmite becomes the predominant product. This shift is due to the greater thermodynamic stability of boehmite at elevated temperatures.

Alternatively, Czech and Troczynski [46] provide a slightly different perspective with more specific temperature ranges. At temperatures below approximately 55 °C, the primary byproduct is bayerite, typically formed in cooler or moderately warm aqueous environments. At temperatures above 90 °C, approaching the boiling point of water, boehmite becomes the dominant product. This transition occurs because the additional thermal energy at higher temperatures facilitates the chemical transformation leading to boehmite formation.

Yield

Milling with salts enables high yields in hydrogen production. The yield depends on several factors (Table 2):

- Water temperature
- Salt molar ratio
- Milling time
- Type of salt

Water temperature

Higher temperatures increase the reaction rate and yield because they facilitate the breakdown of the protective aluminum oxide layer and enhance molecular collisions and reaction kinetics [23,45-49].

Czech et Troczynski [46] verified that at low temperatures (22 °C) the reaction is very slow with yields below 2 %. At moderate temperatures (40–55 °C), the yield significantly improves, reaching a maximum of 80–92 % at 55 °C. Higher temperatures (70–90 °C) further accelerate the reaction, achieving 89 % yield at 70 °C and consuming all available aluminum at 100 °C.

Wang et al. [50] discovered how the initial temperature of the water plays a crucial role in enhancing hydrogen production for Mg60–Al30–Fe10 (wt%) powder. As the temperature increases, the hydrogen generation rate and yield improve significantly. At 0 °C, the conversion yield is 79.93 %, while at 40 °C, it reaches 99.88 %, with a corresponding increase in the hydrogen generation rate from 138 ml.min^{-1}.g^{-1} at 0 °C to 778 ml.min^{-1}.g^{-1} at 40 °C. The heat generated during the hydrolysis reaction further raises the local solution temperature, which promotes faster hydrogen production. Wang et al. achieved higher yields at lower temperatures compared to Czech and Troczynski due to the presence of Mg and Fe, which reduce the activation energy.

Salt molar ratio

The study by Alinejad & Mahmoodi [44] defines the optimal ratio to maximize hydrogen yield and provide the powders with long-term air storage capability. This molar ratio between salt and aluminum powders is 2:1 which reached a yield of 100 % instead of the 60 % yield for the ratio 1:1. Conversely, Czech and Troczynski [46] reported that a lower weight ratio of salt (Al:KCl; 1:1) compared to that used by Alinejad and Mahmoodi was found to be less unfavorable, resulting in the maximum hydrogen production volumes of 1210 ml.g^{-1}H_2 (89 % yield). Therefore, considering the studies by Alinejad & Mahmoodi (Fig. 1) and Czech and Troczynski [46] it can be concluded that an optimal molar Salt: Aluminum ratio is 1.5 or 2.

Wang et al. [50], differently, explored how the concentration of NaCl in the solution affects the hydrogen generation performance for Mg60–Al30–Fe10 (wt%) powder. Low NaCl concentrations produce limited hydrogen, but as the concentration increases, the hydrogen yield and rate increase. For example, increasing the NaCl molarity from 0.05 to 0.6 M, the material increased a hydrogen yield from 88 % to 100 % and a generation rate from 180 to 500 ml.min^{-1}.g^{-1}.

Milling time

Milling aluminum powder increase the specific surface area and decrease average particle size, leading to uniformity and better performance. A higher specific surface area enhances the reactivity of aluminum with water, increasing the rate and efficiency of hydrogen production [22,23,36,47]. Specific surface area can be measured using techniques such as BET (Brunauer-Emmett-Teller) analysis, which quantifies available surface area through gas adsorption.

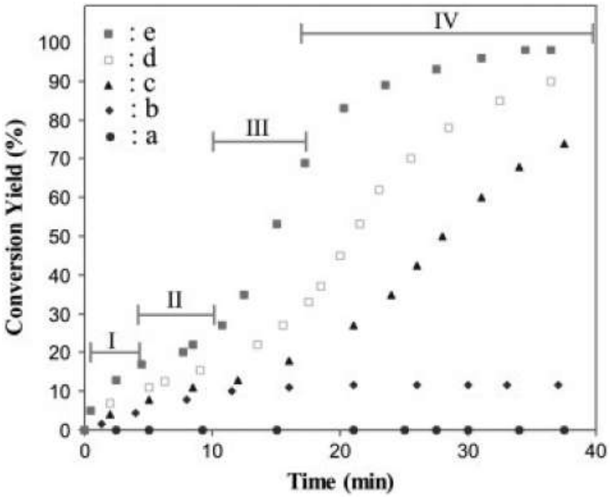

Fig. 1. Effect of various salts: Al mole ratios on the rate and efficiency of hydrogen generation: a) 0.1, b) 0.2, c) 0.5, d) 1 and e) 1.5 [22].[1]

For example, Czech et Troczynski [46] after 15 min of milling obtained an increasing of the specific surface area from 0.30 m^{2}g^{-1} to 9.7 m^{2}g^{-1}, and with 60 min of milling, it can reach 31.6 m^{2}g^{-1}, significantly boosting both reaction rates and hydrogen yield. As shown in the Fig. 2 aluminum milled for 60 min with KCl achieved a maximum yield of 85 %, corresponding to 1200 mL of H_2/g of aluminum, in just 15 min of reaction. In comparison, aluminum milled for 7.5 min with NaCl yielded 42 %, and 600 mL of H_2/g of aluminum, over 15 min of reaction.

On the debit side, Swamy and Shafirovich [23] measured the energy consumed during milling, reporting a consumption of 450 kJ per gram of aluminum for a milling duration of 30 min. Considering the energy balances discussed in the Introduction, the maximum energy yield obtainable from 1 g of aluminum is 16.3 kJ (Eq. (1)), which corresponds to only 3,5 % of the energy consumed during milling. Therefore, the hydrogen production system described in this study is not energetically sustainable, although its efficiency could potentially be improved by increasing the quantity of milled powder.

Wang et al. [50] explored how the ball milling process significantly influences the reactivity of the Mg-Al-Fe material. As the milling time increases, the reactivity improves due to a reduction in particle size and the formation of fresh active surfaces and micro-galvanic cells. Milling for 4 h (the maximum duration test) yielded the best results, with the hydrogen conversion rate increasing from 33.84 % (1h milling) to 99.66 %, and the maximum hydrogen generation rate increasing from 16.60 ml.min^{-1}.g^{-1} to 687.60 ml.min^{-1}.g^{-1}. The longer milling time creates more defects and fresh surfaces, enhancing the material's ability to generate hydrogen.

Dossi [51], in contrast, employed the patented NHEMA technology [52], which involves activating powders through mechanical milling in a stainless steel vessel under dry air for just 15 min achieving a yield greater than 97 %. The milling media consist of stainless steel balls with diameters of 6 mm and 3 mm, and the ball-to-powder size ratio is maintained at 20:1. After milling, the powders are stored under ambient conditions with humidity levels between 20 % and 40 %. Dossi thus identifies an activated powder mixture of Al/Bi/Zn at 90/5/5 wt%, which, utilizing the NHEMA technology, produces 100 g of H_2 per kilogram of aluminum powder.

Type of salt

Swamy and Shafirovich [23] used NaCl that is particularly effective due to its low cost, ease of removal, non-toxicity. Czech et Troczynski [46] compared KCl and NaCl for the same milling duration and KCl proves to be more effective. The superiority of KCl is attributed to its more uniform interaction with aluminum during milling, facilitating the

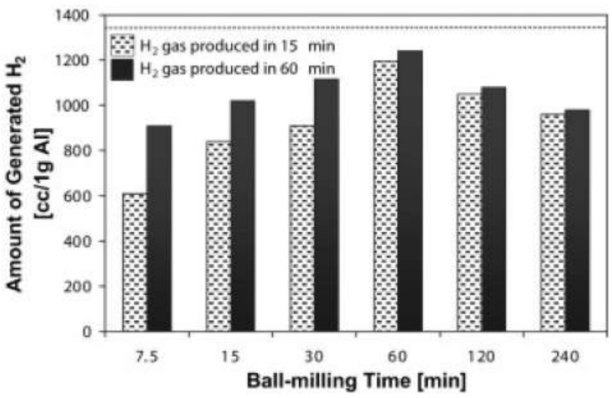

Fig. 2. Effect of ball-milling time on the amount of hydrogen produced from 1 g Al powder after 15 min and 60 min of the Al–H_2O reaction. Al–KCl (50 wt%) system. (T_{water} = 55 °C) [46].[2]

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[2] Reprinted from [46], Copyright (2009), with permission from Elsevier.

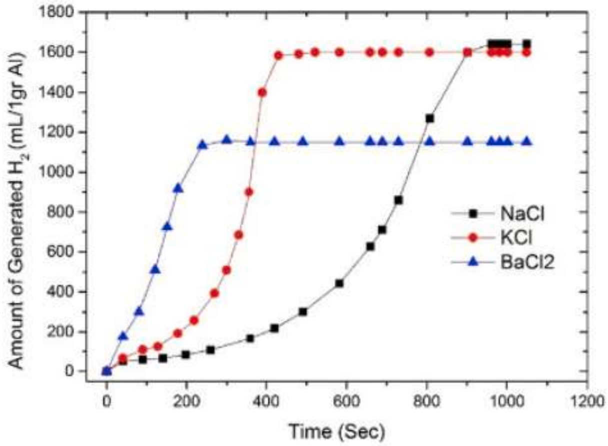

Fig. 3. Effect of type of salt on the hydrogen generation yield after ball milling for 5 h [21].[3]

creation of highly porous and reactive surfaces.

Even Irankhah et al. [21] tested the effect of salt type on hydrogen production comparing NaCl, KCl, and $BaCl_2$. NaCl produced the highest cumulative hydrogen, while $BaCl_2$ yielded the lowest, likely due to its microstructural properties and distinct coating mechanism during milling. The highest hydrogen generation rate was achieved with KCl (857 ml.min^{-1}.g^{-1}), whereas NaCl showed the highest total yield (Fig. 3).

Sodium Stannate and NaOH

In the literature, cross-cutting approaches that employ multiple activation techniques have also been explored. For example, the simultaneous use of NaOH and salts such as Na_2SnO_3.

Sodium stannate (Na_2SnO_3) significantly improves the aluminum-water reaction for hydrogen generation by enhancing efficiency and addressing passivation challenges. It accelerates hydrogen production, achieving higher rates and yields [43,53]. Na_2SnO_3 mitigates the passivation of aluminum by forming metallic tin (Sn), which prevents cohesive oxide layers and ensures sustained hydrogen release [54]. Additionally, it allows for lower NaOH concentrations, reducing system corrosion while maintaining performance [43,53-54]. Indeed, the compound also exhibits synergistic effects when combined with other alkaline additives, further optimizing reaction kinetics [53,43]. These benefits make Na_2SnO_3 a valuable additive for efficient and practical hydrogen generation systems.

In the initial stage of the process, the stannate ion released by dissolving Na_2SnO_3 in a strongly alkaline medium predominantly exists as the $Sn(OH)_6^{2-}$. Metallic aluminum, acting as a reducing agent, partially converts this species into metallic tin (Sn) according to the reaction [53]:

$$4Al + 3Sn(OH)_6^{2-} \rightarrow 4Al(OH)_4^{-} + 3Sn + 2OH^{-} \quad (4)$$

The resulting Sn particles deposit locally on the aluminum surface and, rather than directly accelerating the cathodic reduction of water, they inhibit the repassivation of the aluminum oxide layer. As a consequence, the metallic surface remains chemically accessible, promoting a more efficient attack by water (in the presence of OH^-) and enabling hydrogen generation at lower NaOH concentrations than would otherwise be required.

Dai et al. [53] tested the combination of NaOH and Na_2SnO_3. 1.25 M NaOH with 0.04 M Na_2SnO_3 showed the best performance, achieving a hydrogen generation yield of 100 % (H_2 rate: 2500 ml.min^{-1}.g^{-1}) instead of a yield of 38 % (H_2 rate: 550 ml.min^{-1}.g^{-1}) without Na_2SnO_3. This finding was corroborated by Ga et al. [43], who reported a nearly 100 % yield (H_2 rate: 1800 ml.min^{-1}) within 3 min using a solution of 1 M NaOH and 0.1 M Na_2SnO_3.

Conversely, systems relying solely on NaOH required significantly higher concentrations, such as 3.75 M, to achieve 100 % yield, resulting in lower reaction rates (1420 ml.min^{-1}.g^{-1}). While low concentrations of NaOH (e.g., 0.75 M) resulted in limited hydrogen production, Macanás et al. [54] further substantiated this observation, demonstrating that a NaOH molarity of 0.01 M yielded only 22 % conversion with reduced reaction rates. Ga et al. [43] similarly confirmed this trend, reporting a 60–70 % conversion within 8 min with 1.5 M NaOH, achieving a peak hydrogen generation rate of only 860 ml.min^{-1}.

Regarding the use of sodium stannate (Na_2SnO_3; 0.25 M) not in addition but in place of NaOH, Macanás et al. [54] achieved the highest hydrogen generation rate of 343 ml.min^{-1} (H_2 yield: 33 %), thereby demonstrating that Na_2SnO_3 alone is insufficient and requires combination with NaOH for optimal performance. This conclusion is supported by Ga et al. [43], who observed that 0.3 M Na_2SnO_3 alone resulted in a maximum hydrogen generation rate of only 280 ml.min^{-1}.

Thus, the inclusion of Na_2SnO_3 in conjunction with NaOH enables high hydrogen yields even at moderate alkali concentrations, enhancing the overall versatility of the system.

$BiCl_3$

$BiCl_3$ introduced to the aluminum powder through ball milling enhances the hydrolysis reaction performance of aluminum. This high-energy environment created substantial physical stress on the particles, resulting in the formation of microcracks on the aluminum surface. Under conditions of intense friction, collision, and shear, the brittle and sharp-edged $BiCl_3$ particles further contributed by embedding themselves into the aluminum and disrupting the natural oxide layer, thereby facilitating increased reactivity.

The presence of $BiCl_3$ introduces bismuth (Bi) into the composite. Due to the difference in electrochemical potentials between aluminum and bismuth, micro-galvanic cells are formed. In these cells, aluminum acts as the anode and bismuth as the cathode, accelerating the anodic dissolution of aluminum and thereby enhancing the hydrolysis reaction [55,56].

Gai et al. explored the ball milling process using only $BiCl_3$ in one study [55] and developing an aluminum-based composite, combining $BiCl_3$ with γ-Al_2O_3 (gamma alumina, a catalyst with high mechanical strength [57]) in another [56].

In the first study [55], the Al–$BiCl_3$ composite achieved the highest hydrogen generation rate of 646.0 mL min^{-1} g^{-1}, with a reaction time of 1.6 h and a hydrogen yield of 93.3 % with a 3 h ball milling time compared to a yield of 86.7 % with a 1 h ball milling. This result underscores the efficacy of prolonged ball milling in enhancing the reactivity of the Al–$BiCl_3$ composite for hydrogen generation. Anyway, increasing the milling duration will raise the cost of producing activated Al hydrogen because ball milling is an energy-intensive process.

In the other study the addition of $BiCl_3$ and γ-Al_2O_3 [56] drive a catalytic effect. Its high surface area provides active sites that facilitate the adsorption and dissociation of water molecules, thereby accelerating the reaction kinetics and improving the overall efficiency of hydrogen production (Fig. 4). The highest hydrogen yield observed was 98.5 % for the composite with 5 wt% $BiCl_3$ and 5 wt% γ-Al_2O_3, after 2 h of milling and 5.4 h of reaction time.

Patented technologies

The method patented by Boyle et al. [58] employs both metal oxides (magnesium oxide (MgO) or calcium oxide (CaO)) and inorganic salts (NaCl or KCl) to facilitate the hydrogen production reaction. These materials are arranged in specific configurations (concentric layers, spirals, or zones with variable concentration) to modulate the reaction rate and intensity within cartridges designed to optimize the process.

The analyzed patent does not mention any mechanical pre-treatment for powder activation. This suggests that the described technology has replaced mechanical activation via ball milling with the combined use of salts and metal oxides.

