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Umit B. Demirci. Exploring the technological maturity of hydrogen production by hydrolysis of sodium borohydride. International Journal of Hydrogen Energy, 2023, 10.1016/j.ijhydene.2023.04.176 . hal-04093600

HAL Id: hal-04093600

https://hal.umontpellier.fr/hal-04093600v1

Submitted on 10 May 2023

Exploring the technological maturity of hydrogen production by hydrolysis of sodium borohydride

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Abstract

Sodium borohydride $NaBH_4$ (SB) has been rediscovered in the late 1990s and been presented as a promising hydrogen storage material owing to its high gravimetric hydrogen density of 10.8 wt% and ability to produce H_2 by hydrolysis at ambient conditions. This looked promising, but soon hydrolysis of SB encountered numerous obstacles. In 2015, a progress report (Int J Hydrogen Energy 2015;40:2673-91) showed that the 2000-2014 research did not overcome all of the obstacles, making SB far from being technologically mature. Eight years have passed since 2015. Have we put more effort into all aspects relating to hydrolysis of SB? If so, do we have produced scaled-up technologies and prototypes, of which we would have a better knowledge? Have we been able to gain in technological readiness level? Answering these questions is the main objective of this article. A secondary objective is to summarize the newly acquired knowledge. Five main observations stand out. First, the 2015-2022 period is regrettably similar to the 2000-2014 since, again, catalysts have dominated the field and the other aspects (e.g. recycling of the by-product to regenerate SB, scale-up and implementation) have received little attention. Second, hydrolysis of SB still runs into numerous obstacles, some of the obstacles being known since a long time and other ones being relatively new and unknown. Third, there has been little gain in terms of technological readiness level while few research groups have shown that there is room for new ideas and innovation. Fourth, energy, exergy and economic analyses are needed to evaluate the overall cost of H_2 from SB. Fifth, SB has not effectively thought from the end user perspective. In conclusion, many obstacles remain to be overcome before hydrolysis of SB can be a commercial solution for carrying and producing

H_2. However, all efforts should be dedicated to (i) construct, operate and optimize H_2 production systems (i.e. prototypes and demonstrators), (ii) handle SB at the gram-to-kilogram scale, (iii) make production of SB even more efficient, and (iv) overcome all obstacles while thinking from the end user perspective.

Keywords

Hydrogen carrier; Hydrogen production; Hydrogen storage; Hydrolysis; Sodium borohydride

1. Introduction

Sodium borohydride $NaBH_4$ (SB) was discovered and identified in the 1940s as a hydrogen carrier (gravimetric hydrogen density of 10.8 wt%) capable of producing H_2 by hydrolysis (Eq. 1) at ambient conditions [1,2]:

$$NaBH_4 \text{ (aq or s)} + 4H_2O \text{ (l)} \rightarrow NaB(OH)_4 \text{ (aq or s)} + 4H_2 \text{ (g)} \qquad (1)$$

Producing H_2 at ambient conditions is attractive, but producing H_2 knowing that half comes from water is even more attractive (Figure 1). The theoretical gravimetric hydrogen storage capacity of SB and water in stoichiometric conditions is 7.3 wt%. The hydrolysis reaction is exothermic (ca. –240 kJ mol^{-1}), which makes that H_2 is produced spontaneously. Such a spontaneous production can be mitigated at basic pH, but it is then necessary to use a catalyst or an accelerator to produce H_2 at controllable rates and reach conversions of 100%. The reaction produces sodium tetrahydroxyborate $NaB(OH)_4$, a by-product that is less soluble in water than SB is [3].

SB and hydrolysis of SB were rediscovered in the late 1990s [4]. A prototype using an aqueous alkaline solution of SB was constructed and tested as a H_2 production system for fuel cell vehicles [5]. This looked promising, but hydrolysis of SB encountered obstacles and well-founded criticism. For instance, the US Department of Energy made a no-go decision (for light-duty vehicles application) because of the cost of SB and the inefficiency of the regeneration processes studied at that time [6]. Research on hydrolysis of SB has nonetheless remained active and dynamic as evidenced by a selection of review articles released since 2015 [7-17]. Reading these articles indicates that the research on hydrolysis of SB performed between 2000 and 2015 had mainly focused on catalysts and accelerators, and other equally important aspects (i.e. recycling of the by-product to regenerate SB, scale-up and implementation) had been neglected [18].

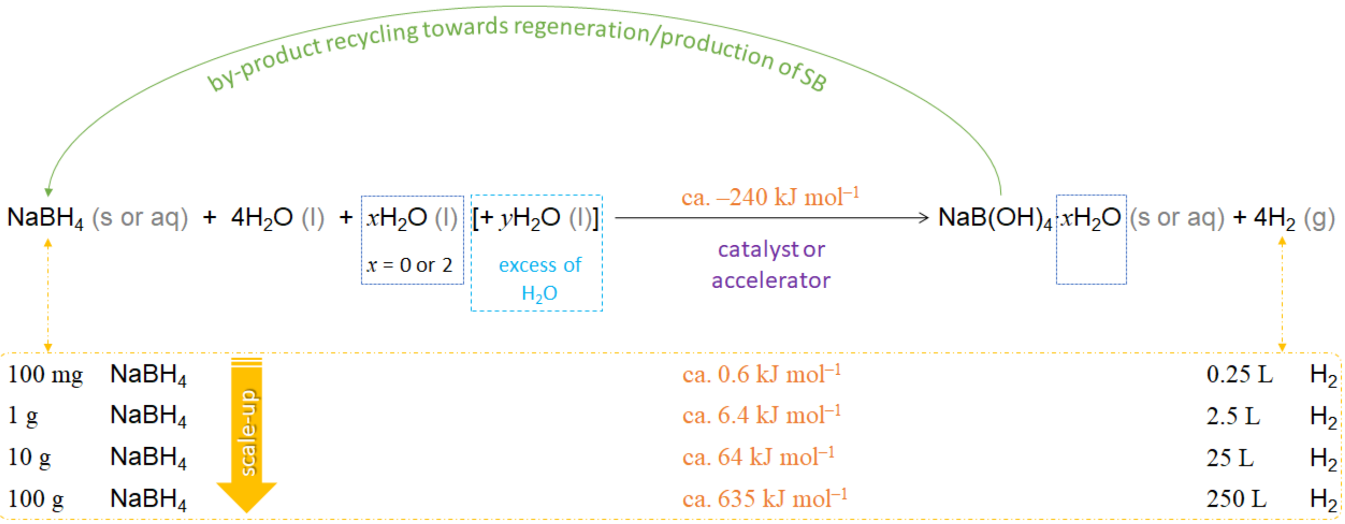

Figure 1. Hydrolysis of SB: the reactants, water in excess as solvent, a catalyst or an accelerator, the heat of the reaction, the by-products, the product H_2, and the amounts of SB and H_2 towards scale-up.

Eight years have passed since 2015. Have we put more effort into all aspects relating to hydrolysis of SB? If so, do we have produced scaled-up technologies and prototypes, of which we would have a better knowledge? Have we been able to gain in technological readiness level? Or, on the contrary, have catalysts or accelerators dominated the field? Answering the above questions is the primary objective of the present article. To that end, it surveys the open literature dedicated to hydrolysis of SB since 2015 and until 2022. The second objective is to summarize the newly acquired knowledge. For the sake of clarity and of consistency, alcoholysis of SB and thermolysis of SB are not discussed herein.

