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CATALYTIC HYDROLYSIS OF SODIUM BOROHYDRIDE FOR HYDROGEN PRODUCTION: STUDY OF THE RECYCLABILITY OF BY-PRODUCT REACTION

FILIPE COSTA

Dissertation submitted for the degree of
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President of the jury:
Adrián Manuel Tavares da Silva, Associate Professor, Department of Chemical Engineering, Faculty of Engineering University of Porto

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Supervisor at the University:
Alexandra Rodrigues Pinto, Associate Professor, Department of Chemical Engineering, Faculty of Engineering University of Porto

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Co-supervisors at the University:
Diogo Silva and Helder Nunes, PhD students, Department of Chemical Engineering, Faculty of Engineering University of Porto

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ABSTRACT

Hydrogen production is increasingly becoming one of the main energy sources presented to use as energy vector. However, the presence of fossil fuels is still very highlighted in daily life, such as in power vehicle engines, in house heating, etc. Due to difficulty in obtaining and storing the molecule of hydrogen in its pure form, chemical hydrides, for example sodium borohydride ($NaBH_4$) show up with hydrogen in their composition which means that, when hydrolyzed, can be converted into pure hydrogen gas and sodium tetrahydroxyborate ($NaB(OH)_4$). It is an alkaline solid compound which can be found in various applications, for example as reducing agent or in detergent's industry. The release of hydrogen gas is an important aspect of the hydrolysis reaction of sodium borohydride, making it a useful reagent in applications such as fuel cells.

However, for $NaBH_4$ to be a competitive hydrogen carrier, it is essential to regenerate it from the hydrolysis reaction's by-product, $NaB(OH)_4$. Therefore, in the current thesis, the by-product of $NaBH_4$ hydrolysis reaction was studied to know how it can be recycled in a better way. Some experiments were performed to see the influence of distinct reducing agents during the ball milling experiment, a mechanical process used to grind and blend the inner material in a rotating form, with the supply of zirconia balls inside. The impact and friction generated by the milling balls makes it easier to mix different compounds and consequently the reduction of their particle size. The number of balls or the reaction time is important due to its direct impact with the production of greater or lower quantities of products. Hereupon, were obtained expected results through x-ray diffraction analysis (XRD). Thus, a regeneration, although $NaBH_4$ was not observed in the final product of the ball milling, it was obtained magnesium oxide (MgO) and sodium carbonate (Na_2CO_3) which proves that it is possible to regenerate $NaBH_4$ from $NaB(OH)_4$ through ball milling.

Keywords: Circular economy, hydrogen production, sodium borohydride hydrolysis, recyclability of sodium tetrahydroxyborate, ball milling process.

RESUMO

A produção de hidrogénio está a tornar-se cada vez mais a tornar-se como uma das principais fontes de energia apresentadas para uso energético. No entanto, a presença de combustíveis fósseis ainda está muito marcada no dia-a-dia, como em motores de veículos, no aquecimento de habitações, etc. Devido à dificuldade em obter e armazenar a molécula de hidrogénio na sua forma pura, os hidretos químicos, por exemplo, o borohidreto de sódio ($NaBH_4$), surgem com átomos de hidrogénio associados à sua composição, o que significa que, quando hidrolisados, podem ser convertidos em hidrogénio gasoso puro e tetrahidroxiborato de sódio ($NaB(OH)_4$). Este é um composto sólido alcalino que pode ser encontrado em diversas aplicações, por exemplo como agente redutor ou na indústria de detergente. A libertação do hidrogénio gasoso é um aspeto importante a reter numa reação de hidrólise de borohidreto de sódio, tornando-o num reagente útil em aplicações como células de combustível.

Contudo, para o $NaBH_4$ ser considerado uma molécula transportadora de hidrogénio competitiva, é essencial regenerá-lo a partir do subproduto $NaB(OH)_4$. Assim, na presente tese, o subproduto da reação de hidrólise do $NaBH_4$ foi estudado para saber como pode ser melhor reciclado. Foram realizadas várias experiências para avaliar a influência de diferentes agentes redutores durante a experiência de *ball milling*, um processo mecânico usado para moer e misturar todo o material interno de forma rotativa, com a ajuda de esferas de zircónio no interior. O impacto e o atrito gerados pelas esferas de moagem facilitam a mistura dos diferentes compostos e, consequentemente, na redução do tamanho das suas partículas. O número de esferas ou o tempo de reação são importantes devido ao seu impacto direto na formação de uma maior ou menor quantidade de produtos bem como o tipo de produtos formados. Obtiveram-se resultados concordantes com o esperado através de uma análise de difração de raios-x (XRD). Apesar de não ter sido observado $NaBH_4$ no produto final da reação de *ball milling*, foi obtido o óxido de magnésio (MgO) e carbonato de sódio (Na_2CO_3) que, por sua vez, indica que é possível regenerar $NaBH_4$ a partir de $NaB(OH)_4$ pelo método de *ball milling*.