Magnesium oxide (MgO) and calcium oxide (CaO), being highly

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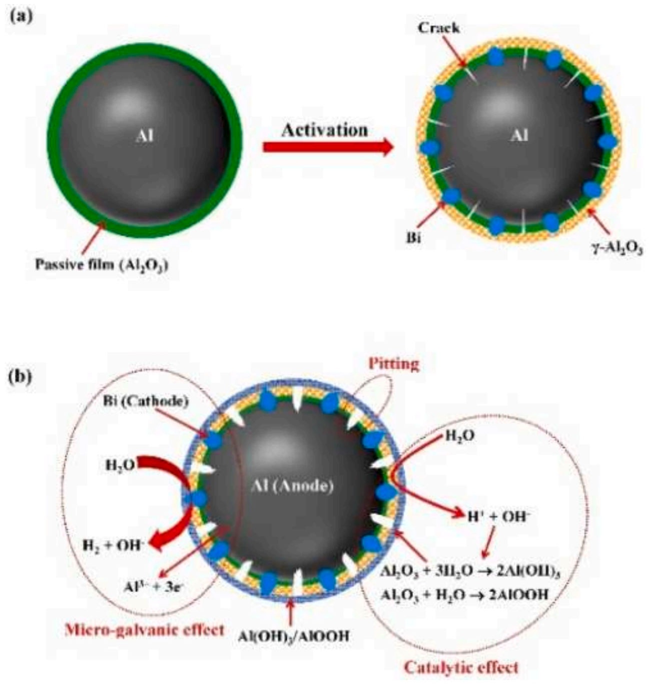

Fig. 4. Activation mechanism (a) and hydrogen production mechanism (b) of Al/$BiCl_3$/γ-Al_2O_3 composite [56].[4]

hygroscopic, react rapidly with water to form their respective hydroxides while releasing thermal energy in the process. These reactions are exothermic, leading to an increase in the local temperature of the reactive mixture, thereby facilitating system activation:

$$CaO + H_2O \rightarrow Ca(OH)_2 \Delta H < 0 \quad (5)$$

$$MgO + H_2O \rightarrow Mg(OH)_2 \Delta H < 0 \quad (6)$$

Simultaneously, the use of soluble inorganic salts (NaCl or KCl) promotes the removal of the passive aluminum oxide (Al_2O_3) layer through a pitting corrosion mechanism. In aqueous solution, the soluble salts dissociate into sodium (Na^+) and chloride (Cl^-) ions. The Cl^- ions exert a corrosive effect on the protective metal oxide layers. By penetrating the micro-defects in the Al_2O_3 layer, the Cl^- ions facilitate its degradation, thereby exposing the underlying metallic aluminum.

This process induces the formation of microscopic cavities (pits), allowing water to directly contact the metal, thereby promoting the aluminum-water reaction and the subsequent hydrogen production.

The method NHEMA patented by Dossi et al. [52] outlines a process for controlled hydrogen gas production using tablets composed of mechanically activated powders. These tablets are created by mixing aluminum powder (70–99 %), bismuth powder (0.5–20 %), and a third component chosen from salts (e.g., NaCl, $MgCl_2$), water-soluble polymers (e.g., PEG, PEO), or sugars (e.g., glucose, sucrose) in proportions ranging from 0.5 % to 20 %. The mixture is processed in an acoustic resonant mixer, which alters the powders' granulometry and reactivity. The activated powders are then compressed into tablets or embedded in a molten polymer to create compact and porous structures. These configurations enable precise modulation of the reaction rate with water, facilitating controlled hydrogen release. The hydrogen release is regulated by design parameters such as the compression level, which slows water penetration, and waterproof coatings on certain surfaces to delay the reaction. The hydrogen yield can reach up to 97 %.

3.1.2. Ball milling with metals

The activation of aluminum powders for reaction with water can be significantly influenced by the introduction of low-melting metals and their alloys, such as gallium (Ga), indium (In), bismuth (Bi), tin (Sn), and zinc (Zn), through mechanochemical treatments [59–63] (Table 1). These elements primarily enhance the reactivity of aluminum by dissolving or disrupting the protective oxide layer on its surface, thereby promoting intergranular fracture and the formation of intermetallic compounds. Activation can be attributed to the Rebinder effect, which reduces the cohesion between metal grains, as well as to the formation of corrosive galvanic cells, in which aluminum serves as the anode during hydrolysis [59,61].

The penetration of these metals into the grain boundaries of aluminum leads to a reduction in the material's mechanical strength, facilitating its milling into powder and accelerating its oxidation process in the presence of water [62,63]. Notably, the use of liquid metals at room temperature prevents the formation of the protective oxide film and enhances the diffusion of aluminum nanoparticles through the liquid phase to the surface, thereby increasing direct interaction with water [60].

Ga-In-Sn-Zn

Ilyukhina et al. [59] explored the activation of aluminum powder with Gallium (Ga) and Indium (In) using planetary ball mill. They first investigated the reaction between water and powders activated through mechanical milling with an alloy composed of Ga-In. The study reported a hydrogen yield of up to 95 % using the alloy at a concentration of 10 wt % across temperatures of 20, 40, and 60 °C, confirming that under these conditions, temperature has no significant impact on the yield. Conversely, the temperature was observed to influence the reaction rate, which increased from 1250 $ml.min^{-1}.g^{-1}$ at 21 °C to 1750 $ml.min^{-1}.g^{-1}$ at 40 °C and further to 2500 $ml.min^{-1}.g^{-1}$ at 59 °C.

Parmuzina et al. [63] explored the activation of aluminum powder using Ga-In and Ga-In-Sn-Zn eutectics. Results show that treated powders, especially smaller particles at higher temperatures (80 °C), produce hydrogen efficiently. Their experiments revealed that the addition of Sn and Zn does not lead to a decisive increase in yield, which only slightly improves from 99.4 % to 99.5 %.

Sevastyanova et al. [62] conducted studies to investigate the effect of salt solutions on hydrogen generation from aluminum-based alloys (Al-20 %Bi) and (Al-7 %Ga-3 %In). In the first case, the addition of salts (NH_4Br, $NaHCO_3$, K_2HPO_4) increased the hydrogen yield (88–95 % compared to 86 % without salts). However, for the Al-7 %Ga-3 %In alloy, the addition of salts (NH_4Cl, NaBr, $KHSO_4$) provided no benefit (89–90 % compared to 97 % without salts).

Manilevich et al. [61] discovered that the addition of 5 wt% Ga-In-Sn eutectic alloy served as a catalyst allowing water to diffuse through the aluminum grains. Indeed, the alloy's low melting point (∼11 °C) facilitated the penetration of water into the activated aluminum particles. Furthermore h-BN (boron nitride, added in small percentages, 1–3 wt%) assisted in reducing cold welding between aluminum particles during the milling process, ensuring that the grains remained separated and reactive. The study obtained that activated aluminum pellets, enriched with 5 wt% Ga-In-Sn eutectic alloy and 1 or 3 wt% h-BN, react efficiently with water at temperatures between 5 and 25 °C, producing over 1000 mL of H_2/g Al. At 25 °C, with 3 wt% h-BN, the hydrogen production rate increases fivefold, achieving a yield of 98.3 %.

Lithium

Lithium can play a key role in enhancing aluminum's hydrolysis reaction by disrupting the oxide layer on its surface and diffusing into the aluminum matrix during the milling process. This diffusion induces structural changes that prevent re-oxidation, increasing reactivity with water. Furthermore, lithium introduces imperfections in aluminum particles and increases their surface area and energy, which are critical for improving hydrolysis efficiency and rate.

The exothermic reaction between lithium and water generates localized heat, further accelerating the process. These combined effects

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Table 1
Comparative table of different studies on the ball milling methodology with metals carried out at ambient pressure, by measuring the hydrogen yield with the water displacement method.

Powder composition	Reaction temperature [°C]	Size [μm]	Mass [g]	Hydrogen generation rate [ml. min^{-1}.g^{-1}]	Ball milling time [h]	Time [min]	Hydrogen yield %	Reference
Al-Li5-Bi5 %wt	25	sub-micron	0.3	609	15	~30	100	[65]
Al-Li10-Bi5 %wt	25	sub-micron	0.3	572	15	~30	100	[65]
Al-Li15-Bi5 %wt	25	sub-micron	0.3	708	15	~30	100	[65]
Al-Li20-Bi5 %wt	25	sub-micron	0.3	988	15	~30	100	[65]
Al-Li10 %wt	25	~10	0.3	233	15	7.5	53	[47]
Al-Li40 %wt	25	~10	0.3	343	15	7.5	84	[47]
Al90-Bi10 wt%	24	13	50	–	5	15	73.9	[14]
Al89-Bi10-NaCl1 wt%	39	13	50	–	5	11	81.3	[14]
Al85-Bi10-NaCl5	42	13	50	–	5	3	85.4	[14]
Al; Ga70-In30 (1–10 wt%)	25	20–100	0.1	1380		10	93	[67]
Al; Ga60-In25-Sn10-Zn5 (1–10 wt%)	80	20–100	0.1	2900		10	96	[67]
Al; Ga70-In30	80	<250	0.1	–	–	25	99	[63]
Al; Ga60-In25-Sn10-Zn5	80	<250	0.1	–	–	12	100	[63]
Al+10wt% $BiCl_3$+10wt% γ-Al_2O_3	40–50	10	0.5–3	362	2	324	98.52	[56]
Al+10wt% $BiCl_3$	40–50	10	0.5–3	161	2	402	88.49	[56]
Al+10wt% γ-Al_2O_3	40–50	10	0.5–3	0.5	2	636	12.69	[56]
Pure Al	40–50	10	0.5–3	–	2	600	27	[56]
Al95; Ga-In-Sn5 wt%	25	≤30	0.2	5.0	4.0	5.3	92.3	[61]
Al94; Ga-In-Sn5, h-BN1 wt %	25	≤30	0.2	15.0	4.0	3.7	95	[61]
Al92; Ga-In-Sn5; h-BN3 wt %	25	≤30	0.2	25.0	4.0	2.5	98.3	[61]

Table 2
Comparative table of different studies on the ball milling methodology with salts and NaOH carried out at ambient pressure.

Additives/ reagents	Powder composition	Molar concentration [M]	Reaction temperature [°C]	Size [μm]	Mass [g]	Hydrogen yield measurement method	Hydrogen generation rate [ml. min^{-1}.g^{-1}]	Ball milling time [h]	Time [min]	Hydrogen yield %	Reference
NaOH	Al_3Mg_2	0.5	55	75	1	weight changes	24.8	2	30	97	[66]
KOH	Al_3Mg_2	0.5	55	75	1	weight changes	24.2	2	30	95	[66]
Stearic acid 1wt %	Mg55-Al30-Fe15 wt%	NaCl 0.6	25	–	0.3	water displacement	687.6	4	10	100	[50]
NaOH, Na_2SnO_3	Al	1.5–4	–	68	1.0	flowmeter	1740	1	3	100	[43]
NaOH	Al	1.5–4	–	68	1.0	flowmeter	860	1	8	90	[43]
Na_2SnO_3	Al	–	–	68	1	flowmeter	280	1	8	80	[43]
Na_2SnO_3	Al	25	25–35	<45	0.2	water displacement	343	/	1	33	[54]
NaOH	Al	0.01	25–35	<45	0.2	water displacement	26	/	70	22	[54]
$NaBO_2$	Al	2.39	25–35	<45	0.2	water displacement	37	/	24	100	[54]
Na_2SiO_3	Al	0.04	25–35	<45	0.2	water displacement	0	/	75	0	[54]
NaOH, Na_2SnO_3	Al	1.25; 0.04	21–94	75–150	2	flowmeter	2500	/	4	100	[53]
NaOH	Al	3.75	21–87	75–150	1	flowmeter	1420	/	2,5	100	[53]
Na_2SnO_3	Al	0.1	75	45	1	flowmeter	1200	/	~3	71	[53]
NaOH	Al	0.75	–	45	1	flowmeter	204	/	~4	100	[53]
NH_4Br	Al80-Bi20 wt %	0.85	25	4	0.1	water displacement	401	0.1	–	89	[62]
$NaHCO_3$	Al80-Bi20 wt %	0.85	25	4	0.1	water displacement	193	0.1	–	95	[62]
K_2HPO_4	Al80-Bi20 wt %	0.1	25	4	0.1	water displacement	158	0.1	–	88	[62]
NH4Cl	Al90-Ga7-In3 %wt	1	25	4	0.1	water displacement	100	0.1	–	89	[62]
NaBr	Al90-Ga7-In3 %wt	0.5	25	4	0.1	water displacement	72	0.1	–	87	[62]
$KHSO_4$	Al90-Ga7-In3 %wt	0.37	25	4	0.1	water displacement	342	0.1	–	90	[62]

Table 3
Comparative table of different studies on atomization methodology by measuring the hydrogen yield with the water displacement method.

Powder composition	Reaction temperature [°C]	Atomization pressure [bar]	Size [μm]	Mass [g]	Hydrogen generation volume [ml.g^{-1}]	Time [min]	Hydrogen yield %	Reference
80 % Al, 10 % Bi, 10 % Sn	0	50–100	–	0.35	–	70	91	[25]
80 % Al, 10 % Bi, 10 % Sn	30	50–100	–	0.35	–	12	91	[25]
80 % Al, 10 % Bi, 10 % Sn	40	50–100	–	0.35	–	3	91	[25]
80 % Al, 10 % Bi, 10 % Sn	50	50–100	–	0.35	–	3	97	[25]
Al	30	50–80	30–60	0.35	~1100	1000	81	[24]
Al-Bi (20 wt%)	30	50–80	30–60	0.35	1100	500	100	[24]
Al-Sn (20 wt%)	30	50–80	30–60	0.35	1050	600	100	[24]
Al85-Bi, Sn	20	–	3	0.05	580	150	52	[26]
Al85-Bi, Sn	30	–	3	0.05	790	95	70	[26]
Al85-Bi, Sn	40	–	3	0.05	950	70	83	[26]
Al85-Bi, Sn	50	–	3	0.05	1050	40	92	[26]
Al-10Bi-3Fe	50	50–80	1–50	0.5	911.8	1500	83	[68]
Al-10Bi-7Fe	50	50–80	1–50	0.5	961	1500	92	[68]
Al-10Bi-10Fe	50	50–80	1–50	0.5	938.8	1500	93	[68]

make Al-Li alloys highly effective for hydrogen generation, although their high reactivity necessitates careful management for practical applications [47,64].

Fan et al. [47] explored that whether lithium content increases from 10 wt% to 40 wt%, the volume of H_2 generated significantly rises from 743 mL/g (53 % efficiency) to 1405 mL/g (92.5 % efficiency), with a corresponding increase in maximum hydrogen generation rate from 233 ml.min^{-1}.g^{-1} to 1405 ml.min^{-1}.g^{-1}. However, for lithium content above 30 wt.%, the reaction becomes less controllable, with most hydrogen produced within the first 30 s. The improvement is attributed to the formation of intermetallic compounds such as Al_2Li_3 and Al_4Li_9, grain size reduction during mechanical milling, and the catalytic effect of LiOH, formed from the reaction of lithium with water.

Fan et al. [65] also explored aluminum alloys activated with lithium and bismuth demonstrated exceptional hydrogen generation capabilities with high efficiency. The Al-20 %Li-5 %Bi alloy (compared to Al-5 %Li-5 %Bi, Al-10 %Li-5 %Bi, Al-15 %Li-5 %Bi) proved to be the most effective, achieving a production of 1340 mL of H_2 per gram of aluminum, corresponding to 100 % of the theoretical maximum yield. Hydrogen generation rates increased with lithium content, reaching a peak of 988 ml.min^{-1} .g^{-1} for the Al-20 %Li-5 %Bi alloy. The high efficiency of the alloys is attributed to the synergistic effects of lithium and bismuth. Lithium reacts with water to produce LiOH, which accelerates aluminum corrosion, while the formation of $BiLi_3$ facilitates the hydrolytic process by acting as an initial catalytic center.