The structure of the present article is based on the different aspects of the hydrolysis reaction as illustrated in Figure 1. The first of the next sections is about the reaction, the reactants and the products. The second one deals with catalysts and accelerators in a brief and concise manner. The third one is entitled scale-up and focuses on scaled-up technologies and prototypes. The fourth, and last one before the conclusion, is about regeneration of SB. Before getting to the heart of the matter, it is worth mentioning that catalyzed hydrolysis of SB has been also considered for other applications such as hydrogenation/reduction of nitro compounds to produce amines [19-38], reduction of azides to anilines [39,40], *N*-cycle hydrogenation of quinolone [41], reduction of carbon dioxide

CO_2 into the formate ion [42], reduction of bromate ions onto bromide ions [43-46], removal of Cr(VI) from aqueous solutions [47-50], degradation of organic dyes [51-53], detoxification of olive-tree pruning hydrolyzates [54], and gas foaming [55].

2. Hydrolysis of SB

SB in solid state degrades if contaminated by moisture and CO_2 of air (upon its storage for example). Such an aspect had been neglected until recently [56]. Such a contamination leads to the formation of sodium polyborates (e.g. $Na_2B_4O_7$) and sodium carbonate Na_2CO_3, and these degradation products cover the SB grains. It then becomes necessary to purify SB before its use. This can be done by using diglyme as solvent, plus ammonia to increase the dissolution of SB, and the process is terminated by the crystallization of SB. This way, a 95%-pure SB can be recovered.

SB and water carry hydrogens that are respectively negatively and positively charged, i.e. $H^{\delta-}$ and $H^{\delta+}$. These hydrogens interact and combine to produce H_2, which implies that dihydrogen bonds $B–H^{\delta-}\cdots H^{\delta+}–O$ form is an intermediate step [57]. This was notably predicted by theoretical calculations [58]. The anion BH_3OH^- is assumed to form as the first short-living reaction intermediate and the corresponding reaction is the rate-determining step [59]. This was experimentally confirmed by using NMR spectroscopy [60]. The formation of BH_3OH^- is followed by that of the consecutive short-living reaction intermediates $BH_2(OH)_2^-$, $BH(OH)_3^-$, and finally, $B(OH)_4^-$. With respect to BH_3OH^-, it was also predicted that it may exist in the form of BH_3 and OH^- separated by water molecules [61]. Because of the intermediates BH_3OH^- and BH_3 (both being able to oscillate), hydrolysis of SB undergoes an oscillatory instability and the consequence is that the production of H_2 is not smooth (i.e. occurrence of fluctuations) [62].

From a practical point of view, it would be more convenient to provide an aqueous solution of SB (instead of SB in solid state and water separately) to the end user. This supposes that the aqueous solution of SB is stabilized by addition of sodium hydroxide NaOH (basic pH), even though this does not totally hinder the occurrence of spontaneous hydrolysis of SB. The question of long-term storage of aqueous alkaline solution of SB then arises. Netskina et al. [63,64] answered it. A solution containing 15 wt% SB and 5 wt% NaOH was kept for one year at 23-25 °C. During this time, 66% of the initial SB hydrolyzed, and the solution pH increased from 11.5 to 12.9. For another solution initially containing 25 wt% SB and 1 wt% NaOH, 76% of SB hydrolyzed after one year, and the pH increased from 11.2 to 13.2. The by-product that formed and precipitated is sodium tetrahydroxyborate dihydrate $NaB(OH)_4 \cdot 2H_2O$. We [65] also answered the above question. We conducted a systematic study by using NMR spectroscopy. The SB concentration was varied from 3.65 to 31.22 wt%, the NaOH concentration from 1 to 16 M, and the storage temperature from –15 to 60 °C; each solution was stored for up to 12 weeks. Hydrolysis took place whatever the conditions (Figure 2). Nonetheless, a relatively good stability of SB was noticed when the solutions with a NaOH concentration of ≥8 M were kept at ≤4 °C. Otherwise, storing at higher temperatures, and above all at the high temperatures that are reached in summer time (>30 °C in Montpellier, France, from June to September, even nowadays from May to October) will pose serious safety concerns.

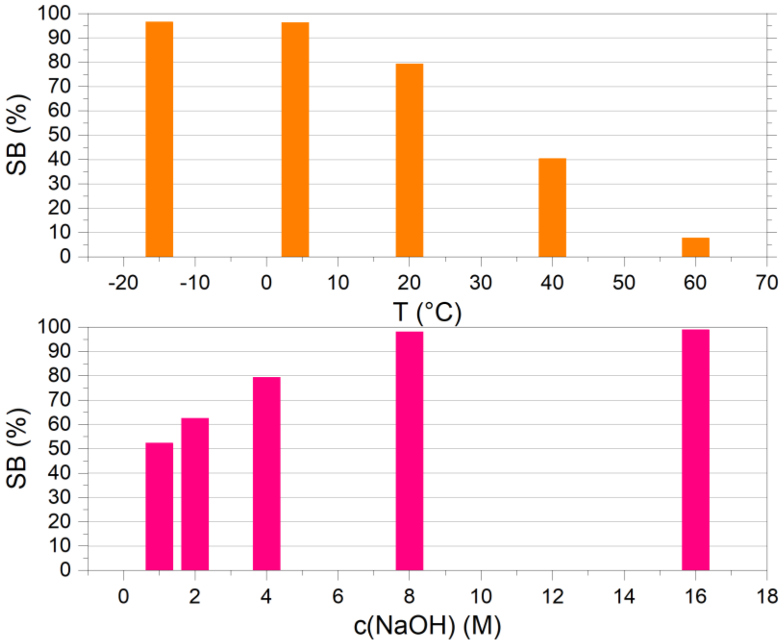

Figure 2. SB remaining (in mole percentage) in aqueous alkaline solution after a storage of 12 weeks: (top) effect of the temperature (-15, 4, 20, 40 and 60 °C) for an aqueous solution of SB (initial concentration of 4 M) having a concentration of NaOH of 4 M; (bottom) effect of the initial concentration of NaOH (1, 2, 4, 8 and 16 M) for an aqueous solution of SB (initial concentration of 4 M) stored at 20 °C.

Water has not been the subject of particular attention until recently. Yet, it is just as important as SB (Eq. 1). For example, what water should we use? At the laboratory scale and to avoid any experimental bias, it is obvious that we have to use distilled water. However, the use of distilled water by the end user will be a constraint and will add to the cost of the H_2 production system. Mosier-Boss et al. [66] studied the effect of distilled water, tap water and seawater, on the $CoCl_2$-catalyzed hydrolysis of SB. They observed slower kinetics of H_2 production when tap water was used, and even slower when seawater was used. Organic species present in both tap water and seawater were found to form complexes with Co^{2+}, thereby impeding an efficient catalysis of the hydrolysis reaction. One cannot generalize these observations because of the use of $CoCl_2$. Indeed, in such conditions, Co^{2+} of $CoCl_2$ is a pre-catalyst, and as such it in situ transforms into a Co-based catalyst (e.g. cobalt boride) when it is put into contact with SB in aqueous solution. The Co-based catalyst, and not Co^{2+}, thus catalyzes the hydrolysis reaction, whereas in this study, a proportion of Co^{2+} did not generate the Co-based catalyst. With less catalyst, the hydrolysis reaction is thus less efficient. Oh et al. [67] reported different results for Co-P-B/C used as catalyst. They found that fresh water (versus distilled water) allows better performance in terms of H_2 production yields and rates. Regrettably, and in conclusion to these paragraph, too little is known about the use of water of different qualities.