Palavras-chave: Economia circular, produção de hidrogénio, hidrólise de borohidreto de sódio, reciclabilidade de tetrahidroxiborato de sódio, *ball milling*.

DECLARATION

I declare, on my word, that this work is original and that all non-original credentials were properly referred with source identification.

Porto, 17th July 2023

Filipe Costa

(Filipe Manuel Figueiredo Costa)

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GLOSSARY

e	Excess of reducing agent
HHV	High Heating Value
m	Mass
M	Molar mass
No	Number
P	Pressure
R	Ideal gas constant
T	Temperature
$V_{molar, STP}$	Molar volume at STP conditions
V	Volume
v	Stoichiometric coefficient
wt.	Weight

Greek Letters

θ	Angle of ray incidence
ρ	Density
η	Yield

List of acronyms

BPR	Ball to Powder Ratio
CEFT	Transport Phenomena Research Centre
DOE	Department of Energy
GHSC	Gravimetric Hydrogen System Capacity
HGR	Hydrogen Generation Rate
MRc	Medium Reactor with conical bottom
PEM	Proton-Exchange Membrane
SDGs	Sustainable Development Goals
SRc	Small Reactor with conical bottom
VHSC	Volumetric Hydrogen System Capacity
NMR	Nuclear Magnetic Resonance
FT-IR	Fourier Transform Infrared Spectroscopy
XRD	X-Ray Diffraction

A. INTRODUCTION

A.1 CIRCULAR ECONOMY

Nowadays it is necessary to consider a new concept about how to minimize waste, maximize resource efficiency, and promote sustainable development. This is because of over-consumption by human beings, depleting all available resources long before their normal time ends. The circular economy is an economic model that seeks to create a closed-loop system where resources are kept in use for as long as possible, in contrast with the traditional linear economy which follows a "take-make-dispose" pattern where resources are extracted, used to create products, and then discarded like garbage. It encourages the implementation of strategies that prioritize reuse, recycling, and regeneration. Instead of seeing waste as a byproduct, the circular economy emphasizes the concept of waste as a resource, such as reducing raw material extraction, minimizing environmental degradation, and reducing pollution [1]. It also promotes innovation and stimulates economic growth, creating new business opportunities and jobs in areas such as recycling, remanufacturing, and renewable energy. A brief explanation of circular economy is represented below (*Figure 1*).

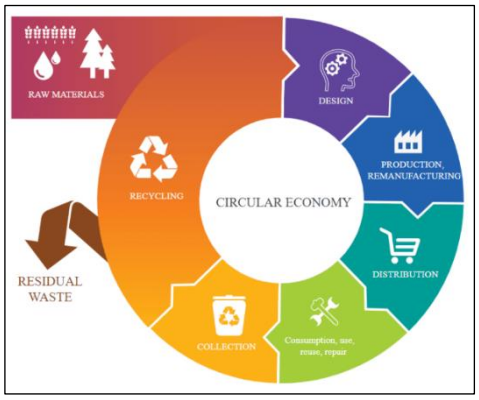

Figure 1 – *Example of a circular economy diagram* [1].

Besides that, there is the need to achieve a better and more sustainable future, which is represented by the Sustainable Development Goals (SDGs). SDGs were designed to address global challenges and promote sustainable development in social, economic, and environmental dimensions and is composed of 17 interconnected goals (*Figure 2*). By embracing the principles and practices of the circular economy, countries and organizations can make considerable progress achieving multiple SDGs simultaneously. The circular economy does not only support sustainable consumption and production patterns but also impacts to economic prosperity, environmental sustainability, and

social well-being [2]. Two of SDGs are highlighted because they are entirely related to this project, such as, no 7 – renewable energy and no 13 – climate action.

Figure 2 – *All 17 global goals of SDGs* [3].

A.2 ABOUT FOSSIL FUELS

As time progresses, there is still talk about lack of natural resources due to the increase of population compared to the regeneration time of these resources. Their excessive use by society makes them less available, while other alternatives will have to be implemented so that none of them runs out. Natural resources like oil, coal, and natural gas are non-renewable resources that despite their high pollution for the environment, are still widely used in industry mostly for energy production, both in developing and developed countries. Furthermore, fossil fuel extraction has expanded to more remote and deeper areas, which puts additional pressure on existing reserves, requiring more advanced technologies and higher costs [4]. However, more than the number of remaining reserves, i.e., the depletion of natural resources, are the environmental concerns like greenhouse gas emissions, and air pollution, which should show more alarm. A transition to cleaner and more sustainable energy sources will reduce the dependence on fossil fuels and mitigate their environmental impacts. Due to its high heating value (*Table 1*) and its abundance in the universe, hydrogen can contribute to reduce the dependence of fossil fuels acting as an energy vector with high potential.