Al_3Mg_2

Naseem et al. [66] investigated hydrogen generation via the hydrolysis of aluminum-magnesium alloys (Al_3Mg_2), fully hydrogenated (MgH_2-Al), enhanced by adding magnesium hydride (MgH_2) and a small amount of sodium hydroxide (NaOH) during ball milling. The milling process refines the particle size and activates aluminum, while MgH_2 contributes both to hydrogen production and the reduction of the reaction's activation energy. The results indicate that with 2 h of milling and the use of alkaline solutions (0.5 M NaOH or 0.5 M KOH), hydrogen yields reach high levels (1488 mL/g in the case of NaOH) with 97.47 % efficiency in 60 min at 55 °C. The formation of by-products such as $Mg_2Al(OH)_7$ further facilitates extended hydrolysis.

3.2. Atomization

The atomization method is a technique used to produce fine and uniform metallic powders. The process begins with the melting of the base metal, which is heated in a protected environment under an inert atmosphere to prevent oxidation and contamination, typically in an induction furnace. Once molten, the metal is transferred into an atomization chamber, where a high-pressure gas jet (commonly argon, at 50–100 bar) breaks it into small droplets, remelting it in the process. These droplets rapidly solidify into powder particles during cooling, resulting in homogeneous particles with spherical or near-spherical shapes. The powders thus obtained are collected in a controlled environment, often maintained under vacuum o low-humidity conditions, to prevent oxidation or degradation. Although they may be briefly exposed to air during collection, the powders are stored in hermetically sealed containers to preserve their chemical and physical properties.

The gas atomization method offers significant technical advantages over other powder production techniques, making it an ideal choice for the development of reactive aluminum-based powders with a specific chemical composition for hydrogen generation. The most notable benefit of this approach is the ability to produce powders with a highly uniform distribution of alloying elements, such as bismuth and tin. This homogeneity ensures consistent hydrolysis performance, which is critical for achieving high hydrogen yields (Table 3). Additionally, the method allows precise control over the microstructure, enabling the formation of specialized morphologies [24–26].

Another key advantage is the significant reduction in grain size, which increases the reactive surface area and accelerates the hydrolysis process. The use of inert gases like argon during atomization minimizes oxidation, resulting in powders with superior stability and reactivity. Furthermore, atomization enables the rapid breaking of the oxide layer while providing precise control over the process. At the same time, it ensures the complete reactivity of the powder, leaving no unreacted material.

However, the method is not without limitations. Compared to simpler techniques such as direct chemical treatments or mechanical milling, gas atomization requires specialized equipment and precise process control, which can increase production costs. Additionally, the process is highly energy-intensive, as aluminum undergoes two melting cycles and pressurization. Another limitation arises from the fact that it is typically applied to aluminum alloys containing bismuth, tin, and iron, as these specific metals activate the powders and enable the subsequent reaction with water.

Wang et al. [25] explored a composite powder (80 % Al, 10 % Bi, 10 % Sn) with high hydrogen generation efficiency, produced through gas atomization. The powders exhibit a unique core/shell microstructure, with a Bi- and Sn-rich phase distributed along the aluminum grain boundaries, which prevents oxidation and promotes reaction with water. At 30 °C, the powders reach a 91.3 % yield within 16 min, while even at 0 °C, the conversion remains high (80.5 %).

Liu et al. [24] explored the performance of pure Al, Al-20Bi, and Al-20Sn powders prepared via gas atomization in hydrogen generation through hydrolysis. Adding Bi and Sn significantly improves hydrogen yield and reduces reaction time compared to pure Al. Both Al-20Bi and Al-20Sn achieved the highest efficiency (100 % yield) within 500 min, while pure Al reached only 81.2 % in 1000 min. Al-20Bi powders also demonstrated superior oxidation resistance, making them suitable for use in ambient conditions.

Chen et al. [26] investigated aluminum conversion efficiency in the presence of low-temperature water vapor. The experiments evaluated hydrogen production using two aluminum-based powders, 95Al-5Bi and 85Al-Bi-Sn, produced via atomization, with water vapor introduced into the reactor at controlled temperatures ranging from 20 °C to 50 °C. The results demonstrated that temperature had a notable impact on the yield of 85Al-Bi-Sn. As the temperature increased from 20 °C to 50 °C, the yield rose significantly from 47 % to 93 %. Furthermore, the 85Al-Bi-Sn alloy consistently outperformed 95Al-5Bi, achieving a yield of 71 % at 30 °C within 100 min and reaching a maximum efficiency of 93 % at 50 °C within one hour. In contrast, 95Al-5Bi exhibited a lower efficiency, peaking at 69 % at 50 °C. The addition of Sn to the alloy significantly enhanced the hydrolysis process by reducing grain boundary strength and promoting the formation of microfractures, which accelerated the reaction.

Experiments conducted by Deng et al. [68] on Al-Bi-Fe alloy powders, produced via gas atomization, have demonstrated that the inclusion of iron in aluminum-based materials significantly enhances hydrogen generation through hydrolysis reactions, even in the absence of Sn.

The addition of iron increases hydrogen yield in Al-Bi-Fe alloys through multiple synergistic effects. These include the formation of micro-galvanic couples, which accelerate aluminum dissolution; the uniform distribution of the Bi-rich phase, which effectively disrupts the passivating film; and the reinforcement of the aluminum matrix, which prevents aggregation and optimizes reactivity. The alloys Al-10Bi-7Fe and Al-10Bi-10Fe achieved the highest hydrogen yields of 92 % and 93 %, respectively. In comparison, the Al-10Bi-3Fe alloy achieved a hydrogen yield of 83 %. These findings underscore that Al-Bi-Fe alloys represent a promising solution for efficient and cost-effective hydrogen production without resorting to tin that would increase the cost of the process.

4. Conversion methods

4.1. Alkaline or acidic solutions

Upon exposure to air, aluminum rapidly oxidizes, creating a surface layer of Al_2O_3 oxide that can be dissolved by both acidic and alkaline solutions at ambient temperature [17].

The aluminum-water reaction, which releases hydrogen gas, is significantly influenced by the type and concentration of alkaline or acidic solutions used as catalysts. In alkaline solutions, the surface passivation layer dissolves more readily than in acidic ones [20].

Literature indicates that the degree of fragmentation of aluminum samples and porosity [69] impact the reaction kinetics. Indeed, the smaller the particle size, the greater the exposed area for interaction between Al and H_2O, and the higher the porosity, the larger the reaction surface area. Consequently, this leads to an increase in reaction kinetics.

Other factors, including temperature, pH, and molar concentration, strongly influence hydrogen production rates in both acidic and alkaline media [20,70,71]. Increasing temperature generally accelerates both aluminum corrosion and hydrogen generation rates, making temperature control an important variable for efficient hydrogen production [71,43].

4.1.1. NaOH

Alkaline solutions, such as sodium hydroxide (NaOH), potassium hydroxide (KOH), are commonly employed due to their effectiveness in disrupting the protective oxide layer on aluminum surfaces, thereby accelerating hydrogen production and reducing reaction induction time [5,12,72-74] (Eq. (7), (11)) (Table 6). Strong alkalis are particularly efficient, with NaOH widely recognized as a low-cost and practical choice for this purpose [5,44,75]. The dissociation of NaOH releases OH^- ions, which dissolve the oxide film on aluminum, exposing fresh metal surfaces for the reaction and creating sodium aluminate and hydrogen gas as in the Eq. (7).

$$2Al + 2NaOH + 6H_2O \rightarrow 2NaAl(OH)_4 + 3H_2 \tag{7}$$

When aluminum reacts with water and NaOH, it primarily forms the soluble ion $[Al(OH)_4]^-$ as the main product and molecular hydrogen (H_2) as a gaseous byproduct. NaOH acts as a catalyst: it is not consumed directly but facilitates aluminum dissolution by consuming water and producing hydrogen. So Eq. (7) can be expressed without NaOH [20]:

$$2Al + 6H_2O + 2OH^- \rightarrow 2\left[Al(OH)_4^-\right] + 3H_2 \tag{8}$$

As the $[Al(OH)_4]^-$ concentration increases, the solution may become saturated, leading to the precipitation of solid aluminum hydroxide, $Al(OH)_3$. This precipitation is accompanied by the regeneration of hydroxide ions (OH^-), as shown in the reaction:

$$Al(OH)_4^- \rightarrow Al(OH)_3(s) + OH^- \tag{9}$$

The regeneration of OH^- during $Al(OH)_3$ precipitation allows the cycle to continue without significant NaOH consumption. This behavior results in a lower final pH compared to the initial pH due to the consumption of hydroxide ions in the primary reaction.

Combining the two processes (formation of $Al(OH)_4^-$ and partial precipitation of $Al(OH)_3$), there is a dynamic cycle in which NaOH facilitates the reaction (Eq. (7)), followed by the possible precipitation:

$$Na[Al(OH)_4] \rightarrow NaOH + Al(OH)_3(s) \tag{10}$$

However, the reaction rate and hydrogen production are dependent on the molar concentration of NaOH. To prevent the termination of the reaction and the precipitation of all aluminum as $Al(OH)_3$, an excess of NaOH is required. This excess not only prevents the aluminum from precipitating as $Al(OH)_3$ but also keeps $NaAl(OH)_4$ soluble in the solution. As a result, the reaction can proceed for a longer duration, leading to an increased hydrogen production [75].

To further boost hydrogen yield, strong alkaline additives like calcium oxide (CaO) can be combined with NaOH in water. This combination has been shown to improve yield significantly [76].

Weakly alkaline salts like sodium aluminate ($NaAlO_2$) and sodium stannate (Na_2SnO_3) can be added to NaOH, mitigating equipment degradation while maintaining a high hydrogen production rate. Sodium aluminate ($NaAlO_2$), for instance, serves as a crystallization nucleus for $Al(OH)_3$ byproducts, generating a mechanism involving directed crystal growth of $Al(OH)_3$ on suspended hydroxide particles. This process effectively limits the formation of an $Al(OH)_3$ layer on the aluminum surface, maintaining the metal's reactivity throughout the reaction [77] [78]. Similarly, adding Na_2SnO_3 to NaOH allows for a reduced NaOH concentration without sacrificing hydrogen output, as Na_2SnO_3 contributes by destabilizing the oxide layer on aluminum and forming metallic Sn on the aluminum surface, which further prevents repassivation [43,53]. Other non-toxic inorganic salts, like ferric sulfate ($Fe_2(SO_4)_3$) and magnesium chloride ($MgCl_2$), can enhance the aluminum-water reaction when combined with NaOH [54,79,80].

Additionally, research has shown that using choline hydroxide as a promoter offers another viable approach due to its lower corrosiveness than NaOH. Its equilibrium constant facilitates a slower initial dissociation, followed by enhanced OH^- regeneration, leading to a stable hydrogen output over time [72].

Bolt et al. [29] extensively described the reaction of aluminum with sodium hydroxide solution. The generation of hydrogen and its rate were monitored using a flow meter and an H_2 analyzer. As highlighted in Fig. 5, the amount of H_2 increases over time, but the rate of generation

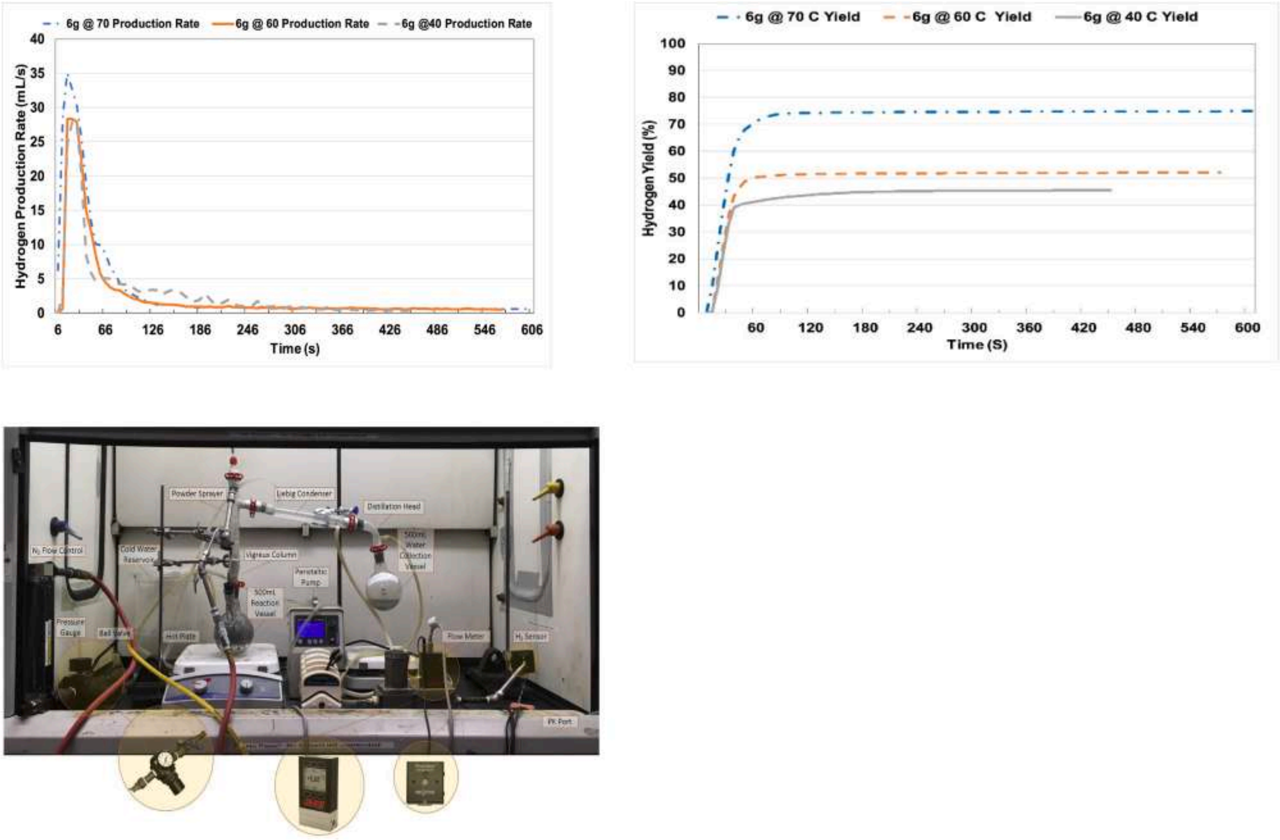

Fig. 5. Hydrogen yield (6 *g* aluminum samples), varying water temperature test conditions. Experimental testing work station [29].[5]

starts to decrease thereafter: the two graphs are inversely proportional because most of the H_2 production occurs in the first minute due to the strong triggering effect caused by the soda, which, thanks to its high alkalinity, acts rapidly. The quantities of the reactants (aluminum, NaOH, and water) are in their stoichiometric proportions, ensuring an optimal reaction process. The reaction rate is positively influenced by temperature and smaller-sized particles due to the increased specific surface area of aluminum. The process is as follows: a sprayer introduces aluminum powder mixed with soda into the reactor where there is water. Since the reaction is exothermic, it causes the vapor and gaseous hydrogen to rise upward. From there, they are led into a condensation system where the hydrogen is separated from the vapor, which is condensed. The hydrogen is then directed into a flow meter to measure its flow rate and finally into a gas analyzer.

Testa et al. [12] systematically investigated the interplay between temperature (−5 °C, 25 °C, and 50 °C) and molar concentration of NaOH solution on the aluminum-water reaction. Their findings revealed that increasing the NaOH concentration markedly decreased the reaction time, achieving a hydrogen production volume of 1200 mL within 40 s, compared to 240 s under lower concentration conditions (Fig. 6, Table 5). Furthermore, the elevated NaOH concentration substantially enhanced the hydrogen generation rate, as quantitatively summarized in Table 4. These results confirm the findings of Bolt et al. [29], who achieved a maximum yield of 95.44 % using 1.5 times the stoichiometric quantity of NaOH. The study also demonstrated that temperature critically influenced the kinetic energy of the reactant particles, thereby accelerating reaction kinetics. In contrast, subzero conditions (−5 °C) were found to significantly decelerate the reaction, corroborating theoretical predictions on the strong temperature dependence of reaction rates.