The by-product that forms upon hydrolysis of SB is $NaB(OH)_4$. It is less soluble than SB is in water (16 vs 55 g in 100 mL of water), and precipitates when SB solutions are concentrated (as mentioned above) [69]; this is an issue (see section 4). $NaB(OH)_4$ forms when the mole ratio Na/B is 1 as in the case of the use of SB without addition of NaOH, and when the mole ratio Na/B is >1 as in the case of aqueous alkaline solutions [68]. When the mole ratio Na/B is lower than 1 (e.g. 0.33), polyborate anions (B_3-, B_4-, B_5-based) form [70]. Sodium polyborates are more water-soluble than $NaB(OH)_4$. Note that a mole ratio of e.g. 0.33 assumes that a boron-containing compound like boric acid $B(OH)_3$ has to be added to the SB solution. Another option would be to use sodium octahydrotriborate NaB_3H_8 instead of SB.

The value-added product of hydrolysis of SB is H_2, and the reaction (Eq. 1) suggests that the produced H_2 is pure. However, the situation is not quite as simple as that. Because of the reaction exothermicity, water vapor is transported along with H_2, and this water vapor contains Na^+ and $B(OH)_4^-$ [71,72]. This poses a constraint and a question. The constraint is that the produced H_2 must be purified (owing to downstream traps; see section 4) or the reactor design should be thought so that $NaB(OH)_4$ remains within it. The question is, what will be the purity of H_2 when its production will be considered for greater amounts of SB and water? A response and actions are required, but an experiment based on the use of a lot of SB requires an appropriate and secured facility (1 kg of SB for example, is able to produce more than 2500 liters of H_2 at 20 °C).

3. Catalysts and accelerators

This article does not intend to explore the complete list of catalysts and accelerators reported since 2015. It aims to be concise, to focus on the essentials (i.e. new findings and knowledge), and to present a selection of catalysts and accelerators that can be defined as being out of the ordinary and/or that offer obvious prospects for scale-up and implementation. That represents 15 articles (see below), knowing that a total of 466 articles with catalysts or accelerators as central topic were found for the period 2015 to 2022.

The remaining 451 articles (listed as supplementary material) can be summarized as follows. Most of them report on catalysts, synthesized via chemical or physical methods, and intended to be used many times: e.g. mono-/bi-/tri-metallic or multi-element catalysts supported onto a support like mesoporous silica, carbonaceous materials (e.g. graphene, carbon nanotubes, biosourced carbons) and metal organic frameworks (among other ones); mono-/bi-/tri-metallic catalysts (including alloys) in the form of nanostructures, being dense or porous, and with or without magnetic properties; metallic catalysts contained into polymer capsules; polymer- and ionic liquid-based composites containing a metallic active phase; supported or unsupported metal oxides; alkali metal oxides; salts or hydroxides of metal cations; and, boron- and nitrogen-doped, functionalized and/or surface-charged carbon dots. Cobalt remains the most studied metal, though it is often combined with at least one p-block element (e.g. B or P) or one other transition metal. Metals like platinum, ruthenium, nickel and gold were also reported. Some articles report on photocatalysts (based on e.g. titanium oxide) as well as single-use accelerators (e.g. acids, polyols, oxides or clays with H^+-treated surfaces, sulfonated polymers, metal chlorides). Beyond the routinely studied aspects (e.g. kinetics and thermodynamics), reusability and stability of the catalysts over cycles (generally 5 to 10) were studied, and the majority of the catalysts show more or less pronounced loss of activity upon cyclic use. Such a loss is mainly explained by catalyst poisoning due to surface adsorption of borates. Another explanation, in the case of the cobalt catalysts, is the loss of the active phase by formation of cobalt hydroxide and oxyhydroxide and their detachment from the catalyst surface [73]. To go beyond this summary, the reader is invited to refer to a selection of review articles [7-17].

Singh et al. reported a catalyst that is out of the ordinary [74]. They synthesized Pt-black/Ti Janus microparticles, in fact micromotors (Figure 3), to catalyze the production of H_2 by hydrolysis of SB. The Janus microparticle is made of a catalytically active side (i.e. Pt-black) and an inactive one (i.e. Ti), which allows the microparticles moving in the solution owing to the propulsion created by the production of H_2 onto the Pt-black surface. The efficiency of these micromotors was demonstrated by feeding with H_2 a polymer exchange membrane fuel cell (PEMFC) model car.

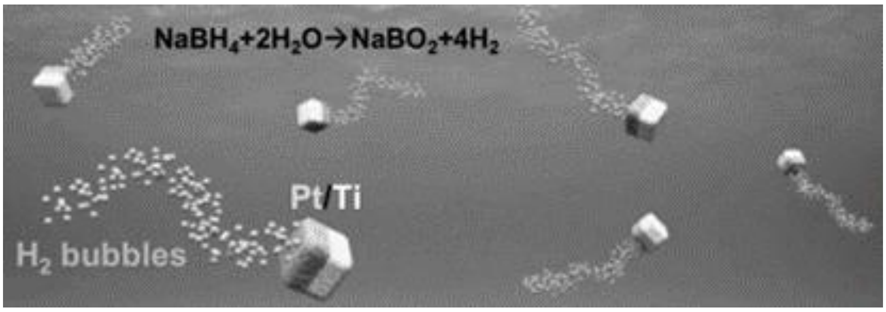

Figure 3. Schematic representation of the Pt-black/Ti Janus micromotors by the production of H_2 microbubbles by hydrolysis of SB. Reproduced from ref. [74] with permission granted by John Wiley and Sons (January 6, 2023).

With powdery catalysts, handling is tedious and material losses are almost inevitable. It is more convenient to develop one-block catalysts, at least from a practical point of view. First examples of one-block catalysts are based on nickel foam that is used as support of an active phase like the binary Co-P. Oh et al. [75] optimized such a catalyst. Co-P was loaded onto nickel foam by electroless deposition, and the most efficient one was selected to produce H_2 for a 200-watt PEMFC. In a subsequent study, the PEMFC was successfully operated for 30 min, stopped for 30 min, and re-operated for 30 min [76]. A 500-watt PEMFC was successfully operated in the same way [77], as well as a 100-watt one [78]. Pure cobalt can also be loaded onto nickel foam, which is done by electrodeposition at –2 $V_{Ag/AgCl}$ [79]. Aluminum-surface modified nickel foams, obtained through a three-step process including aluminization, post-annealing and selective aluminum selective leaching, are also potential catalysts [80]. Second examples of one-block catalysts are based on ceramic monoliths.

Marchionni et al. [81] explored cordierite honeycomb monoliths as supports of Co-B. Dai et al. [82] also studied cordierite honeycomb monoliths onto which alumina was wash-coated and then platinum was deposited by incipient wet impregnation. The as-obtained monolithic catalysts catalyzed a continuous and stable H_2 production (e.g. 0.6 L min^{-1}) by hydrolysis of SB (10 wt%) in aqueous alkaline (5 wt% NaOH) solution (feed rate of 2 mL min^{-1}). Other examples include mesh nickel [83], dealloyed ruthenium on Teflon substrate [84], Ru/MgO wash-coat onto a magnesium substrate [85], and platinum-decorated polydopamine-coated wood pulp sponge [86].

There is also an alternative approach, not using a catalyst, as proposed by Sankir et al. [87]. One chamber was filled with the SB solution, another chamber with an acid solution (e.g. 18 M H_2SO_4), and both chambers were separated by a proton exchange membrane made from a disulfonated poly(arylene ether sulfone) copolymer (Figure 4). Protons were provided by the acid, via the membrane, to the SB solution in order to initiate the hydrolysis reaction. The H_2 production rate was controlled by tailoring the proton conductivities of the membranes, which was possible by varying the degrees of disulfonation. This H_2 production system was coupled to a 8-watt PEMFC that worked for about 300 h.