Table 1 – *High Heating Value (HHV) for different fuels at 0ºC and 1 bar* [5].

Fuel	HHV (*MJ/kg*)
Glycerin	19.0
Gasoline	46.4
Methane	55.5
Hydrogen *gas*	141.7

A.3 HYDROGEN

Hydrogen has been associated as an alternative fuel in the search for sustainable and clean energy sources due to its potential environmental advantages. For example, this gas when is used by fuel cells to generate electricity does not emit any harmful pollutants or toxic gas such as carbon dioxide (CO_2) or other typical atmospheric pollutants (CH_4, CO, O_3, NO_x, SO_x, PM), making it an attractive option for reducing air pollution and better impact on climate change. These hydrogen to electricity converters minimizes the needs for external hydrogen storage and transport infrastructure, turning out to be more compact and user-friendly systems. Especially, Proton-Exchange Membrane (PEM) fuel cells (*Figure 3*) are expanding right through clean energy technology due to their high efficiency and operational flexibility, like in personal vehicles or electronics. Once the hydrogen gas enters directly to PEM fuel cell, a redox reaction takes place facilitating the production of electricity [6].

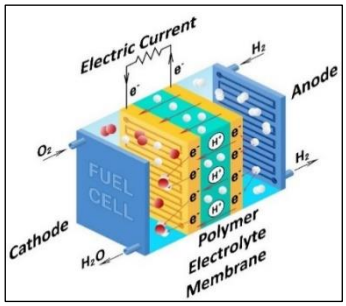

Figure 3 – *Example of a PEM fuel cell [7].*

Additionally, redox reactions are also present in the reverse process of obtaining H_2 (and O_2) from the water molecule by using electricity. In the PEM electrolyzer, for example, an external electric current is applied. At the anode, water molecules lose electrons and are oxidized to produce oxygen gas, protons, and electrons. The protons are transported through the electrolyte to the cathode. At the cathode, the protons combine with electrons from the external circuit to form hydrogen gas [8].

Hydrogen also has the smallest atomic number (*Figure 4*), or in other words, the primary chemical element to appear on the periodic table and the most abundant element in the universe (can be found beyond our planet in the Sun along with planets like Jupiter and Saturn [9]). Three times in amount as much helium, the next most widely occurring element, hydrogen is present in atmosphere and, of course, in any mass of water unlike entire composition of Earth's crust which is reduced. As part of carbon compounds,

hydrogen is present in all animal and vegetable tissue also as in petroleum (named as hydrocarbons). Even though it is often said that there are more known compounds of carbon than of any other element, the truth is that, since hydrogen is contained in the majority of almost all carbon compounds, it is possible that hydrogen compounds are more numerous [10]. However, molecular hydrogen (H_2) is not abundant in its preferential form, therefore it must be produced. Also, this gas has lower density than air, comparing their characteristics presented in table below (*Table 2*), so its production must be handle with safety to avoid its release and mixture with other compounds, including air.

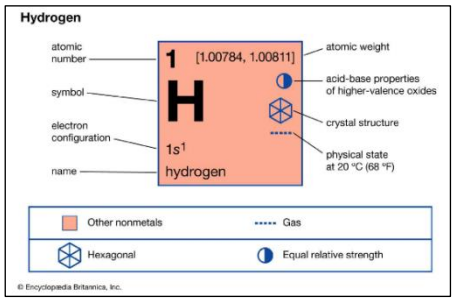

Figure 4 – *Chemical properties of hydrogen [10].*

Table 2 – *Properties of hydrogen (H_2) at 25ºC and 1 atm* [11].

Molecular mass (*g/mol*)	2.016
Specific gravity, air = 1	0.070
Specific volume (m^3/kg)	12.10
Absolute viscosity (N/m^2)	9.0×10^{-6}
Specific heat (*kJ/kg·K*)	14.31
Melting point (*K*)	14.05
Boiling point (*K*)	20.40
Latent heat of fusion (*kJ/kg*)	58
Latent heat of evaporation (*kJ/kg*)	447

A.4 HYDROGEN PRODUCTION

When we talk about energy recyclability it refers to the ability to reuse or recover waste energy after it has been used in various applications. The point is to maximize energy efficiency and reduce overall energy waste. There are two ways to "recycle" energy: by renewable energy sources or non-renewable sources. The first ones are those that are naturally restocked and have a minimal impact on the environment, i.e., they are considered sustainable because they can be used indefinitely without depleting finite resources. Some examples are the case of solar energy, wind power, hydropower, biomass energy, and geothermal energy. On the other hand, non-renewable energy sources are finite for the reason that they have limited availability whose formation lasts over millions of years and cannot be replenished within an human time scale. For example, nuclear energy and all fossil fuels such as coal, oil, and natural gas [12]. Below is represented a chart with some hydrogen production sources and their ratio (*Figure 5*).