Regarding another type of aluminum waste, specifically aluminum chips, Amrani et al. [81] demonstrated that the hydrogen production volume can be enhanced through the application of copper-based metal oxide, such as CuO and Cu_2O. These catalysts break the protective aluminum oxide (Al_2O_3) layer, increase the reactive surface area, and lower the activation energy required for the reaction. For instance, under standard conditions (0.4 M NaOH, 50 °C), reactions employing CuO result in a hydrogen production of 295 mL compared to 225 mL in the absence of a catalyst, while reactions using Cu_2O achieve 290 mL, also in contrast to 225 mL without a catalyst. This corresponds to an increase of approximately 23–24 % (Fig. 7). Although the increase in yield is relatively modest, this study highlights that copper-based metal oxides have the potential to enhance the efficiency of the reaction.

In addition to the direct attack by NaOH to dissolve the oxide layer, an alternative approach, explored by Hammad et al. [82], involves the manual mixing aluminum powders with NaH, followed by a second step of adding H_2O to trigger the reaction.

After simple mixing, the NaH-Al mixture powder exhibits a core-shell structure, where aluminum is embedded within the NaH.

During the hydrolysis process, NaH reacts readily with water, producing NaOH, which creates an alkaline environment. This compound dissociates into OH^- and Na^+ ions, with the OH^- ions rapidly removing the protective oxide layer (Eq. (7)–(9)). This allows water to directly attack the fresh aluminum surface, initiating the Al-water reaction.

This method can achieve a yield of 98 % in a ratio Al:NaH 1:1 and a 0.9 M NaH. This method offers the advantage of greater control over the reaction, as NaH, during the mixing process, penetrates the surface of the particles effectively, thus allowing for a more homogeneous dissolution of the surface oxide.

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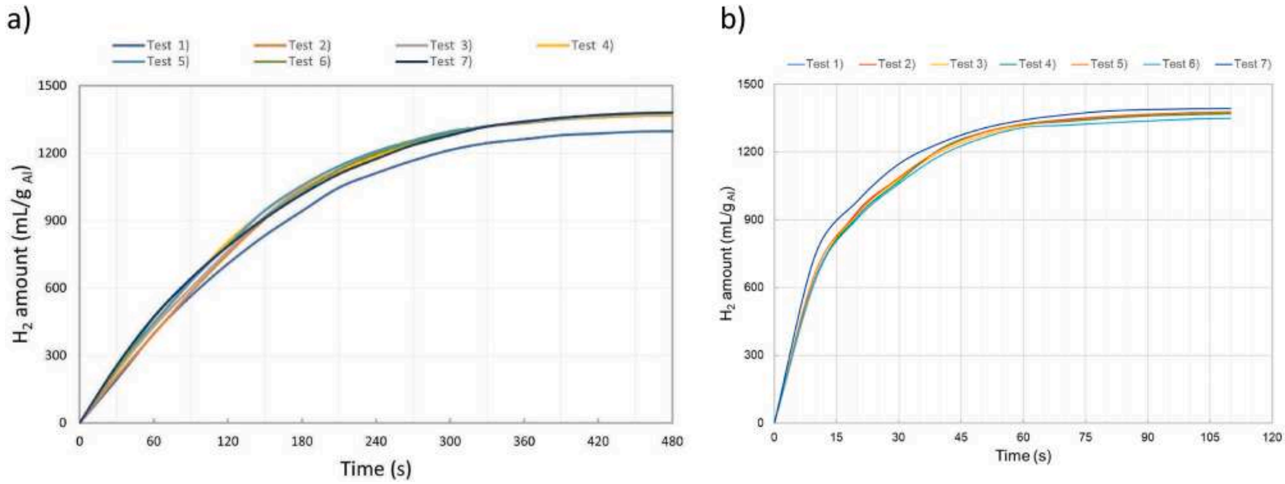

Fig. 6. Aluminum powder reacting with 1 M NaOH aqueous solution (a) and with 5 M NaOH aqueous solution (b) [12].[6]

Table 4
Hydrogen production rate and specific production rate for the various tested configurations [12].

Temperature (°C)	Molar concentration (alkaline solution)	H_2 production rate [ml. $min^{-1}.g^{-1}$]
−5	5 M	80
25	1 M	250
25	5 M	1600
50	1 M	1800
50	5 M	> 3000

Table 5
Hydrogen volume produced at 25 °C by aluminum powder reacting with 1 M NaOH/water solution: comparison between stoichiometric and measured values [12].

Conducted test	Stoichiometric H_2 volume (mL)	Measured H_2 volume (mL)
1	83.6	79.0
2	84.6	84.3
3	85.2	85.0
4	86.6	86.6
5	89.5	90.0
6	92.6	93.0
7	95.5	96.1

4.1.2. KOH

As in the case of NaOH, KOH also acts as a catalyst without directly participating in the reaction:

$$2Al+6H_2O+2KOH\rightarrow 2KAl(OH)_4+3H_2 \tag{11}$$

$$KAl(OH)_4\leftrightarrow KOH+Al(OH)_3 \tag{12}$$

$$2Al+6H_2O\rightarrow 2Al(OH)_3+3H_2 \tag{13}$$

As well as for NaOH the excess of potassium hydroxide KOH is essential for the formation of $KAl(OH)_4$ as it ensures a highly alkaline environment necessary to maintain aluminum in solution in the form of $Al(OH)_4^-$ ions. Under high pH conditions, the equilibrium of the Eq. (12) is shifted to the left, preventing the precipitation of insoluble aluminum hydroxide ($Al(OH)_3$), which, if formed, would inhibit the reactivity of aluminum with water. Consequently, the availability of $Al(OH)_4^-$ promotes the oxidation reaction of aluminum and the production of hydrogen, as described by the Eq. (11) [83].

Shmelev et al. [75] explored the reaction between aluminum powders, H_2O, and KOH with the addition of copper, which penetrates the aluminum powder surface either through pressing or continuous copper addition during the reaction. The objective was to assess the possibility of maintaining a low molarity (≤ 1 M) of the alkaline solution by introducing copper. Indeed, the presence of copper induces an electrochemical reaction due to the significant difference in the electrolytic potentials of the two metals (Al: −1.662 V; Cu: +0.337 V). Shmelev et al. demonstrated that this electrochemical reaction leads to intense aluminum corrosion, resulting in a six-fold increase in H_2 production rate.

Regarding the effect of temperature, it was more significant at an aqueous KOH concentration of 0.5 M compared to 1 M. As the temperature increased from 50 to 70 °C, the time required for the reaction with 0.5 M KOH decreased substantially. Results indicate that temperature had a greater impact on the water-splitting reaction with 0.5 M compared to 1 M KOH. The optimal addition of Ga was 90 % wt for 0.5 M and 75 % wt for 1 M KOH.

4.1.3. HCl

Acidic solutions, such as hydrochloric acid (HCl) and sulfuric acid (H_2SO_4), can also trigger the aluminum-water reaction. Initially, the acid reacts with the Al_2O_3 layer, exposing the underlying aluminum and releasing hydrogen gas (Eq. (14)). As the reaction progresses, and once the acid supply is reduced, however, the concentration of H^+ ions in the solution diminishes due to their consumption in the reaction with aluminum (Eqs. (15), and (16)). This reduction in H^+ ion concentration leads to a corresponding decrease in the reaction rate, as these ions are essential for sustaining the production of hydrogen gas. Once the acid is significantly depleted, the reaction rate cannot be maintained at its initial level. This limitation underscores the reduced efficiency of acidic solutions for prolonged reactions compared to alkaline solutions, which provide a more stable chemical environment for dissolving the Al_2O_3 passivation layer, thereby ensuring sustained reactivity [20].

$$2Al\ +\ 6HCl\rightarrow 2AlCl_3+\ 3H_2 \tag{14}$$

$$Al+3H^++3OH^-\leftrightarrow Al^{3+}+3OH^-+\frac{3}{2}H_2 \tag{15}$$

$$Al+3H^+\rightarrow Al^{3+}+\frac{3}{2}H_2 \tag{16}$$

As with alkaline solutions, the quantity of water is also a significant factor in acidic solutions. Excess water beyond the required

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Table 6
Comparative table of different studies on alkaline and acidic solutions carried out at ambient pressure.

Alkaline/ acidic solutions	Molar concentration [M]	Reaction Temp [°C]	Size [μm]	Mass [g]	Hydrogen yield measurement method	Hydrogen generation rate [ml.min^{-1}.g^{-1}]	Time [min]	Hydrogen yield %	Reference
HCl	2	50	150	0.30	water displacement	–	15	93	[64]
KOH	–	35	150	0.30	water displacement	–	10	–	[64]
NaOH	0.5:1	60	75–150	10	flowmeter	–	123	94.6	[84]
KOH	0.5:1	60	75–150	10	flowmeter	–	126	93.1	[84]
KOH	1	25	10	0.1–1	water displacement	–	15	20	[75]
NaOH	1	25	5–23	0.06	water displacement	250	5	94–100	[12]
NaOH	5	25	5–23	0.06	water displacement	1600	1	94–100	[12]
NaOH	1	50	5–23	0.06	water displacement	1800	5	100	[12]
NaOH	5	50	5–23	0.06	water displacement	6300	1	100	[12]
NaOH	5	−5	5–23	0.06	water displacement	80	–	–	[12]
NaOH	0.4	50	chips	–	volumetric measurement	2250	20	–	[81]
NaOH; CuO	0.4	50	chips	–	volumetric measurement	2800	15	–	[81]
NaOH; Cu_2O	0.4	50	chips	–	volumetric measurement	2750	15	–	[81]

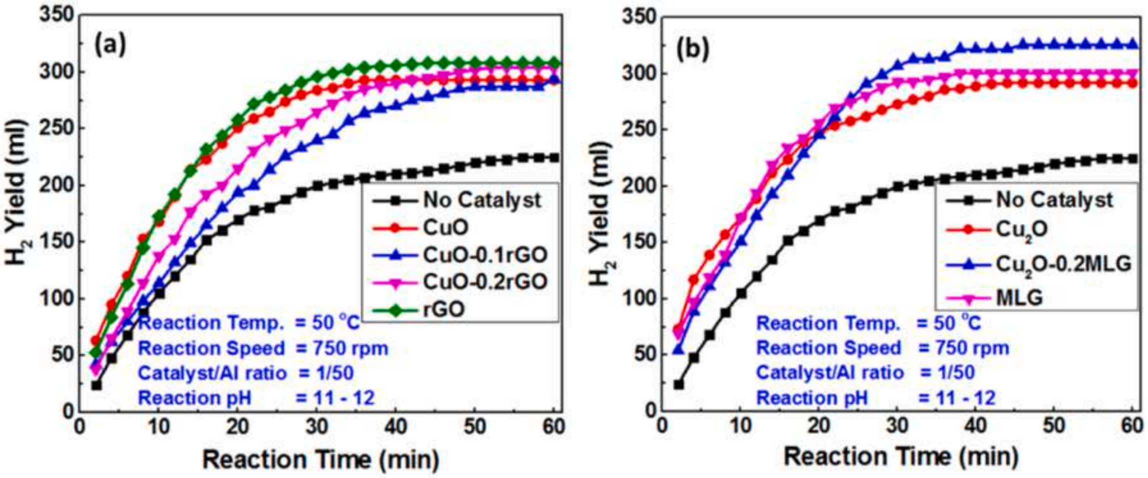

Fig. 7. Comparison graphs of H_2 production yield versus reaction time, with the help of various nanocatalysts: (a) CuO and (b) Cu_2O [81].

stoichiometric amount can actually slow down the reaction, as it first leads to the formation of boehmite (AlOOH), which, if further hydrated, then transforms into bayerite ($Al(OH)_3$), inhibiting H_2 production.

The reaction kinetics are highly vigorous, resulting in the release of substantial amounts of heat and hydrogen. Two main approaches can be employed to carry out the reaction. The first involves diluting hydrochloric acid in water and allowing the entire solution to react with aluminum powder (e.g., 0.3 g of Al, 30 mL of 2 M HCl at 50 °C, producing 348 mL of hydrogen, equivalent to 1160 mL/g) [64]; the second approach involves mixing aluminum powder with water and gradually adding hydrochloric acid dropwise while continuously stirring the reactor (e.g., 4 g of Al powder, 100 mL of 6 M HCl; the amount of hydrogen produced was not quantified) [69].

4.2. Steam oxidation

The steam-based approach to facilitate the reaction between aluminum powders and water remains relatively underexplored in the scientific literature compared to other methodologies, primarily due to the high temperatures required, which complicate maintaining a sustainable energy balance. Nevertheless, by utilizing elevated pressures, it is feasible to avoid such extreme temperatures. Furthermore, the heat from the water vapor can be efficiently recovered using a steam turbine [85,86]. In addition to the energy considerations, this approach is also challenged by the difficulty of establishing a continuous operation system, owing to the inherent use of high pressures or temperatures during the process [32]. Implementing this methodology as a continuous hydrogen production system introduces further complexities. Beyond the essential safety measures for handling hydrogen production and presence, there would be a need to design additional safety systems to manage the high temperatures or pressures involved. One possible strategy to overcome the challenge of continuous operation under high temperature and pressure conditions is to melt the aluminum powders and allow the liquid aluminum to react directly with steam, as illustrated in the system developed by Milani et al. [87]. However, achieving the complete melting of aluminum powders requires a significant energy input, as these powders are coated with aluminum oxide, which has a high melting point of 2072 °C. This oxide layer acts as a thermal barrier, further increasing the energy demand required to sustain the reaction.

On the other hand, the potential to develop a system that enables hydrogen production from aluminum powders without resorting to additives or catalysts is highly compelling. This methodology is particularly promising because the high temperatures or pressures required can serve as key variables that initiate and sustain the reaction without the addition of catalysts or additives which can produce unacceptable byproducts from a circular economy perspective.

Existing studies in the literature provide a basis for comparing hydrogen production efficiencies in relation to the different temperatures and pressures applied (Table 9).

The use of steam for aluminum oxidation offers notable advantages compared to liquid water. Steam can easily penetrate the porous oxide layers that form on the aluminum surface, ensuring the reaction proceeds efficiently, whereas liquid water is hindered by surface tension and fails to reach the aluminum beneath the oxide layer. Furthermore, steam enhances the reaction's efficiency by interacting with a larger surface area of the aluminum due to its higher diffusivity [88].

Reaction phases

The reaction between aluminum and water progresses through a well-defined sequence of stages, each characterized by distinct mechanisms governing oxidation and the generation of hydrogen and heat (Fig. 8).

During the induction phase, aluminum particles are initially covered by a protective layer of aluminum oxide (Al_2O_3), which acts as a passivation barrier. When aluminum comes into contact with water, a weak and transient oxidation process occurs; however, this phenomenon is quickly interrupted by the resistance of the oxide layer. Toward the end of the induction phase, the protective oxide layer undergoes hydrolysis, leading to the weakening of the passivation barrier and allowing the aluminum core to react directly with water. The degradation of the oxide layer is a critical step, as it enables the reaction to progress to the subsequent phase.

Once the protective layer has been compromised, rapid oxidation is initiated. At this stage, the reaction accelerates significantly, producing large quantities of hydrogen gas and releasing substantial amounts of heat due to its highly exothermic nature. This represents the most active and productive phase of the process.

Finally, the reaction transitions to the quenching phase, during which the formation of stable oxides and hydroxides, such as aluminum hydroxide ($Al(OH)_3$), which deposits in the pores where the reaction occur, gradually slows the process until it ceases entirely. At this stage, a portion of the aluminum core may remain unreacted, thereby limiting the overall yield of the reaction [11,32,89–92].

4.2.1. *High temperature and ambient pressure oxidation*

Thermal treatment and reaction at 90 °C

Buryakovskaya et al. [93] explored the effect of thermal treatment on aluminum particles oxidation kinetics in water for hydrogen production. Samples were thermally treated at temperatures ranging from 120 °C to 600 °C and then reacted with distilled water at 90 °C for two hours. A series of experiments employing multiple alternating cycles of oxidation and thermal treatment at 500 °C revealed a gradually declining hydrogen yield per cycle (due to significant thickening of the protective aluminum oxide layer), with a total yield of 53.46 % after six cycles. The treatment's efficacy is linked to crack formation in the alumina shell, exposing the aluminum core to water and promoting the reaction. Nonetheless, temperatures above 500 °C result in excessively thick oxide layers that hinder the interaction between water and aluminum.