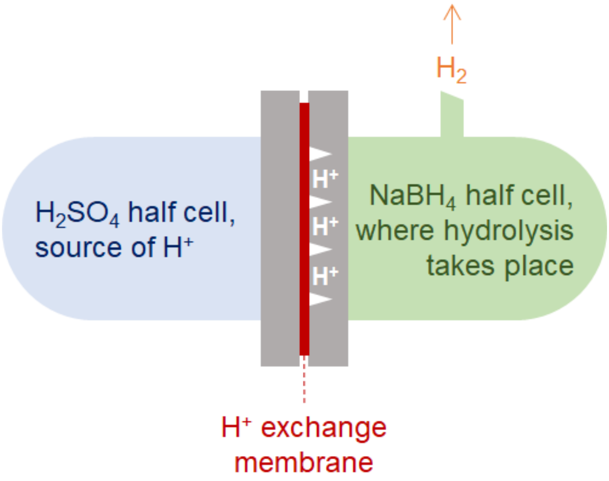

Figure 4. Scheme of the H_2 production system, based on two half-cells, as proposed in ref. [87]. The H_2SO_4 half cell is separated from the SB half cell by a proton exchange membrane (disulfonated poly(arylene ether sulfone) copolymer), and the H_2 produced in the latter cell is vented through an outlet.

4. Scale-up

Hydrolysis of SB at the milligram scale has been much studied over the past twenty years and we have learned about the issues that the reaction is encountering. However, hydrolysis of SB at the gram-to-kilogram scale has not been thoroughly studied yet [88,89], and our knowledge of the issues that are inevitably exacerbated due to effect of scale is limited. In addition, it remains possible that we are not yet aware of issues that would be specific to the use of SB at the gram-to-kilogram scale. We have to expend more effort on closing these gaps, which involves developing and studying prototypes and demonstrators (e.g. H_2 production systems feeding fuel cells powering unmanned aerial vehicles [90,91]).

The period 2015-2022 was punctuated with interesting studies, showing a real dynamic around scale-up of hydrolysis of SB. From here on, these studies will be discussed from two perspectives: a selection of the prototypes developed so far will be presented (Table 1) [92-101], and the lessons learned from the operation of these prototypes (with particular emphasis focused on the challenges to be met) will be summarized. For more details about the operation conditions (e.g. catalyst amounts, H_2 yields and operation pressures), and the algorithms used for maintaining a constant H_2 production and a constant power supply, the reader is invited to refer to the articles discussed hereafter.

As shown in Table 1, the H_2 production systems were dimensioned to produce pure H_2 to feed 20-watt to 3000-watt PEMFCs, and in most of the case to power unmanned aerial vehicles. SB was used in solid state or in aqueous alkaline solution. In the former case, water, containing an acid for example, is pumped or injected into the SB containing reactor, and the by-product is kept inside the reactor. Various acids can be used, with typical examples being hydrochloric acid, sulfuric acid, acetic acid and citric acid [102-104]. Lee et al. [92] identified an issue not really seen before. They noticed that reactor pressurization is an important factor for stable system operation, that is, for constant H_2 production rates. In case SB is in aqueous alkaline solution, it is pumped onto a one-block catalyst (e.g. Co-P loaded onto nickel foam), and the aqueous alkaline solution of the by-product is either purged out the system or stored in a tank placed at the outlet of the catalytic chamber. The fluids circulation are allowed by a pump. Known et al. [93] demonstrated that the energy density of a H_2 production system using SB in solid state is 1.3 times higher than a system using an aqueous alkaline solution of SB.

Table 1. H_2 production systems, coupled or not to a fuel cell (PEMFC) as reported in references [92-101]. Information (when available from the articles) about the state of SB (solid or in aqueous solution), the nature of the catalyst or accelerator used, how the reaction was made start, the cooling technology used, how the by-product was managed during hydrolysis, the power of the fuel cell, the H_2 production rate recorded, the total volume of H_2 measured, and the gravimetric hydrogen storage capacity (GHSC) of the system, are given.

State of SB	Cat./Accel.	How the reaction starts	Cooling approach	By-product management	Fuel cell power	H_2 production rate	Volume of H_2	GHSC	Reference
SB as a solid	Aqueous HCl (2.5-4 M)	Pumping HCl onto SB	Fan (2.4 W)	Kept in the reactor	20 to 100 W	0.2-0.9 L min^{-1}	11-49 mL	3.1-4.2 wt% H	[92]
SB as a solid	Aqueous $NaHCO_3$	Pumping $NaHCO_3$ onto SB	Fan	Kept in the reactor		7-9 L min^{-1}	3464 L from 283 g SB	5.1 wt% H	[93]
SB as a solid	Aqueous $NaHCO_3$	Pumping $NaHCO_3$ onto SB	Fins and fans						[94]
SB as a solid	Aqueous $FeCl_3$ (1g vs. 10g SB)	Injection of $FeCl_3$ onto SB		Kept in the reactor	20 W	1.17 L min^{-1}			[95]
Aqueous SB (25 wt%)	Co-B supported on Ni foam	Pumping SB onto the catalyst	Fins and fans	Purged out	100 W	1.2-1.7 L min^{-1}		3.55 wt% H	[96]
Aqueous SB (20 wt%)	Co-P supported on Ni foam	Pumping SB onto the catalyst	Fan	Purged out	300-500 W	4.5-5.9 L min^{-1}			[97-99]
Aqueous SB (20 wt%)	Not mentioned	Pumping SB into the reactor	Cooling coil	Stored after the cooling coil	200 W				[100]
Aqueous SB (5-15 wt%)	Cobalt oxide on Ni foam	Pumping SB onto the catalyst	Four 4-W fans	Waste tank	3000 W			31.7-149.9 L	[101]

Within the last two years, Avrahami and co-workers developed alternative H_2 production systems. On the one hand [105], they constructed five designs of lightweight reactors for which SB in solid state (powder or 3-mm granulates) is dropped into tap water containing a catalyst suspension of 1 wt% ruthenium black. The reactors design allows on-demand production of H_2 with an almost constant flow of about 400 mL min^{-1} for 5-7 h of operation. All the reactors however faced technical and mechanical problems, mainly because of gumming of SB in the presence of water vapor rising from the exothermic hydrolysis reaction. Another problem was mentioned. Leakage of H_2 is unavoidable especially at pressures higher than 0.5 bar. On the other hand [106], they constructed a modified reactor with the aim of taking advantage of the aforementioned gumming of SB (Figure 5). This reactor allowed the production of 110 L of H_2 at a flow rate of 290 mL min^{-1}, the conversion of SB reached 98 %, and the prototype was successfully coupled to a 30-watt PEMFC.

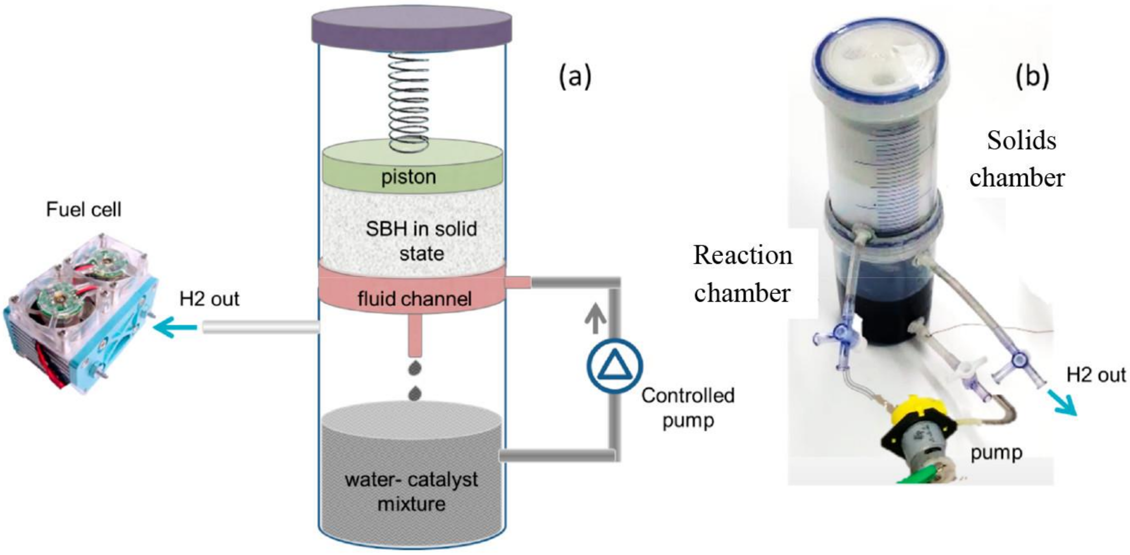

Figure 5. Avrahami and co-workers' pump-based circulation generator: (a) schematic concept (with SBH for sodium borohydride as denoted by the authors); (b) photograph of the generator described in (a). Reprinted with permission from reference [106]. Copyright 2021 American Chemical Society.