Low-Temperature Steam

Gao et al. [32] investigated the reaction between aluminum powders and low-temperature steam (90–200 °C). The experimental results confirmed that the product from aluminum powder reaction consist in $Al(OH)_3$ (Eq. (1)). In addition to temperature, another factor influencing the reaction yield is the amount of porosity. The highest H_2 yield is recorded at 150 °C for powders with a particle size of 25 μm, which have a higher specific surface area (0.644 m^2/g). For this particle size and at this temperature, the highest H_2 yield is 31.9 %. At higher temperatures, specifically between 150 °C and 200 °C, there is a decrease in the H_2 production rate. This decrease is due to the major deposition of aluminum hydroxide within the pores during H_2 production. Such accumulation reduces the reaction interface, thereby decreasing the reactivity of the powders.

High-Temperature Steam (300–650 °C)

Etminanbakhsh and Reza Allahkaram [30] investigated the reaction between aluminum powders and steam at temperatures up to 600 °C in a reactor containing superheated steam. This study addressed the challenge posed by the formation of aluminum oxide using a graphite rod. By passing an electric current through the rod for 2–3 s within the reactor, the oxide layer was disrupted, enabling the reaction between the steam and the aluminum powder.

However, the study does not exclude the possibility of initiating the reaction by raising the steam temperature above 600 °C, particularly beyond aluminum's melting point of 658 °C. The method applied in this study resolves the oxide layer issue through an electric discharge rather than relying on elevated steam temperatures. Regarding the amount of hydrogen produced, the study does not provide any data.

Li et al. [94] analyzed in detail the ignition temperature of aluminum powders and the maximum combustion temperature through the system shown in Fig. 9. The study analyzes the effect of adding $NaBH_4$ to aluminum powders in the reaction with steam.

However, since $NaBH_4$ can be hydrolyzed in the presence of water without the involvement of aluminum, this review considered only the results obtained for the samples without $NaBH_4$. Therefore, only the black curves (sample Al-1) in Figs. 10 and 11 and 11 have to be considered.

The study demonstrates that a minimum temperature of 550 °C is required for the combustion to occur. The effect of temperature is significant, as an increase in reaction temperature generally enhances hydrogen production by accelerating reaction kinetics and improving efficiency.

The volumetric concentration of hydrogen increases from 8 000 ppm (Al-1 at 450 °C) to 16 000 ppm (Al-1 at 550 °C) and then slightly decreases to 14 000 ppm (Al-1 at 650 °C), as shown in Fig. 11(a), (b), (c). Therefore, raising the temperature to 650 °C does not provide significant advantages in terms of hydrogen yield but primarily results in a slightly reduction of the ignition time, which decreases from 65 s (Al-1 at 550 °C) to 25 s (Al-1 at 650 °C) and a decrease in the ignition temperature from 350 °C to 190 °C, along with an increase in the maximum combustion temperature from 1220 °C to 1310 °C (Fig. 10). Thus, increasing the temperature up to 650 °C is not particularly advantageous; instead, a temperature of 550 °C is sufficient to initiate the ignition of aluminum powders in steam atmosphere.

Considering the hydrogen production yield expressed as a percentage, it can be observed that the maximum yield achieved is 0.8 % at 450 °C and increases to 1.6 % at 550 °C and to 1.4 % at 650 °C.

Very high-temperature steam (600 and above)

The research conducted by Barelli et al. [33] investigated the aluminum-steam reaction at elevated temperatures, offering a noteworthy contribution to the development of a circular energy system devoid of chemical additives. Notably, substantial hydrogen yields are only achieved at 900 °C, a temperature considerably exceeding the melting point of aluminum. In particular, the aluminum conversion rate (%CR) increases significantly with temperature: below the aluminum melting point (550–650 °C), the %CR remains low, with limited improvements due to the inhibiting effect of the surface oxide layer. Above the melting point (750–850 °C), the %CR rises considerably, reaching a peak of 31 % at 850 °C, as molten aluminum enhances reaction kinetics. At 900 °C, the highest conversion rate (CR) of 73 % is achieved, highlighting the critical role of high temperatures in optimizing the reaction.

Zhu et al. [95] also investigated the high-temperature reaction, but with a specific focus on the addition of sodium fluoride (NaF) to aluminum powder, demonstrating that it significantly enhances the ignition and combustion properties of aluminum in steam.

Their investigation specifically concentrated on the ignition and combustion temperatures, rather than on the production of hydrogen. Notably, they found that NaF greatly lowers the ignition temperature. For instance, without NaF, aluminum ignites at approximately 960 °C when heated to 1000 °C, while with 10 % by weight of NaF, the ignition temperature drops to 743 °C. This effect is due to NaF's ability to weaken the aluminum oxide layer that typically protects the particle surface, allowing steam to reach the fresh aluminum more easily and accelerating the reaction.

Halter et al. [96] demonstrated combustion at significantly higher temperatures using a burner specifically designed for the combustion of

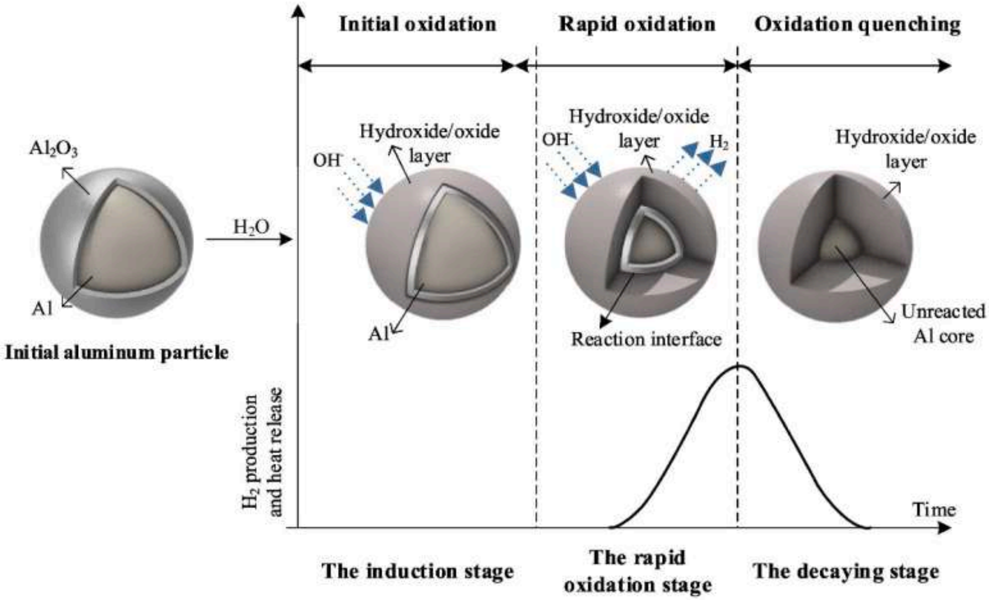

Fig. 8. The diagram of the aluminum-water reaction [32].[7]

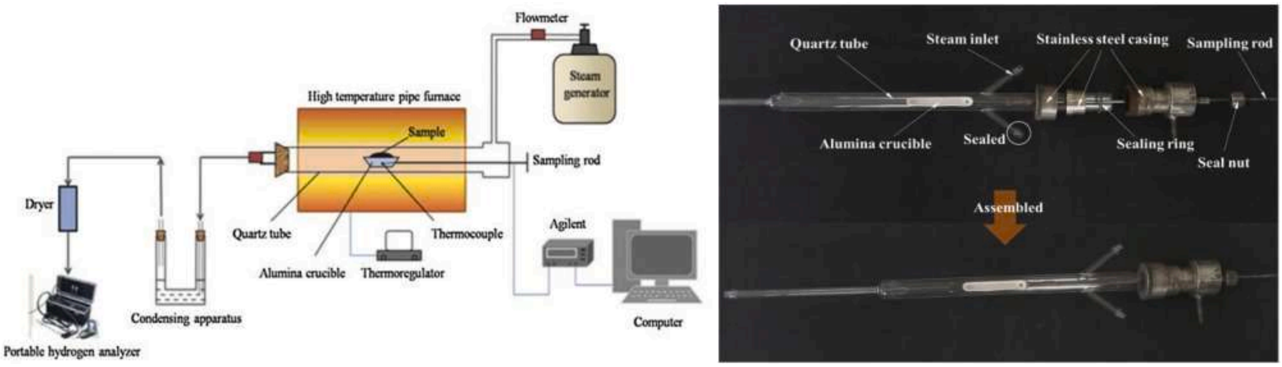

Fig. 9. The system studied by Li et al. consists of the following components: a pipe furnace with a quartz tube, a steam generator with a flow meter, a condensation system, a dryer and a portable hydrogen analyzer [94].[8]

a gas mixture containing dispersed aluminum particles. A methane-rich flame, combined with argon and oxygen, created a high-temperature environment (2444 °C). The combustion of methane completely depleted the available oxygen, promoting the oxidation of aluminum primarily through its reaction with water vapor and, to a lesser extent, with carbon dioxide, leading to the formation of carbon monoxide.

The system included a quartz cylinder and shielded by an argon flow to prevent contamination. Gas Chromatography analysis confirmed a conversion rate (X_{H_2}=0,16) of water vapor into hydrogen. Aluminum combustion followed two distinct phases: the preheating of incandescent particles, followed by an intense, highly luminous reaction, indicating significant thermal energy release. The temperature in the reactive zone exceeded 2727 °C.

The results provide an experimental demonstration of the co-generation of heat and hydrogen via high-temperature aluminum oxidation in water vapor, achieving an efficient conversion of the metal's chemical energy.

4.2.2. *High pressure and high temperature oxidation*

The use of high temperatures and pressures is a highly effective approach for optimizing aluminum-water reactions to produce hydrogen, heat, and alumina. These conditions significantly enhance hydrogen yield by increasing aluminum reactivity and improving the contact with water vapor, while also mitigating issues such as surface passivation and bubble formation [97,88].

Furthermore, high temperatures induce particles fracturing, generating porous structures in the powder that enhance surface area and reactivity [98]. When temperature and pressure exceed 374 °C and 22.1 MPa, water enters a supercritical state, exhibiting properties such as high density and enhanced diffusivity. In this state, water effectively penetrates internal cracks and voids within the aluminum particles (Fig. 12), ensuring optimal contact with unreacted aluminum and

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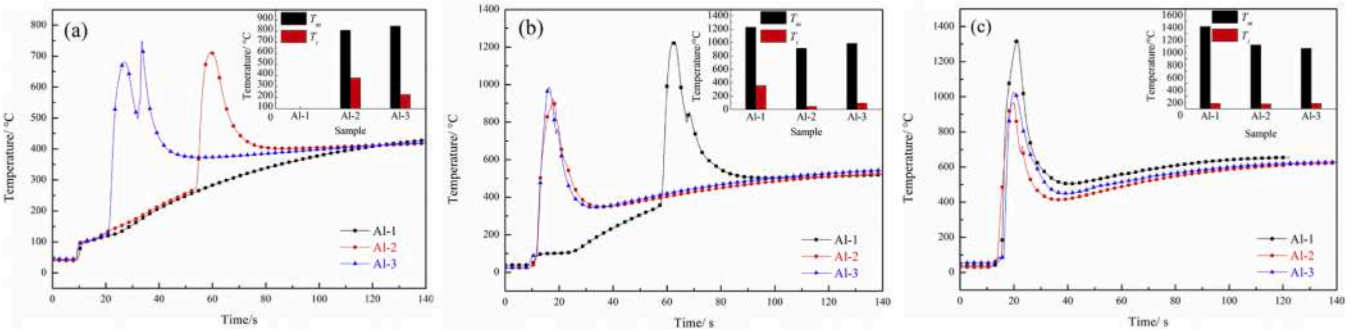

Fig. 10. Combustion temperatures evolution curves of the samples at different temperatures (a) 450 °C, (b) 550 °C, and (c) 650 °C. T_m: maximum combustion temperature; T_i: the ignition temperature [94].[9]

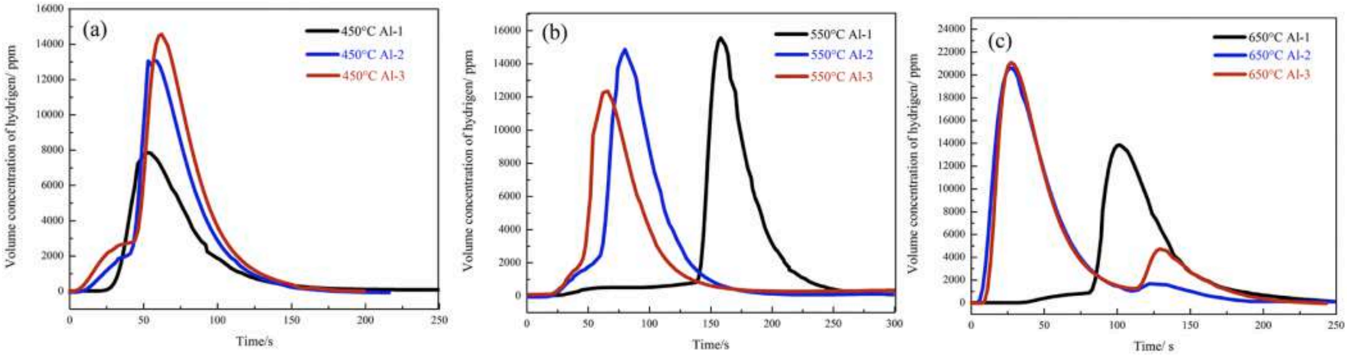

Fig. 11. Hydrogen generation processes of the samples at different temperatures (a) 450 °C, (b) 550 °C and (c) 650 °C [94].[10]

enabling nearly complete metal conversion [97,99,100].

Despite these advantages, high-pressure and high-temperature conditions pose engineering and operational challenges. Such conditions necessitate robust equipment and advanced safety systems, while maintaining these conditions requires significant energy input, which may undermine energy sustainability. Therefore, achieving a balance between enhanced efficiency and operational complexity is essential to optimize the overall process.

Pressure and temperature are crucial factors in enhancing the efficiency of the aluminum-water reaction and increasing hydrogen yield. High temperature facilitates the diffusion of OH^- ions through the passive oxide layer covering the aluminum, improving contact between water molecules and the metal. This accelerated interaction boosts the reaction's effectiveness. For instance, Gao et al. [91] experimented that, at 264 °C and 5 MPa, the hydrogen yield is 60.87 %; increasing the pressure to 9.7 MPa at 312 °C raises the yield to 91.12 %. At 343 °C and 13.7 MPa, the reaction achieves a 100 % yield. These results confirm that higher pressure enhances water penetration and overall reaction efficiency.

Gao et al. in the same work [91] proved that also temperature plays a key role, as it impacts the destruction of the passive oxide layer that initially hinders the reaction. At lower temperatures, breaking this barrier is challenging, which limits both the oxidation of aluminum and hydrogen production. Once the temperature of 180 °C is exceeded, the oxide layer is more effectively destroyed, allowing the reaction to proceed more completely. Between 180 °C and 312 °C (Fig. 13), the hydrogen yield increases significantly with rising temperature.

Gao et al. [99] also compared the performance of millimeter-scale aluminum powders with previously studied micron-sized powders [91]. As shown in Fig. 14 while the micron powders produce hydrogen at 90 °C and form $Al(OH)_3$, millimeter-scale particles exhibit negligible hydrogen generation below 250–280 °C and pressures between 4.0 MPa and 6.4 MPa, emphasizing the influence of particle size and operating conditions on reaction efficiency (Fig. 14). In an analysis of supercritical water reactions, millimeter-scale aluminum powders achieved complete conversion to AlOOH within 60 min at 374 °C and 22.2 MPa, and in just 30 min at 376 °C and 23.5 MPa. In contrast, subcritical conditions at 370 °C and 21.0 MPa yielded a hydrogen production rate of 90.7 % after 60 min, demonstrating lower efficiency compared to supercritical reactions.

Similar to Gao et al., Setiani et al. [31] experimented with the reaction between aluminum powder and steam at temperatures between 230 °C and 340 °C under high pressures (25–150 bar). At these temperatures, the reacted aluminum powder formed boehmite (AlOOH). They utilized a gas sorption analyzer to measure the surface porosity, which was found to be 0.713 m^2/g and gas chromatography to measure the hydrogen produced. This study examined the reaction kinetics at various temperatures and pressures. Through XRD analysis of the reaction products, the study led to the following conclusions (Table 7):

- $T \leq 270$ °C: aluminum reacted only partially, producing aluminum and boehmite (AlOOH), even after 24 h.
- $T \geq 280$ °C: aluminum reacted completely, although full reactions require 24 h.