At the scale of a H_2 production system, the exothermic nature of hydrolysis of SB is a substantial issue. Cooling fins, fans, coils and/or traps (Table 1) have to be incorporated to the system to manage the evolving heat [98]. For example, Lee et al. [92] observed a temperature increase up to 110-120 °C in the absence of an appropriate cooling system. Kwon et al. [93] observed that the side of their reactor that was cooled down thanks to a fan kept its temperature below 30 °C whereas the top side, free of a fan, attained a temperature of 65 °C. Heat removal is important to avoid heat damages, fuel cell inundation because of evaporated water, as well as uncontrollable and unpredictable hydrolysis rates [107,108].

Lapena-Rey et al. [100] published an excellent article where all the recurring issues that a H_2 production system feeding a 200-watt PEMFC to power an unmanned aerial vehicle is able to encounter. The issues are shown in Figure 6. These issues were actually rather well identified (as discussed above and in the previous sections). For example, the catalyst deactivation issue is known since many years now and is still reported [109,110]. Nevertheless, it must be admitted that the Lapena-Rey et al.'s study clearly underlines how critical the issues are when SB is used at the gram-to-kilogram scale.

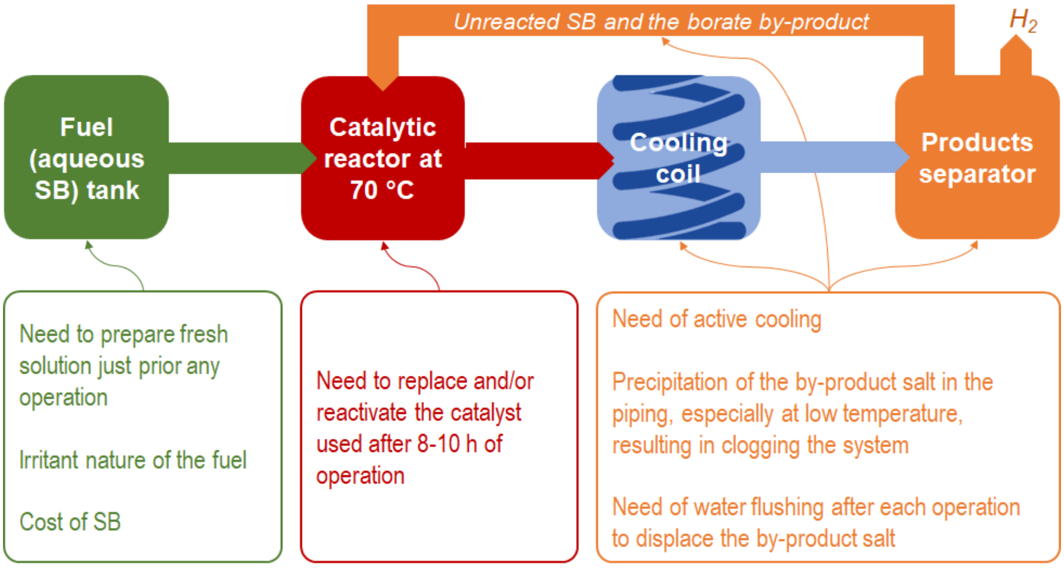

Figure 6. The recurring issues encountered by a H_2 production system, as reported by Lapena-Rey et al. [100].

Other issues were reported elsewhere (Table 2) [100,108,111,112]. One of them is specific to the aircraft applications as it is about the importance of keeping stable the center of gravity of the plane even when the SB tank is depleted [100]. Another issue is related to the alkaline pH values (up to 12) that are reached upon hydrolysis of SB and/or when the solution is stabilized with NaOH. Corrosion is likely to occur with stainless steel [108] and is unavoidable with aluminum alloys [111]. Coating of the internal walls of reactors will thus be required for long-term utilizations. Polytetrafluorethylene coating is a possibility [108]. A last issue concerns the weight of the constituent materials of a H_2 production system, and specifically that of the reactor materials. Nunes et al. [112] pointed out the negative impact on gravimetric hydrogen storage capacities when stainless steel is used. Lighter materials and reactors are required, especially for small portable applications. A similar conclusion was made by Gang et al. [98], and they even stated that their portable electric fuel cell system is not optimized in terms of weight as shown in Figure 7. Indeed, the weight fraction of the SB solution is only 31% of the total weight. This is lower than the 50% that we generally target when discussing about the storage capacities of a H_2 production system [89]. The net gravimetric hydrogen storage capacity (i.e. the capacity for the system as a whole) is limited to 1.3 wt% in such a case. There is nevertheless room for improvement. One of the main challenges is just to make the system lighter without compromising security.

Table 2. Other issues to be encountered by H_2 production systems and reactors, as reported in references [100,108,111,112].

Studied device or system	Issue	Consequence / Risk	Reference
Complete H_2 production system	Depletion of the tank containing the SB fuel	Risk of disrupting the aircraft center of gravity	[100]
Complete H_2 production system	Increase of pH up to 12	Leaching of the stainless steel pressure vessel, implying coating with inert material	[108]
Aluminum alloy as light material for low weight reactor	Corrosion of aluminum (dissolution with alkali) with formation $Al(OH)_3$	Unavoidable degradation of the reactor	[111]
Stainless-steel mini-reactor	Use of stainless steel	Negative impact on the gravimetric hydrogen storage capacities	[112]

There are few other articles including simulation works that are worth being briefly mentioned. Tomoda et al. [113] used a reactor simulation model to simulate hydrolysis of an aqueous alkaline solution of SB at 90 °C. Shabunya et al. [114] modeled heat- and mass-transfer processes in a circulating-type reactor. Chen and Lin [115] studied the dynamic response of a reactor between the input of the aqueous solution of SB and the output of the produced H_2. Jung et al. [116] studied the H_2 pressures and the H_2 production rates for different geometries of their system channels. For a H_2 production system that will gain in maturity, simulation and optimization will bring much more studies in these topics. Scale-up is the only option to leapfrog towards hypothetical commercialization.

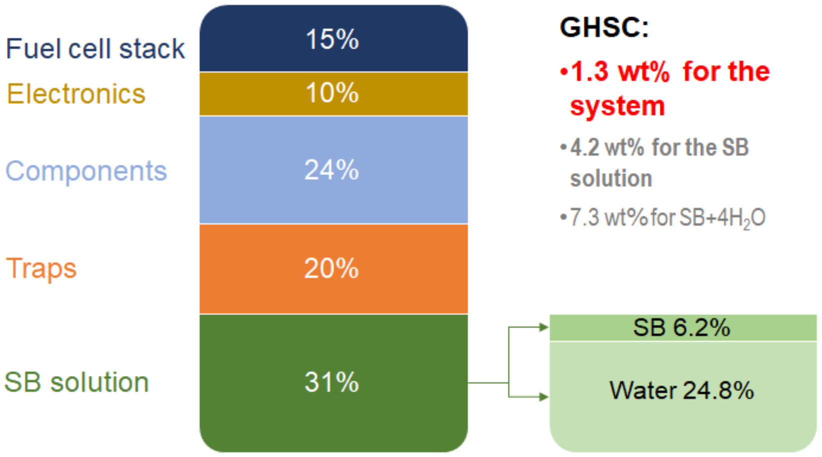

Figure 7. Weight percentage of the SB solution for the H_2 production system reported in reference [98]; this original scheme was drawn from the data available in this reference. The system is simply described by five items such as the SB solution, the traps (water and silica and their containers), the components (fuel tank, hydrogen generator, separator, pumps, cooling fan and fittings), the electronics (controller, monitoring device and DC-DC converter), and the fuel cell stack. The gravimetric hydrogen storage capacity for the system as a whole is given, as well as for the SB solution and for the couple SB+4H_2O (as shown in Eq. 1).

Since 2018, our group has placed a renewed focus on scaling-up. We constructed a prototype, and we are working on its evolution and optimization with the objective to produce at least 100 liters of H_2 to feed a 200-W PEMFC. We have learned a lot about the change in scale (from e.g. 120 mg SB to 40 g SB), and though a large part of our results are confidential (due to partnerships), I am able to share our experience. Firstly, we do confirm the main observations reported and discussed above, such as the importance of heat removal, fast deactivation of cobalt and even ruthenium-alumina catalysts (commercial ones) requiring then reactivation, the fact that the H_2 production rates are not constant during the reaction, hygroscopicity of SB resulting in its gumming, and lowered gravimetric hydrogen storage capacities because of the weight of the stainless vessel we currently use. Secondly, we are faced with three other problems. The reactor design has an impact in terms of H_2 production rates and thus times of completion of hydrolysis, even though the experimental conditions are identical. When SB is used in solid state, and under certain conditions, the results are sometimes not reproducible; we observed that, for instance, the way water is put into contact with SB can lead to differences in terms of H_2 production rates. Upon the completion of the H_2 production, emptying the reactor containing the aqueous alkaline solution of the by-products, as well as a precipitate of the by-products, requires care and several rinses; this makes the process tedious. In summary, many obstacles remain to be overcome before we achieve the ultimate optimization.

Last, not least, there is an aspect that is just as critical as the technical and economic challenges discussed above. As well pointed out by Yao et al. [117], it is essential to gain approval from the regulatory bodies to facilitate the applications of hydrolysis of SB.

5. Regeneration of SB

The hydrogen cycle and the boron cycle must be closed. Recycling $NaB(OH)_4$ to regenerate and thus produce SB remains a major challenge.

The achievements reported between 2015 and 2022 are summarized and discussed in the next paragraphs. Before, it is pertinent to briefly remind the main regeneration processes developed until 2014. These are the modified Brown-Schlesinger process, the modified Bayer process, the reduction processes using reducing agents such as methane CH_4, H_2, and the pair carbon-H_2, and the electrochemical reduction process (Figure 8). To enter the detail of these, the reader is invited to refer to the following review articles [118-124].

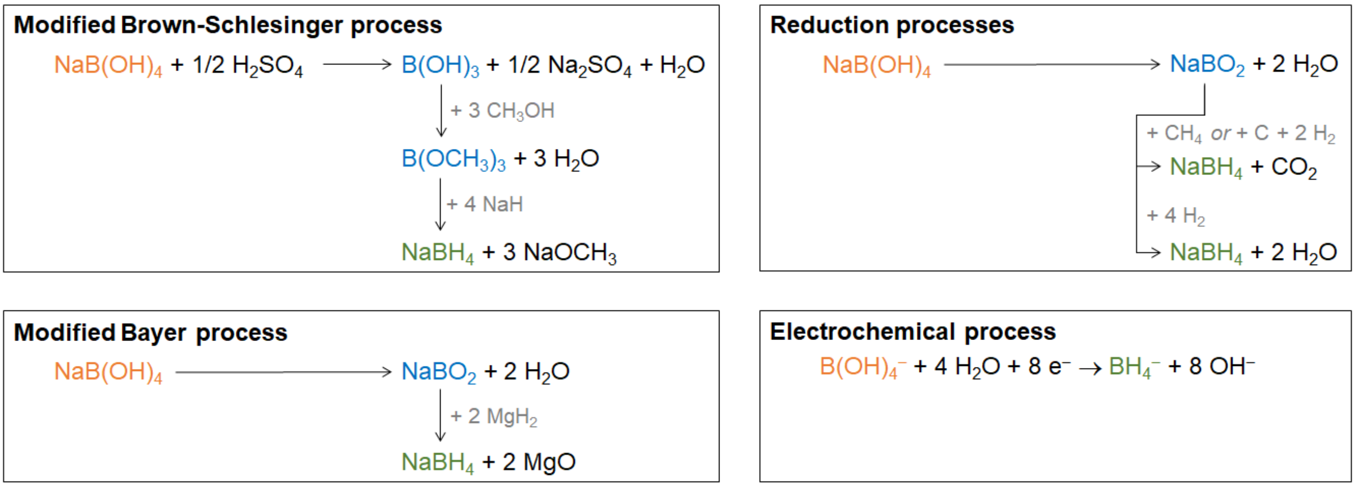

Figure 8. The main SB regeneration processes developed until 2014, as surveyed in references [118-124].

SB can be produced from anhydrous sodium metaborate $NaBO_2$ that is obtained by dehydration of the by-products $NaB(OH)_4$ and $NaB(OH)_4 \cdot 2H_2O$ at >350 °C [125]. It is however preferable to produce SB directly from $NaB(OH)_4$ and $NaB(OH)_4 \cdot 2H_2O$ to save energy (the one that would be required to get $NaBO_2$) and decrease the SB production costs. It is with this logic in sight that Ouyang and co-workers have developed effective regeneration processes over the past years (Figure 9). At room temperature and atmospheric pressure [126], either $NaB(OH)_4$ or $NaB(OH)_4{\cdot}2H_2O$ was ball-milled with magnesium hydride MgH_2, using a high-energy shaker mill. The milling conditions were as follows: 1 mol $NaB(OH)_4$, 5.5 mol MgH_2, a ball-to-powder ratio of 30:1, and 15 h of milling while alternating 30 min of milling and 30 min of rest; 1 mol $NaB(OH)_4{\cdot}2H_2O$, 8.25 mol MgH_2, a ball-to-powder ratio of 50:1, and 20 h of milling while alternating milling and rest. In these conditions, SB was produced:

$$NaB(OH)_4\ (s) + 4MgH_2\ (s) \rightarrow NaBH_4\ (s) + 4MgO\ (s) + 4H_2\ (g) \qquad (2)$$

$$NaB(OH)_4{\cdot}2H_2O\ (s) + 6MgH_2\ (s) \rightarrow NaBH_4\ (s) + 6MgO\ (s) + 8H_2\ (g) \qquad (3)$$