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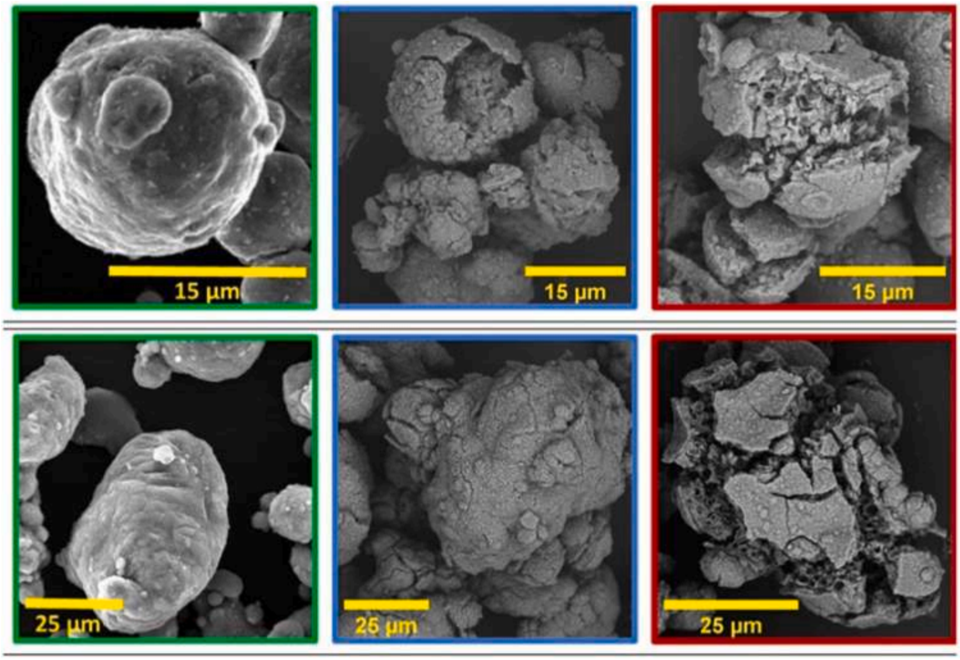

Fig. 12. SEM images show particles from the left: unreacted, unignited, ignited [97] .[11]

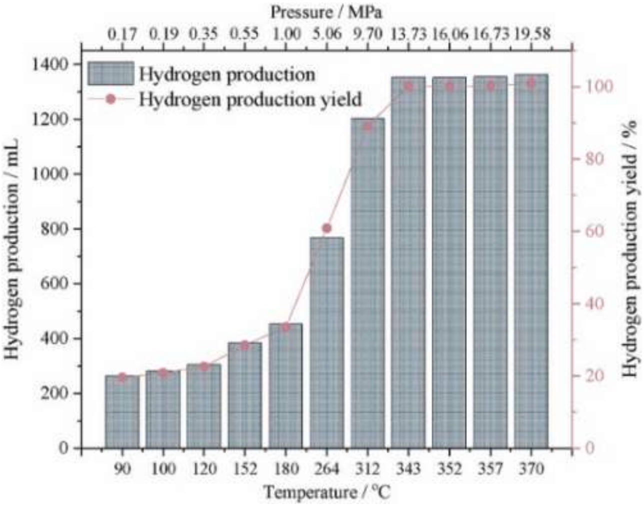

Fig. 13. Hydrogen production and yield at various temperatures and pressures [91] .[12]

- $T \geq 290$ °C: aluminum reacted completely, and after 1 hour, only boehmite was present.

Setiani et al. [31] reported that the reaction is significantly influenced by both temperature and pressure, which together accelerate the reaction kinetics. Specifically, a minimum pressure of 62 bar and a temperature of at least 280 °C are required to effectively initiate the process with a duration of 24 h. To reduce the reaction time to 1 h, an increase in operating conditions to 290 °C and 69 bar is necessary. Notably, the maximum yields observed in this study exceed 90 %, significantly surpassing the yields reported in the literature where high-pressure conditions are not applied [30,32,33]. This highlights the critical role of pressure in optimizing hydrogen yield. In fact, no studies have reported yields exceeding 73 % at ambient pressure, even at temperatures as high as 900 °C [33].

Kirton et al. [97] investigated the thermal oxidation of aluminum powders in pressurized water, with the aim to produce hydrogen, heat, and alumina. Reactions were carried out in a batch reactor by using aluminum powders with nominal diameters of 1, 2, 10, and 45 μm. Operational pressures ranged from 34 to 138 bar, with reaction

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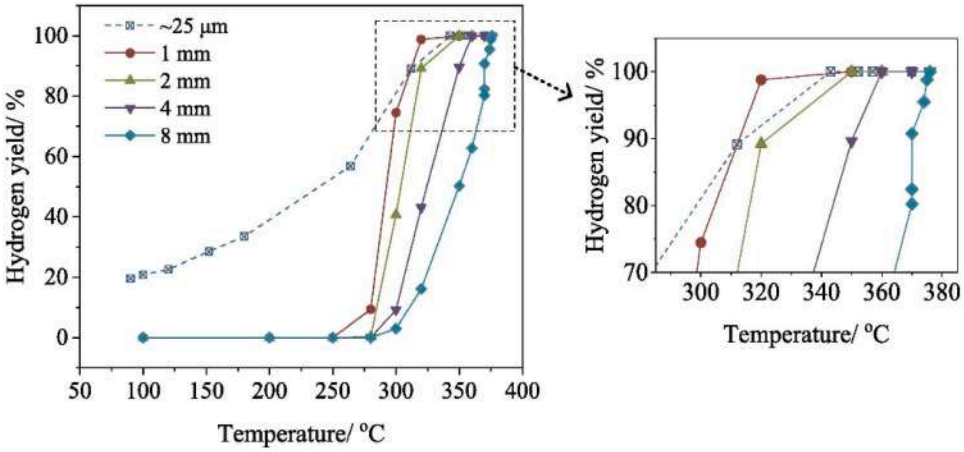

Fig. 14. Variation of hydrogen generation from the aluminum-water reaction at 90–376 °C and 0.1–23.5 MPa for various particle sizes and forms [99].[13]

Table 7
Hydrogen production from reactions of water and aluminum [31].

Temperature (°C)	Pressure (bar)	Time (h)	H_2 (mmol)	Hydrogen conversion rate (%)
230	25	24	15.84	26 %
250	40	24	22.28	37 %
270	55	24	30.42	51 %
280	62	24	56.6	94 %
290	69	1	55.01	92 %
300	85	1	59.06	98 %
340	150	1	57.47	96 %

temperatures exceeding 450 °C during thermal ignition. Larger particles (i.e., 10 and 45 μm) showed higher efficiency, achieving hydrogen yields of up to 80 % at 138 bar (Table 8). The byproduct mainly consisted of alumina at temperatures above 450 °C, whereas boehmite prevailed under lower-temperature conditions.

Trowell et al. [89] analyzed the use of supercritical water for catalyst-free oxidation of aluminum to produce hydrogen. Various aluminum morphologies, including particles up to 120 μm in diameter, were subjected to temperatures between 202 °C and 377 °C under corresponding vapor saturation pressures. The critical point of 374 °C and 220 bar proved essential for achieving complete hydrogen yield using water as the oxidizing agent. Below 277 °C, efficiency remained low, with yields under 30 %. However, above 277 °C, a significant increase in yield was observed, with full hydrogen production achieved within the supercritical range. This enhancement is attributed to the high ionic product of water at these conditions, acting as a self-neutralizing catalyst, and the low viscosity that facilitates mass transfer, preventing the formation of passivating oxide layers.

Patented technologies

Schraud et al. [101] developed and patented a commercial hydrogen production system which combines two methodologies: premixing of aluminum powder with NaOH and $NaAlO_2$ ascribable to the ball milling technique, and reaction with steam at high temperatures and pressures. Both methodologies independently could yield effective results. However, their combination undoubtedly accelerates the reaction, while also inheriting the disadvantages associated with both approaches. The process can be divided into three distinct phases.

During the dry mixing phase, aluminum powder is mechanically combined with sodium hydroxide (NaOH) and sodium aluminate ($NaAlO_2$) within a rotary drum, ensuring a homogeneous distribution of the promoters on the aluminum surface. This process facilitates the formation of a surface coating on the metal particles, enhancing the contact between the reactants in the subsequent reaction phase. Specifically, NaOH can alter the natural passivating layer of aluminum oxide (Al_2O_3), reducing its stability and increasing the metal's exposure to steam, while $NaAlO_2$ can form a thin surface film that prevents the reformation of oxidative passivation. These chemo-mechanical modifications optimize the reactivity of aluminum, promoting complete conversion during its subsequent reaction with steam.

Subsequently, the prepared mixture is exposed to high-temperature and high-pressure steam. This step is critical as it facilitates the breakdown of the aluminum's surface oxide layer, enabling the underlying aluminum to react more readily with steam. The mechanism underlying this phase is detailed in Chapter 4.2.

The final phase involves the production of hydrogen gas along with the generation of thermal energy. This energy-efficient reaction highlights the dual utility of the system, which not only produces clean hydrogen but also provides thermal energy as a by-product, potentially

Table 8
Reaction yield 1, 2, 10 and 45 μm powder [97].

Pressure (bar)	H_2 production Yield %			
	1 μm	2 μm	10 μm	45 μm
34	58 %	35 %	–	–
52	60 %	40 %	–	–
69	55 %	55 %	62 %	–
86	50 %	50 %	78 %	58 %
103	55 %	55 %	62 %	70 %
121	–	–	68 %	78 %
138	55 %	57 %	80 %	80 %

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Table 9
Summary and comparative table of different studies on the water vapor reaction for aluminum powder.

Powder composition	Reaction temperature [°C]	Atomization pressure [bar]	Size [micron]	Mass [g]	Hydrogen yield measurement method	Hydrogen generation volume [ml. g^{-1}]	Hydrogen generation rate [ml.min^{-1}.g^{-1}]	Time [min]	Hydrogen yield %	Reference
Al	90	1	35	–	flowmeter	5.46	–	120	5	[93]
Partially oxidized Al	90	1	35	–	flowmeter	1.47	–	120	5	[93]
Partially oxidized Al	90	1	35	–	flowmeter	3.36	–	120	17	[93]
Partially oxidized Al	90	1	35	–	flowmeter	10.05	–	120	27	[93]
Partially oxidized Al	90	1	35	–	flowmeter	8.36	–	120	36	[93]
Partially oxidized Al	90	1	35	–	flowmeter	11.59	–	120	43	[93]
Partially oxidized Al	90	1	35	–	flowmeter	7	–	120	48	[93]
Partially oxidized Al	90	1	35	–	flowmeter	1.53	–	120	53	[93]
Al	90	1	~25	0,3	water displacement	333	10	133	23	[32]
Al	130	1	~25	0,3	water displacement	367	6	233	27	[32]
Al	200	1	~25	0.3	water displacement	183	16	233	15	[32]
Al	90	1,7	~25	1	water displacement	280	–	30	19.57	[32]
Al	264	50,6	~25	1	water displacement	800	–	30	60.87	[32]
Al	343	137	~25	1	water displacement	1300	–	30	100	[32]
Al	355	235	~25	1	gas analyzer	–	–	60	100	[32]
Al	600	–	40	–	–	–	–	3	(100)	[30]
Al	650	1	0.05	0.1	portable hydrogen analyzer	–	–	1.75	1.4	[94]
Al	230	25	100	1.08	gas chromatography	–	–	1440	26	[31]
Al	250	40	100	1.08	gas chromatography	–	–	1440	37	[31]
Al	270	55	100	1.08	gas chromatography	–	–	1440	51	[31]
Al	280	62	100	1.08	gas chromatography	–	–	1440	94	[31]
Al	290	69	100	1.08	gas chromatography	–	–	60	92	[31]
Al	307	220	12	1	pressure difference	1200	40	30	100	[89]
Al	327	220	55	1	pressure difference	1200	40	30	100	[89]
Al	317	220	120	1	pressure difference	200	10	30	100	[89]
Al	382	~45	10	0.33	pressure difference	1260	675	3	100	[13]
Al	382	~20	10	0.33	pressure difference	–	220	–	97	[13]
Al	382	~5	10	0.33	pressure difference	–	120	–	51	[13]
Al	382	~45	120	0.33	pressure difference	1000	300	5	92	[13]
Al	382	~20	120	0.33	pressure difference	–	120	–	78	[13]
Al	382	~5	120	0.33	pressure difference	–	100	–	43	[13]

enhancing the system’s overall efficiency and sustainability.

5. Comparative evaluation of various methodologies

The comparative analysis of various hydrogen production methodologies summarized in Table 10 highlights the advantages and challenges associated with each technique. Each method provides unique opportunities for hydrogen generation, but their applicability and scalability depend on specific technological, economic, and environmental considerations.

Ball milling with salts emerges as a highly effective methodology for activating aluminum powders due to its simplicity and the use of low-cost additives. The absence of metallic chemical agents in milling with salts provides a significant environmental advantage. However, the energy consumption associated with milling reduce its overall energy sustainability.

Conversely, ball milling with metals presents similar advantages and disadvantages but introduces the additional challenge of recycling byproducts consisting of aluminum mixed with Ga, In, Sn, Zn, or Bi. Additionally, the economic feasibility of this method is significantly impacted by the high market prices of Ga and In, which represent a major cost constraint.

Atomization appears as a promising method for the rapid and continuous production of hydrogen, leveraging ultrafine aluminum particles. However, a significant limitation lies in the necessity of employing aluminum alloys containing bismuth, tin, and iron, as these elements are essential for activating the powders and enabling their reaction with water. Consequently, these metallic elements will inevitably be present in the process by-products. Furthermore, the method involves a high energy demand due to the two melting cycles and the pressurization required for generating aluminum powders.

The use of alkaline or acidic solutions stands out for its simplicity of implementation and low reagents and equipment costs. This approach ensures high hydrogen production but poses significant environmental and safety challenges. The generation of alkaline or acidic byproducts, the toxicity of chemical agents, and equipment corrosion represent critical obstacles, requiring targeted interventions for environmental impact management and equipment maintenance.

The reaction with water vapor is notable for its low environmental impact, producing only alumina as a byproduct, an inert and recyclable material [102]. However, this methodology requires high temperatures and high pressures, complicating system design and increasing energy consumption. Nonetheless, the thermal energy of the steam can be recovered, enhancing the system’s energy sustainability.

Table 10
Advantage and disadvantages comparative table of different methods for activation of aluminum powder and hydrogen production.

Methodology	KPI	Advantages	Disadvantages
Ball milling with metals	Environment	–	Metal by-products
	System Design	Simple activation and basic design	–
	Hydrogen Production	High hydrogen yield and production rate	Long milling time for activation
	Energy Balance	–	High energy consumption during milling
	Costs	Low-cost equipment	Expensive metals; Difficulty in recovering metals
	Safety	Safe system	–
Ball milling with salts	Environment	Salt by-products	–
	System Design	Simple activation and basic design	–
	Hydrogen Production	High hydrogen yield and production rate	Long milling time for activation
	Energy Balance	–	High energy consumption during milling
	Costs	Low-cost additives and equipment	–
	Safety	Safe system	–
Atomization	Environment	–	Metal by-products
	System Design	–	Complex design
	Hydrogen Production	High hydrogen yield and production rate	–
	Energy Balance	–	High energy consumption (two melting and pressurization)
	Costs	–	High-cost equipment
	Safety	–	High pressure conditions
Alkaline or acidic solutions	Environment	–	Alkaline or acidic by-products
	System Design	Simplicity of implementation and design	Possible corrosion of the equipment
	Hydrogen Production	High hydrogen yield and production rate	–
	Energy Balance	No energy consumption by the system	–
	Costs	Low-cost materials and equipment	–
	Safety	–	Presence of toxic substances
High temperature and high pressure oxidation	Environment	No catalyst required; environmentally friendly; only alumina as a by-product	–
	System Design	–	Complex design, requires high pressure, difficulty in creating a continuous system (batch process)
	Hydrogen Production	High yield (only with high temperature and high pressure)	–
	Energy Balance	Possibility of waste heat recovery	High energy consumption
	Costs	–	High-cost equipment
	Safety	–	High pressure conditions

In summary, each approach offers unique advantages, but the optimal methodology depends closely on the application context. While the first three methods (ball milling, atomization, alkaline or acidic solutions) are limited by the need to manage basic or acidic or metallic byproducts, dependence on expensive materials, or unrecoverable energy consumption, the high temperature and high pressure oxidation methodology represent promising pathways, particularly from the perspective of environmental sustainability and circular economy, as energy consumption can be mitigated through the recovery of steam thermal energy.