In both reactions, some H_2 is produced. It could be recovered to hydrogenate the magnesium product MgO to regenerate MgH_2; in doing so, the magnesium cycle would be closed. SB was separated by extraction using anhydrous ethylenediamine $C_2H_4(NH_2)_2$ as solvent. The SB yields were 90 and 83.3% respectively. In other studies, Ouyang and co-workers explored alternatives to MgH_2. They used Mg [127], Mg_2Si [128,129], a mixture of Mg and Mg_2Si [130], and a magnesium-aluminum alloy $Mg_{17}Al_{12}$ [131,132], with attractive results though the SB yields were lower than those reported above. In yet other studies, Ouyang and co-workers considered other borates. On the one hand, the aforementioned process was successfully applied to $NaBO_2$, the SB yield being 89% [133]:

$$NaBO_2\ (s) + 2MgH_2\ (s) \rightarrow NaBH_4\ (s) + 2MgO\ (s) \qquad (4)$$

On the other hand, a polyborate such as $Na_2B_4O_7{\cdot}10H_2O$ that is the main constituent of naturally abundant borax mineral was selected [134]. This approach is interesting in two counts. First, $Na_2B_4O_7{\cdot}10H_2O$ is the raw material of the industrially-applied Brown-Schlesinger process for production of SB. Second, $Na_2B_4O_7{\cdot}10H_2O$ is known to form by reaction of CO_2 with e.g. $NaB(OH)_4$ in aqueous solution:

$$4NaB(OH)_4\ (aq) + CO_2\ (aq) + 2H_2O\ (l) \rightarrow Na_2B_4O_7{\cdot}10H_2O\ (aq) + Na_2CO_3\ (aq) \qquad (5)$$

Similar to what has been described above, $Na_2B_4O_7{\cdot}10H_2O$ (without separating Na_2CO_3) was ball-milled with Mg, resulting in the production of SB (yield of 78.9%):

$$Na_2B_4O_7{\cdot}10H_2O\ (s) + Na_2CO_3\ (s) + 20Mg\ (s)$$
$$\rightarrow 4NaBH_4\ (s) + 20MgO\ (s) + CH_4\ (g) \qquad (6)$$

Higher yields were attained with the use of additives such as sodium hydride NaH [135]. For instance, a SB yield of 93.1% was achieved when the system MgH_2-NaH-$Na_2B_4O_7{\cdot}5H_2O$ was ball-milled 3.5 h. A SB yield of 85.2% was obtained with the system $Mg_{17}Al_{12}$-NaH-$Na_2B_4O_7{\cdot}10H_2O$ after a milling of 20 h [136]. The use of aluminum (without or with silicon) to hydrogenate $Na_2B_4O_7{\cdot}10H_2O$ was also explored, and the SB yields were lower than 62%

[137]. In the main, Ouyang and co-workers have been much active and are currently the leading researchers on this matter [138].

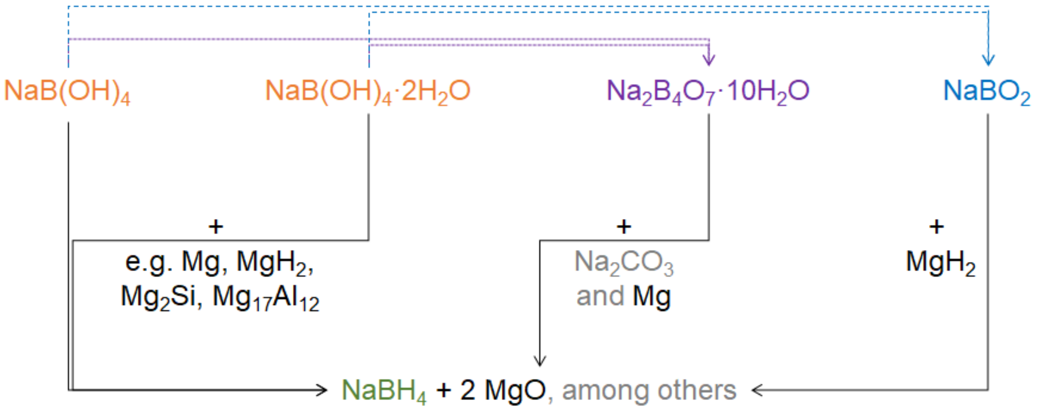

Figure 9. The SB regeneration processes developed by Ouyang and co-workers [126-137].

Few other studies are also of interest. Ar et al. [139] produced SB from boron oxide B_2O_3, MgH_2 and sodium amide $NaNH_2$, by mechanosynthesis carried out at room temperature:

$$B_2O_3\ (s) + NaNH_2\ (s) + MgH_2\ (s) \rightarrow NaBH_4\ (s) + 2MgO\ (s) + NH_4BH_4\ (s) \qquad (7)$$

SB was extracted by using ethylenediamine as solvent. For a reaction lasting 500 min and using an excess of 30% of MgH_2, the SB yield was 84%. According to the authors, ammonium borohydride NH_4BH_4 (Eq. 7) formed as by-product. However, no evidence of its formation is given. It is however unlikely that NH_4BH_4 forms. Indeed, this compound is much unstable in the conditions mentioned above [140]. Le et al. [141] used a magnesium-aluminium alloy (76 wt% Mg and 13.6 wt% Al, plus other elements like Ca, Cu, Mn, Nd, Zn, Y, Ag) that was ball-milled with either $NaBO_2$ or $NaB(OH)_4 \cdot 2H_2O$ under H_2 pressure (70 bar) and at room temperature:

$$NaBO_2\ (s) + 2Mg\ (s) + 2H_2(g) \rightarrow NaBH_4\ (s) + 2MgO\ (s) \qquad (8)$$

$$NaB(OH)_4 \cdot 2H_2O\ (s) + 6Mg\ (s) \rightarrow NaBH_4\ (s) + 6MgO\ (s) + 2H_2\ (g) \qquad (9)$$

Yields of 99.5%, upon extraction of SB by ethylenediamine, were found.

Progress has been made. However, there are two outstanding questions. How simple and safe is the extraction of SB from the ball-milled mixture? Our recent attempts (unpublished work) taught us two things. When the ball-milling is too harsh, the particles size of the magnesium products is so small that they remain in suspension after weeks of storage. Even centrifugation turns out to be complicated. The other point is that the aforementioned small particles are pyrophoric, and ethylene diamine is a highly flammable solvent. This makes the extraction/separation process very constraining. These observations bring up the second question. What is the cost of the as-produced SB, and that of the H_2? It is difficult to answer this question because there is a lack of energy, exergy and economic analyses. The only study available is that of Rivarolo et al. [142]. They carried out a thermo-economic analysis for a process where the electricity is from photovoltaic panels, H_2 is produced by electrolysis of water, and SB is synthesized from $NaBO_2$ in the presence of Mg and H_2 (Eq. 8). The total cost of H_2 was found to be 15.5 € per kilogram. At such a cost price, SB is not economically viable, except perhaps for niche applications.

6. Conclusions and prospects

The first conclusion that can be drawn is that the 2015-2022 period is regrettably too similar to the 2000-2014 (surveyed in reference [18]). Again, catalysts or accelerators have dominated the field, the other aspects have received little attention (Figure 10), and there has been little gain in terms of technological readiness level. There is now substantial literature on catalysts and accelerators showing a potential use in hydrolysis of SB. However, it is important to mention that the prototypes reported so far were based on the use of a one-block catalyst (e.g. cobalt supported on Ni foam) or an accelerator among very few ones (e.g. HCl or $NaHCO_3$). There is clearly a gap between the hundreds (in fact >1000 since the early 2000s) of different catalysts or accelerators reported so far and the very few catalysts and accelerators tested on a prototype.

The 47 articles dated 2015-2022 and dealing with aspects other than catalysts or accelerators give valuable insights into hydrolysis of SB towards scaling up. These insights are much interesting, have been discussed above, and deserve to be put into perspective with a view of the end user.