Limitations and future perspectives

Scientific literature has extensively investigated the ball milling technique, highlighting its effectiveness. A significant contribution for this methodology is the patent by Dossi et al. [52], which proposes the activation of aluminum powders through an acoustic resonant mixer, a method of potential interest for process optimization. Future developments should focus on reducing the energy consumption of ball milling, potentially by decreasing the required processing time while enhancing the efficiency of the mixer. This could be achieved by incorporating suitable additives, as long as they do not produce byproducts that cannot be recycled. Conversely, the activation methodology based on atomization, while ensuring an effective yield, it has the disadvantage to have energy consumption not recoverable, thereby making the process less sustainable from an energy perspective.

Regarding the main conversion techniques, scientific literature has thoroughly examined the approach based on alkaline solutions. The primary issue of this method is the corrosiveness of alkaline or acidic compounds, as well as the need to manage and recover the alkaline or acidic byproducts generated during the process. Future studies could investigate which additives may work in combination with alkaline or acidic solutions to mitigate their corrosive effects, while also exploring sustainable methods for recycling alkaline or acidic byproducts.

Similarly, the oxidation method conducted at high temperatures and high pressures has also been extensively studied, demonstrating very high yields, up to 100 % conversion into hydrogen. A particularly noteworthy contribution that integrates ball milling activation with the high-temperature and high-pressure oxidation process is the patent by Schraud et al. [101], which proposes a combined approach aimed at optimizing the overall efficiency of these two methods.

However, the main challenge associated with steam oxidation lies in the operational complexity arising from the required high temperatures and high pressures. From a future perspective, further research could explore strategies to recover steam heat in order to balance the system's energy consumption. This could be achieved, for instance, by reutilizing the heat within the system to maintain the reactor at high temperatures or by implementing heat recovery solutions such as a heat exchanger or a steam turbine.

6. Conclusion

This paper reviewed numerous studies investigating the reaction between aluminum powder and water. However, initiating this reaction requires the destabilization of the aluminum oxide layer, which naturally forms on aluminum surfaces and has a high melting point (2072 °C). This destabilization can be achieved through various approaches, including chemical treatments with corrosive substances, the addition of other elements, mechanical processing, melting with other metals, or the application of high temperatures and high pressures. This review analyzed the advantages and limitations of these different approaches, in particular of the activation methods (ball milling and atomization), as well as the conversion techniques (alkaline solutions and steam oxidation), comparing the hydrogen yield under the different experimental conditions of each study.

Considering all aspects discussed in Chapter 5, this review highlights that high-temperature and high-pressure oxidation appears to be the most promising methodology for hydrogen production from aluminum powders considering environmental sustainability and hydrogen yield efficiency as key factors and assuming that the energy required for steam production can be effectively recovered.

Thus, utilizing aluminum powders, whether derived from industrial waste or commercially available sources, for hydrogen production represents a viable strategy to overcome key challenges associated with hydrogen storage and transportation. Moreover, this approach offers a potential solution to mitigate the intermittency of renewable energy sources during the energy transition. Therefore, it can be concluded that pure aluminum powder is particularly well-suited for on-site hydrogen generation due to its environmental compatibility and high hydrogen yield when reacting with high-pressure steam.

CRediT authorship contribution statement

Nicola Musicco: Writing – original draft, Writing – review & editing, Conceptualization, Data curation, Formal analysis, Methodology. **Marcello Gelfi:** Writing – original draft, Writing – review & editing, Conceptualization, Methodology, Supervision. **Paolo Iora:** Writing – original draft, Writing – review & editing, Conceptualization, Methodology, Supervision. **Matteo Venturelli:** Writing – original draft, Writing – review & editing, Methodology, Supervision. **Nancy Artioli:** Writing – review & editing, Methodology, Supervision, Visualization. **Luca Montorsi:** Writing – review & editing, Methodology, Supervision, Project administration. **Massimo Milani:** Writing – review & editing, Methodology, Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

References

[1] S.A. Alnuaim, Energy transition or Energy advancement!, in: Proceedings - SPE Annual Technical Conference and Exhibition, 2023, https://doi.org/10.2118/215050-MS.

[2] S. Ghosh, B. Ghosh, Fossil fuel consumption trend and global warming scenario: energy overview, Glob. J. Eng. Sci. 5 (2020) 1–5, https://doi.org/10.33552/GJES.2020.05.000606.

[3] I Energy Agency, "World Energy Outlook 2024," 2024. [Online]. Available: www.iea.org/terms.

[4] I. Zaiter, M. Ramadan, A. Bouabid, A. Mayyas, M. El-Fadel, T. Mezher, Enabling industrial decarbonization: framework for hydrogen integration in the industrial energy systems, Renew. Sustain. Energy Rev. 203 (2024), https://doi.org/10.1016/j.rser.2024.114782.

[5] A. Bolt, I. Dincer, M. Agelin-Chaab, Energy and exergy analyses of hydrogen production process with aluminum and water chemical reaction, Energy 205 (2020), https://doi.org/10.1016/j.energy.2020.117978.

[6] C. Gunathilake, et al., A comprehensive review on hydrogen production, storage, and applications, R. Soc. Chem. (2024), https://doi.org/10.1039/d3cs00731f.

[7] E.S. Akyüz, E. Telli, M. Farsak, Hydrogen generation electrolyzers: paving the way for sustainable energy, Int. J. Hydrogen Energy 81 (2024) 1338–1362, https://doi.org/10.1016/j.ijhydene.2024.07.175.

[8] S.E. Hosseini, M.A. Wahid, Hydrogen production from renewable and sustainable energy resources: promising green energy carrier for clean development, Renew. Sustain. Energy Rev. 57 (2016) 850–866, https://doi.org/10.1016/j.rser.2015.12.112.

[9] L. Mulky, et al., An overview of hydrogen storage technologies – Key challenges and opportunities, Mater. Chem. Phys. 325 (2024), https://doi.org/10.1016/j.matchemphys.2024.129710.

[10] J.M. Bergthorson, et al., Metal-water combustion for clean propulsion and power generation, Appl. Energy 186 (2017) 13–27, https://doi.org/10.1016/j.apenergy.2016.10.033.

[11] J.M. Bergthorson, Recyclable metal fuels for clean and compact zero-carbon power, Elsevier Ltd (2018), https://doi.org/10.1016/j.pecs.2018.05.001.

[12] V. Testa, M. Gerardi, L. Zannini, M. Romagnoli, P.E. Santangelo, Hydrogen production from aluminum reaction with NaOH/H2O solution: experiments and insight into reaction kinetics, Int. J. Hydrogen Energy 83 (2024) 589–603, https://doi.org/10.1016/j.ijhydene.2024.08.152.

[13] K. Trowell, S. Goroshin, D. Frost, J. Bergthorson, Hydrogen production rates of aluminum reacting with varying densities of supercritical water, RSC Adv. 12 (20) (2022) 12335–12343, https://doi.org/10.1039/d2ra01231f.

[14] M.Q. Fan, L.X. Sun, F. Xu, Experiment assessment of hydrogen production from activated aluminum alloys in portable generator for fuel cell applications, Energy 35 (7) (2010) 2922–2926, https://doi.org/10.1016/j.energy.2010.03.023.

[15] S. Xu, X.H. Yang, S.S. Tang, J. Liu, Liquid metal activated hydrogen production from waste aluminum for power supply and its life cycle assessment, Int. J. Hydrogen Energy 44 (33) (2019) 17505–17514, https://doi.org/10.1016/J.IJHYDENE.2019.05.176.

[16] C. Chen, J. Lu, B. Zhang, T. Liang, F. Xiao, Study on synergistic hydrogen generation from aluminum-based composites in different forms of water, Phys. Chem. Chem. Phys. 26 (22) (2024) 15987–15998, https://doi.org/10.1039/d3cp05429b.

[17] D.M. Taher, et al., All-electric ship on-board continuous sustainable H2 generation from aluminum scrap and seawater, in: 2023 IEEE Electric Ship Technologies Symposium, ESTS 2023, Institute of Electrical and Electronics Engineers Inc., 2023, pp. 211–217, https://doi.org/10.1109/ESTS56571.2023.10220471.

[18] M.A.E. Soberanis, et al., Temperature dependence on hydrogen production from hydrolysis reaction of recycled aluminum, Clean. Technol. Environ. Policy. 25 (1) (2023) 35–49, https://doi.org/10.1007/s10098-022-02386-y.

[19] F. Xiao, R. Yang, Z. Liu, Active aluminum composites and their hydrogen generation via hydrolysis reaction: a review, Elsevier Ltd (2022), https://doi.org/10.1016/j.ijhydene.2021.09.241.

[20] V.N. Alviani, et al., Mechanisms and possible applications of the Al–H2O reaction under extreme pH and low hydrothermal temperatures, Int. J. Hydrogen Energy 44 (57) (2019) 29903–29921, https://doi.org/10.1016/J.IJHYDENE.2019.09.152.

[21] A. Irankhah, S.M. Seyed Fattahi, M. Salem, Hydrogen generation using activated aluminum/water reaction, Int. J. Hydrogen Energy 43 (33) (2018) 15739–15748, https://doi.org/10.1016/j.ijhydene.2018.07.014.

[22] B. Alinejad, K. Mahmoodi, A novel method for generating hydrogen by hydrolysis of highly activated aluminum nanoparticles in pure water, Int. J. Hydrogen Energy 34 (19) (2009) 7934–7938, https://doi.org/10.1016/j.ijhydene.2009.07.028.

[23] A.K. Narayana Swamy, E. Shafirovich, Conversion of aluminum foil to powders that react and burn with water, Combust. Flame 161 (1) (2014) 322–331, https://doi.org/10.1016/j.combustflame.2013.08.017.

[24] Y. Liu, X. Liu, X. Chen, S. Yang, C. Wang, Hydrogen generation from hydrolysis of activated Al-Bi, Al-Sn powders prepared by gas atomization method, Int. J. Hydrogen Energy 42 (16) (2017) 10943–10951, https://doi.org/10.1016/j.ijhydene.2017.02.205.

[25] C. Wang, et al., A novel self-assembling al-based composite powder with high hydrogen generation efficiency, Sci. Rep. 5 (2015), https://doi.org/10.1038/srep17428.

[26] X. Chen, et al., Popcorn-like aluminum-based powders for instant low-temperature water vapor hydrogen generation, Mater. Today Energy 19 (2021), https://doi.org/10.1016/j.mtener.2020.100602.

[27] D.H. Xuan, Y.P. Qiu, P. Wang, Rapid hydrogen generation from the reaction of aluminum/activated charcoal composite with alkaline solution, J. Alloys. Compd. 947 (2023), https://doi.org/10.1016/j.jallcom.2023.169611.

[28] Y. Sun, R. Sun, B. Zhu, Y. Wu, Effects of additives on the hydrogen generation of Al–H2O reaction at low temperature, Int. J. Energy Res. 41 (14) (2017) 2020–2033, https://doi.org/10.1002/er.3761.

[29] A. Bolt, I. Dincer, M. Agelin-Chaab, Experimental study of hydrogen production process with aluminum and water, Int. J. Hydrogen Energy 45 (28) (2020) 14232–14244, https://doi.org/10.1016/j.ijhydene.2020.03.160.

[30] M. Etminanbakhsh, S. Reza Allahkaram, Reaction of aluminum particles with superheated steam to generate hydrogen gas as a readily usable clean fuel, Fuel 332 (2023), https://doi.org/10.1016/j.fuel.2022.126011.

[31] P. Setiani, N. Watanabe, R.R. Sondari, N. Tsuchiya, Mechanisms and kinetic model of hydrogen production in the hydrothermal treatment of waste aluminum, Mater. Renew. Sustain. Energy 7 (2) (2018), https://doi.org/10.1007/s40243-018-0118-8.

[32] X. Gao, C. Wang, W. Bai, Y. Hou, D. Che, Experimental investigation of the catalyst-free reaction characteristics of micron aluminum powder with water at low and medium temperatures, J. Energy Storage 59 (2023), https://doi.org/10.1016/j.est.2022.106543.

[33] L. Barelli, L. Trombetti, A. Di Michele, L. Gammaitoni, J. Asenbauer, S. Passerini, Aluminum steam oxidation in the framework of long-term energy storage: experimental analysis of the reaction parameters effect on metal conversion rate, Energy Technol. 10 (9) (2022), https://doi.org/10.1002/ente.202200441.

[34] H. Zhang, Y. Sun, F. He, X. Yu, Z. Zhao, Preparation and characterization of activated aluminum powder by magnetic grinding method for hydrogen generation, Int. J. Energy Res. 38 (8) (2014) 1016–1023, https://doi.org/10.1002/er.3123.

[35] E.L. Dreizin, M. Schoenitz, Correlating ignition mechanisms of aluminum-based reactive materials with thermoanalytical measurements, Prog. Energy Combust. Sci. 50 (2015) 81–105, https://doi.org/10.1016/J.PECS.2015.06.001.

[36] S.P. du Preez, D.G. Bessarabov, On-demand hydrogen generation by the hydrolysis of ball-milled aluminum composites: a process overview, Int. J. Hydrogen Energy 46 (72) (2021) 35790–35813, https://doi.org/10.1016/J.IJHYDENE.2021.03.240.

[37] K.G. Raghavendra, et al., Synthesis and characterization of Fe-15wt.% ZrO2 nanocomposite powders by mechanical milling, Powder Technol. 287 (2016) 190–200, https://doi.org/10.1016/j.powtec.2015.10.003.

[38] S.P. du Preez, D.G. Bessarabov, Hydrogen generation by the hydrolysis of mechanochemically activated aluminum-tin-indium composites in pure water, Int. J. Hydrogen Energy (2018) 21398–21413, https://doi.org/10.1016/j.ijhydene.2018.09.133.

[39] S.P. du Preez, D.G. Bessarabov, The effects of bismuth and tin on the mechanochemical processing of aluminum-based composites for hydrogen generation purposes, Int. J. Hydrogen Energy 44 (39) (2019) 21896–21912, https://doi.org/10.1016/j.ijhydene.2019.06.154.

[40] F. Xiao, R.-J. Yang, J.-M. Li, Preparation and characterization of mechanically activated aluminum/polytetrafluoroethylene composites and their reaction properties in high temperature water steam, J. Alloys. Compd. 761 (2018) 24–30, https://doi.org/10.1016/j.jallcom.2018.05.087.

[41] S.S. Razavi-Tousi, J.A. Szpunar, Effect of structural evolution of aluminum powder during ball milling on hydrogen generation in aluminum–water reaction, Int. J. Hydrogen Energy 38 (2) (2013) 795–806, https://doi.org/10.1016/J.IJHYDENE.2012.10.106.

[42] E.L. Dreizin, M. Schoenitz, Mechanochemically prepared reactive and energetic materials: a review, J. Mater. Sci. 52 (20) (2017) 11789–11809, https://doi.org/10.1007/s10853-017-0912-1.

[43] G.L. Ma, H. Bin Dai, D.W. Zhuang, H.J. Xia, P. Wang, Controlled hydrogen generation by reaction of aluminum/sodium hydroxide/sodium stannate solid mixture with water, Int. J. Hydrogen Energy 37 (7) (2012) 5811–5816, https://doi.org/10.1016/j.ijhydene.2011.12.157.

[44] K. Mahmoodi, B. Alinejad, Enhancement of hydrogen generation rate in reaction of aluminum with water, Int. J. Hydrogen Energy 35 (11) (2010) 5227–5232, https://doi.org/10.1016/j.ijhydene.2010.03.016.

[45] S. Yolcular, S. Karaoglu, M. Karasoglu, Hydrogen generation performance of waste aluminum alloy chips and powders, Energy Sources, Part A: Recov. Utiliz. Environ. Effects 44 (1) (2022) 1529–1540, https://doi.org/10.1080/15567036.2020.1822468.