Storage of SB gives rise to constraints. SB in solid state must be kept far from air contamination to avoid its degradation (by reaction with moisture and CO_2). Aqueous alkaline solution of SB suffers from spontaneous hydrolysis even for high concentrations of NaOH and low temperatures, and its storage will require special care (e.g. chemically inert high-pressure vessel, ventilated storage areas). May one impose such constraints to the end user knowing that one should do because of the safety concern related to uncontrolled H_2 production by spontaneous hydrolysis? From what we know at present, the answer to the question is in the negative, and one may regret that there is no study and data about kilograms of SB stored in various conditions and in different vessels.

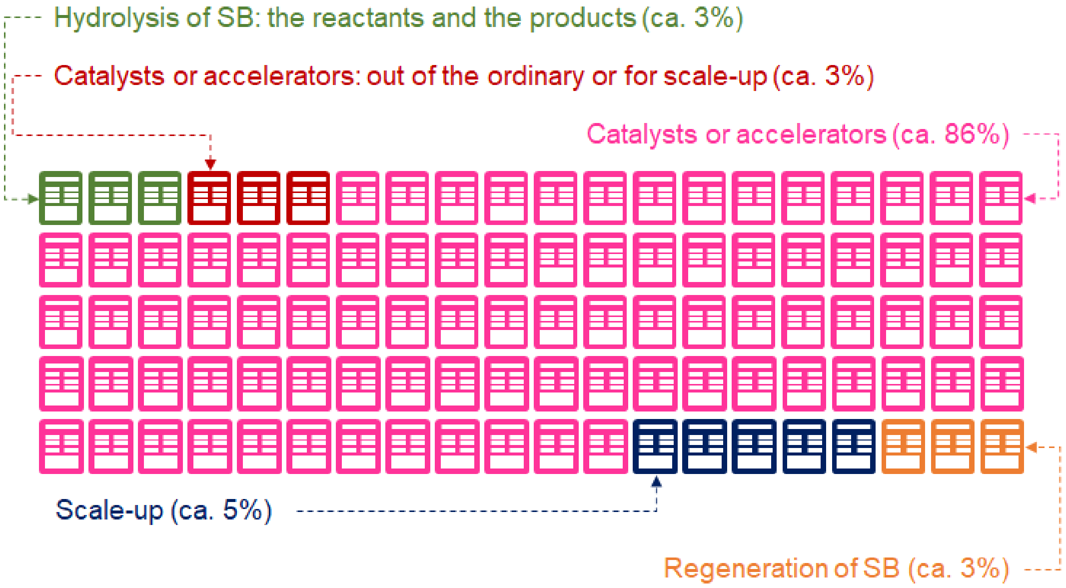

Figure 10. Percentage of articles dealing with the different aspects related to hydrolysis of SB, knowing that a total of 523 articles (for the period 2015-2022) were analyzed.

Perhaps, one may consider that the end user prepares a fresh aqueous alkaline solution of SB when it is required. But, is this conceivable? Perhaps the answer is yet for professionals. However, the normal end user should not have to handle chemicals like solid SB and NaOH because this could poses significant constraints and safety concerns. In fact, the question does not have a definite answer, but it is unquestionable that a SB-based technology must be easy and safe to operate.

Another, less critical, question raises from the discussion above. Which water should we use for preparing a fresh SB solution? Actually, we cannot answer the question from the point of view of the performance. There are only two studies dealing with the nature of water. This fact reflects how the aspects other than catalysts or accelerators have been little investigated or neglected. In any case, tap water or seawater for example would be preferable, at least because they are cheaper and more accessible than distilled water. More studies on water quality (including also rainwater, bottled water, etc.) could lead to a better understanding of the impact of the species present in water on the overall performance of the hydrolysis reaction and of the catalyst. We however have to keep in mind that any species in water will complicate the already complex issue related to recycling of the hydrolysis by-product.

The articles dealing with prototypes represent a mine of information. Three types of issues can be identified. The first type of issues are those that have been identified a long time ago: need of active cooling of the system because of the exothermic nature of the hydrolysis reaction; deactivation of the catalyst requiring its reactivation or replacement; and, precipitation of the by-product resulting in clogging the system and/or requiring water flushing after each operation. Each of these issues have to be well managed, otherwise they have a greater or lesser impact on the system as a whole (including the PEMFC). It should be noted that, though these issues are known, they remain unexplored for a use of SB at the kilogram scale. The second type of issues was less known and documented: need of reactor pressurization for constant H_2 production rates; leakage of H_2; and, risk of corrosion of stainless steel implying coating with inert material. All of these issues are related to the system and on its operation, and further development should allow further improvements. The third type of issues is typical of a specific type of reactor (e.g. gumming of SB) or of a specific application (e.g. risk of disrupting the aircraft center of gravity because of depletion of the tank containing the SB fuel). Other issues will obviously pop up as new prototypes will be constructed, tested and presented. Thus, the only conclusion to be drawn from this is that, we must expand our efforts to address each of these issues.

Even now SB is very often presented as being technologically much promising thanks to the 10.8 wt% of hydrogen atoms of which it is formed. This is both true and untrue. SB has indeed a gravimetric hydrogen density of 10.8 wt%, however this is far from the net gravimetric hydrogen storage capacities that could be reached with a H_2 production system integrated to a fuel cell-powered device. Net gravimetric hydrogen storage capacity takes into account the weight of each component of the system taken as whole and that of SB and water, and only a net value can give the real performance of the couple SB-water as hydrogen carriers. The only measure available is 1.3 wt% as discussed in section 4, and this illustrates how low is the net capacity in comparison to the gravimetric hydrogen density of SB. There is still room for improvement because there are few levers. For example, every components of a H_2 production system (e.g. reactor) may be lightened by exploring and using light materials instead of heavy ones (e.g. steel). Further optimization with respect to the hydrolysis reaction may allow using an aqueous solution of highly concentrated SB; in doing so, less water would be embarked, positively affecting the net capacity. A last example is of using SB in solid state as the energy density of a H_2 production system using solid SB would be 1.3 times higher than a system using an aqueous alkaline solution of SB. In any case, we have to keep in mind the following values: SB and four equivalents of water have a gravimetric hydrogen density of 7.3 wt%; for a system where the weights of SB and water (both embarked) represent 50% of the system weight, the highest gravimetric hydrogen storage capacity would be about 3.7 wt%; and, for a system where the weights of SB and water is 31% (as in Figure 7), the highest capacity would be 2.3 wt%.

Last but not least, SB must be produced back from its by-products. Since 2015, significant progress has been made. It is now possible to produce SB by ball milling $NaB(OH)_4$ and MgH_2 at room temperature, and one of the highest yield reported so far is 90%. This presupposes that half of an initial amount of SB would not be 'lost' after 7 regeneration cycles. Improvement is thus still necessary, and the yield of 100% should be the target. We could also take inspiration from what is being done with electrochemical conversion of CO_2 in order to explore other possibilities. Improvement is all the more necessary in that the cost of H_2 from SB is still too high. With relation to that, another noteworthy observation is that energy, exergy and economic analyses are needed to better evaluate the overall cost of H_2 from SB.

After more than 20 years of research and innovation, many obstacles (as listed above) remain to be overcome before hydrolysis of SB can be a commercial solution for carrying and producing H_2. In my view, our aim should be to answer the following question: does SB really offer prospects in terms of technological implementation and commercial deployment? We do not have the insight necessary to answer this question yet. But we have to answer it. To do so, we should overcome the obstacles at first, which means more efforts dedicated to construct, operate and optimize H_2 production systems, as well as more efforts to make production of SB from its by-product more efficient and cheaper. That is the only way to reach technological maturity. Next, other questions about the technology deployment will come (how will SB be distributed, how will SB be stored at the end user's home, how will the by-products be stored at home, how will the by-products will be recovered, how many recycling sites will be available, what will be the transportation and distribution cost, and so forth?).

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