[46] E. Czech, T. Troczynski, Hydrogen generation through massive corrosion of deformed aluminum in water, Int. J. Hydrogen Energy 35 (3) (2010) 1029–1037, https://doi.org/10.1016/j.ijhydene.2009.11.085.

[47] M.Q. Fan, et al., Microstructure of Al-Li alloy and its hydrolysis as portable hydrogen source for proton-exchange membrane fuel cells, Int. J. Hydrogen Energy 36 (16) (2011) 9791–9798, https://doi.org/10.1016/j.ijhydene.2011.05.096.

[48] X. Zhang, et al., Hydrogen production from aluminum-water reactions at low temperatures: based on an in-situ two powders of different particle sizes, Front. Energy Res. 12 (2024), https://doi.org/10.3389/fenrg.2024.1441155.

[49] S.S. Razavi-Tousi, J.A. Szpunar, Effect of addition of water-soluble salts on the hydrogen generation of aluminum in reaction with hot water, J. Alloys. Compd. 679 (2016) 364–374, https://doi.org/10.1016/j.jallcom.2016.04.038.

[50] C. Wang, T. Yang, Y. Liu, J. Ruan, S. Yang, X. Liu, Hydrogen generation by the hydrolysis of magnesium-aluminum-iron material in aqueous solutions, Int. J. Hydrogen Energy 39 (21) (2014) 10843–10852, https://doi.org/10.1016/j.ijhydene.2014.05.047.

[51] S. Dossi, Using Al-based activated powders for on-demand hydrogen production: possibilities and perspectives of the 'white' Hydrogen, Adv. Sci. Technol. Innov. (2024) 415–418, https://doi.org/10.1007/978-3-031-43922-3_94.

[52] S. Dossi, "Process for the production of a tablet for generating gaseous hydrogen from water and its control," 102021000017624, Jul. 05, 2023.

[53] H.B. Dai, G.L. Ma, H.J. Xia, P. Wang, Reaction of aluminium with alkaline sodium stannate solution as a controlled source of hydrogen, Energy Environ. Sci. 4 (6) (2011) 2206–2212, https://doi.org/10.1039/c1ee00014d.

[54] J. Macanás, L. Soler, A.M. Candela, M. Muñoz, J. Casado, Hydrogen generation by aluminum corrosion in aqueous alkaline solutions of inorganic promoters: the AlHidrox process, Energy 36 (5) (2011) 2493–2501, https://doi.org/10.1016/j.energy.2011.01.041.

[55] W.Z. Gai, et al., In situ hydrogen production from Al–BiCl3 hydrolysis for small-sized fuel cell, J. Power Sources. 606 (2024), https://doi.org/10.1016/j.jpowsour.2024.234567.

[56] W.Z. Gai, W.Y. Wang, J.W. Yang, Y.Y. Shi, H. Jia, Z.Y. Deng, A novel Al/BiCl3/γ-Al2O3 composite for small-sized fuel cell: fabrication, performance and mechanisms, Int. J. Hydrogen Energy 84 (2024) 929–938, https://doi.org/10.1016/j.ijhydene.2024.08.311.

[57] R. Prins, On the structure of γ-Al2O3, J. Catal. 392 (2020) 336–346, https://doi.org/10.1016/J.JCAT.2020.10.010.

[58] J.F. Boyle, S.II. Mclntosh, and D.J. cade, "Methods and apparatus for controlled production of hydrogen using aluminum-based water-split reactions," US 2012/0225010 Al, May 12, 2012.

[59] A.V. Ilyukhina, O.V. Kravchenko, B.M. Bulychev, Studies on microstructure of activated aluminum and its hydrogen generation properties in aluminum/water reaction, J. Alloys. Compd. 690 (2017) 321–329, https://doi.org/10.1016/j.jallcom.2016.08.151.

[60] F.D. Manilevich, Y.K. Pirskyy, A.V. Kutsyi, V.V. Berezovets, V.A. Yartys, Studies of mechanochemically activated aluminum powders for generating hydrogen from water, Powder Metall. Metal Ceramics 60 (5–6) (2021) 268–277, https://doi.org/10.1007/s11106-021-00237-x.

[61] F.D. Manilevich, Y.K. Pirskyy, A.V. Kutsyi, V.V. Berezovets, V.A. Yartys, Aluminium as an efficient energy storage substance for the catalysed generation of hydrogen from water, J. Energy Storage 96 (2024), https://doi.org/10.1016/j.est.2024.112748.

[62] L.G. Sevastyanova, S.N. Klyamkin, V.A. Stupnikov, A.V. Ilyukhina, B. M. Bulychev, On mechanism of hydrogen generation at oxidation of activated aluminum in aqueous solutions, Int. J. Hydrogen Energy 54 (2024) 428–436, https://doi.org/10.1016/j.ijhydene.2023.07.224.

[63] A.V. Parmuzina, O.V. Kravchenko, Activation of aluminium metal to evolve hydrogen from water, Int. J. Hydrogen Energy 33 (12) (2008) 3073–3076, https://doi.org/10.1016/j.ijhydene.2008.02.025.

[64] D. Rohendi, A. Rachmat, N. Syarif, M. Said, I. Rihsansah, The production of hydrogen from aluminum waste by aluminum-water methods at various conditions, in: IOP Conference Series: Earth and Environmental Science, Institute of Physics Publishing, 2019, https://doi.org/10.1088/1755-1315/396/1/012009.

[65] M.Q. Fan, D.S. Mei, D. Chen, C.J. Lv, K.Y. Shu, Portable hydrogen generation from activated Al-Li-Bi alloys in water, Renew. Energy 36 (11) (2011) 3061–3067, https://doi.org/10.1016/j.renene.2011.03.029.

[66] K. Naseem, H. Zhong, H. Wang, L. Ouyang, M. Zhu, Promoting Al hydrolysis via MgH2 and NaOH addition, J. Alloys. Compd. 831 (2020), https://doi.org/10.1016/j.jallcom.2020.154793.

[67] A.V. Ilyukhina, O.V. Kravchenko, B.M. Bulychev, E.I. Shkolnikov, Mechanochemical activation of aluminum with gallams for hydrogen evolution from water, Int. J. Hydrogen Energy 35 (5) (2010) 1905–1910, https://doi.org/10.1016/j.ijhydene.2009.12.118.

[68] R. Deng, et al., Development of cost-effective Sn-free Al-Bi-Fe alloys for efficient onboard hydrogen production through Al–Water reaction, Materials (Basel) 17 (20) (2024), https://doi.org/10.3390/ma17204973.

[69] Y.F. Adans, A.R. Martins, R.E. Coelho, C.F. Das Virgens, A.D. Ballarini, L. S. Carvalho, A simple way to produce γ-alumina from aluminum cans by precipitation reactions, Mater. Res. 19 (5) (2016) 977–982, https://doi.org/10.1590/1980-5373-MR-2016-0310.

[70] S.P. Tekade, D.Z. Shende, and K.L. Wasewar, "Hydrogen generation in water splitting reaction using aluminum: effect of NaOH concentration and reaction modelling using SCM," vol. 16, no. 7, 2018, doi:10.1515/ijcre-2017-0250.

[71] H. Yang, H. Zhang, R. Peng, S. Zhang, X. Huang, Z. Zhao, Highly efficient hydrolysis of magnetic milled powder from waste aluminum (Al) cans with low-concentrated alkaline solution for hydrogen generation, Int. J. Energy Res. 43 (9) (2019) 4797–4806, https://doi.org/10.1002/er.4621.

[72] H. Wang, Z. Wang, Z. Shi, X. Gong, J. Cao, M. Wang, Facile hydrogen production from Al-water reaction promoted by choline hydroxide, Energy 131 (2017) 98–105, https://doi.org/10.1016/j.energy.2017.05.031.

[73] J. Oh, S. Yoon, W. Kim, Hydrogen production by water splitting using commercial Al pellets in a circulating NaOH flow reactor, Fuel 374 (2024), https://doi.org/10.1016/j.fuel.2024.132510.

[74] R. Moreno-Flores, F. Loyola-Morales, E. Valenzuela, P.J. Sebastian, Design and performance evaluation of a prototype hydrogen generator employing hydrolysis of aluminum waste, Clean. Technol. Environ. Policy. 25 (2) (2023) 747–753, https://doi.org/10.1007/s10098-022-02276-3.

[75] V. Shmelev, V. Nikolaev, J.H. Lee, C. Yim, Hydrogen production by reaction of aluminum with water, Int. J. Hydrogen Energy 41 (38) (2016) 16664–16673, https://doi.org/10.1016/j.ijhydene.2016.05.159.

[76] H. Liu, F. Yang, B. Yang, Q. Zhang, Y. Chai, N. Wang, Rapid hydrogen generation through aluminum-water reaction in alkali solution, Catal. Today 318 (2018) 52–58, https://doi.org/10.1016/J.CATTOD.2018.03.030.

[77] L. Soler, A.M. Candela, J. Macanás, M. Muñoz, J. Casado, Hydrogen generation by aluminum corrosion in seawater promoted by suspensions of aluminum hydroxide, Int. J. Hydrogen Energy 34 (20) (2009) 8511–8518, https://doi.org/10.1016/J.IJHYDENE.2009.08.008.

[78] L. Soler, A.M. Candela, J. Macanás, M. Muñoz, J. Casado, Hydrogen generation from water and aluminum promoted by sodium stannate, Int. J. Hydrogen Energy 35 (3) (2010) 1038–1048, https://doi.org/10.1016/J.IJHYDENE.2009.11.065.

[79] N. Fadhilah, F.R. Maulana, R.A. Wahyuono, M. Raditya, D.D. Risanti, Hydrogen generation from waste aluminum foil AA 1235 promoted by sodium aluminate in sodium hydroxide solutions, Key. Eng. Mater. 965 (2023) 113–118, https://doi.org/10.4028/p-UR11a3.

[80] N. Fadhilah, et al., Kinetic study of the aluminum–Water reaction using NaOH/NaAlO2 catalyst for hydrogen production from aluminum cans waste, Bull. Chem. Reaction Eng. Catal. 18 (4) (2023) 615–626, https://doi.org/10.9767/bcrec.20041.

[81] M.A. Amrani, et al., Productive and sustainable H2 production from waste aluminum using copper oxides-based graphene nanocatalysts: a techno-economic analysis, Sustainability (Switzerland) 14 (22) (2022), https://doi.org/10.3390/su142215256.

[82] A. Hammad, et al., Aluminum hydrolysis for hydrogen generation enhanced by sodium hydride, Int. J. Hydrogen Energy 77 (2024) 138–148, https://doi.org/10.1016/j.ijhydene.2024.06.174.

[83] P. Deebika, M.P. Saravanakumar, Utilization of RO rejects and waste aluminum scraps for hydrogen generation, Int. J. Hydrogen Energy 48 (91) (2023) 35516–35531, https://doi.org/10.1016/j.ijhydene.2023.06.015.

[84] W. Tang, L. Yan, K. Li, Y. Juan, C. Fu, J. Zhang, A comparison study on aluminum-water reaction with different catalysts, Mater. Today Commun. 31 (2022), https://doi.org/10.1016/j.mtcomm.2022.103517.

[85] M. Pini, et al., Life cycle assessment of an innovative cogeneration system based on the aluminum combustion with water, Renew. Energy 154 (2020) 532–541, https://doi.org/10.1016/j.renene.2020.03.046.

[86] A. Farmani, F. Eskandari Manjili, Modelling and assessment of hydrogen combined cycle power plant using aluminum-water reaction as renewable fuel, Int. J. Hydrogen Energy 50 (2024) 276–291, https://doi.org/10.1016/j.ijhydene.2023.08.239.

[87] M. Milani, et al., Experimental and numerical analysis of a liquid aluminium injector for an Al-H2O based hydrogen production system, Int. J. Thermofl. 7–8 (2020), https://doi.org/10.1016/j.ijft.2020.100018.

[88] M.S. Vlaskin, G.E. Valyano, A.Z. Zhuk, E.I. Shkolnikov, Oxidation of coarse aluminum in pressured water steam for energy applications, Int. J. Energy Res. 44 (11) (2020) 8689–8715, https://doi.org/10.1002/er.5561.

[89] K.A. Trowell, S. Goroshin, D.L. Frost, J.M. Bergthorson, The use of supercritical water for the catalyst-free oxidation of coarse aluminum for hydrogen production, Sustain. Energy Fuels. 4 (11) (2020) 5628–5635, https://doi.org/10.1039/d0se00996b.

[90] X. Wang, G. Li, R.K. Eckhoff, Kinetics study of hydration reaction between aluminum powder and water based on an improved multi-stage shrinking core model, Int. J. Hydrogen Energy 46 (67) (2021) 33635–33655, https://doi.org/10.1016/J.IJHYDENE.2021.07.191.

[91] X. Gao, C. Wang, Y. Hou, L. Zhao, W. Bai, D. Che, Experimental study on catalyst-free high-temperature and high-pressure aluminum-water reaction characteristics using metal as energy carrier, Int. J. Hydrogen Energy 50 (2024) 1338–1357, https://doi.org/10.1016/j.ijhydene.2023.09.216.

[92] F. Halter, V. Glasziou, M. Di Lorenzo, S. Gallier, C. Chauveau, Peculiarities of aluminum particle combustion in steam, Proc. Combust. Institute 39 (3) (2023) 3605–3614, https://doi.org/10.1016/j.proci.2022.07.120.

[93] O.A. Buryakovskaya, M.S. Vlaskin, A.V. Grigorenko, Effect of thermal treatment of aluminum core-shell particles on their oxidation kinetics in water for hydrogen production, Materials (Basel) 14 (21) (2021), https://doi.org/10.3390/ma14216493.

[94] F. Li, B. Zhu, Y. Sun, W. Tao, Hydrogen generation by means of the combustion of aluminum powder/sodium borohydride in steam, Int. J. Hydrogen Energy 42 (6) (2017) 3804–3812, https://doi.org/10.1016/j.ijhydene.2016.07.015.

[95] B. Zhu, et al., Enhancing ignition and combustion characteristics of micron-sized aluminum powder in steam by adding sodium fluoride, Combust. Flame 205 (2019) 68–79, https://doi.org/10.1016/J.COMBUSTFLAME.2019.02.007.

[96] F. Halter, et al., Demonstration of the co-generation of heat and hydrogen by high-temperature oxidation of aluminum in steam, Int. J. Hydrogen Energy 102 (2025) 1140–1142, https://doi.org/10.1016/j.ijhydene.2025.01.116.

[97] T. Kirton, F. Saceleanu, M. Salehi Mobarakeh, M.R. Kholghy, Cogeneration of hydrogen, alumina, and heat from aluminum-water reactions, Int. J. Hydrogen Energy 68 (2024) 115–127, https://doi.org/10.1016/j.ijhydene.2024.04.038.

[98] Y. Yavor, S. Goroshin, J.M. Bergthorson, D.L. Frost, Comparative reactivity of industrial metal powders with water for hydrogen production, Int. J. Hydrogen Energy 40 (2) (2015) 1026–1036, https://doi.org/10.1016/j.ijhydene.2014.11.075.

[99] X. Gao, C. Wang, Y. Hou, L. Zhao, W. Bai, D. Che, Experimental study on characteristics and mechanism of hydrogen production from aluminium–water reaction for carbon-free power generation, Fuel 380 (2025), https://doi.org/10.1016/j.fuel.2024.133206.

[100] M.S. Vlaskin, E.I. Shkolnikov, A.V. Bersh, Oxidation kinetics of micron-sized aluminum powder in high-temperature boiling water, Int. J. Hydrogen Energy 36 (11) (2011) 6484–6495, https://doi.org/10.1016/j.ijhydene.2011.02.131.

[101] E.I. Schraud, H. Dong Nguyen, and M. Schraud, “Hydrothermal process for producing hydrogen,” US 2022/0371884 A1, Nov. 11, 2022.

[102] D. Brough, H. Jouhara, The aluminium industry: a review on state-of-the-art technologies, environmental impacts and possibilities for waste heat recovery, Elsevier B.V (2020), https://doi.org/10.1016/j.ijft.2019.100007.