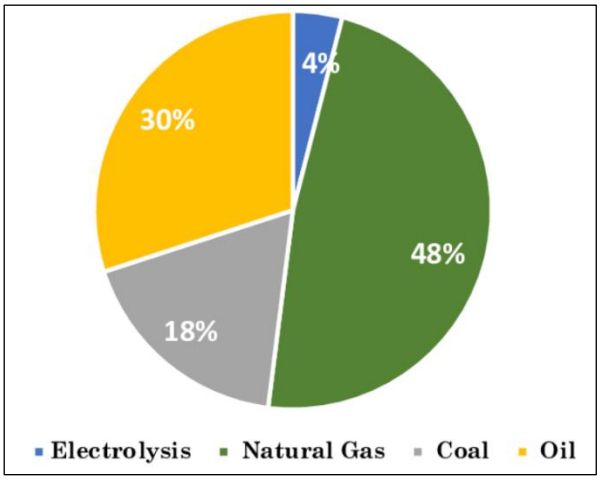

Figure 5 – *Hydrogen production sources and their ratio [13].*

Hydrogen is considered a clean and versatile renewable energy carrier or a secondary fuel that can be produced from primary energy sources, such as natural gas, biomass, or electrolysis of water, and can be used in various sectors, including transportation, industry, or power generation. Hydrogen production is an important aspect of maximizing its potential as a sustainable energy source and helps to reduce the overall demand for additional hydrogen production, making the process more sustainable and cost-effective. Additionally, it contributes to the circular economy minimizing waste and maximizing resource efficiency. Hydrogen production is widely used by different methods including oil refinery, steam methane reforming, oil reforming, coal gasification, and

hydrolysis. These processes require energy inputs from primary sources to extract hydrogen, which is unavailable in its pure form, from compounds like water or hydrocarbons. Because of the easy way that electricity can convert water into hydrogen and oxygen through electrolysis and can be converted back into electrical power, hydrogen is widely regarded as an ideal energy storage facility [14].

Although the deployment of hydrogen as an alternative energy vector has long been discussed, it has not been realized since the lack of low-cost hydrogen generation and conversion technologies. The recent turning point in the cost of some renewable energy technologies such as wind and photovoltaics has mobilized continuing interest in renewable hydrogen through water splitting.

It is worth bear in mind that while hydrogen production is an important aspect, it is also crucial to ensure the overall sustainability of hydrogen production methods. The source of hydrogen production, such as renewable energy or low-carbon sources, plays a significant role in determining the environmental impact and overall sustainability of the hydrogen cycle [15]. From the several methods to produce hydrogen, chemical hydrides and more specifically sodium borohydride ($NaBH_4$) has particular interest for off-grid and on-demand hydrogen generation, storage and usage. This source of hydrogen is therefore the subject of my work.

A.5 AIM OF THE WORK and THESIS ORGANIZATION

The curiosity to know beyond my daily life as an environmental engineer awoke in me my secret passion in chemistry. Also, because there are practically no curricular units related to chemistry in my course. So, I chose to escape from my comfort zone, not if I have more or less knowledge about that, but because I do not study chemistry every college day.

The main objective of this thesis is recycling the $NaBH_4$ hydrolysis reaction by-product, over mechano-chemical methods (such as ball milling), in order to close the cycle of H_2 production systems through $NaBH_4$. Therefore, quantitative and qualitative results should be achieved in order to demonstrate practical observations and valuable considerations for future studies developed.

This thesis is composed by a first chapter already presented, *Introduction* (chapter A). In the introduction, the necessary basic information in order to simplify the framing of objectives and results is showed.

Settling up the remaining chapters, the next will be the *State of the Art* (chapter B), a more detailed observation of sodium borohydride and their capacity to store hydrogen, according to published articles.

Methods and Experimental Procedure (chapter C) are described in the following chapter in detail, starting with the production of sodium tetrahydroxyborate and afterward, the recyclability steps back to sodium borohydride.

In the following chapter, *Results and Discussion* (chapter D) are presented and *Main Conclusions* (chapter E) will be discussed in the last chapter together with future work that must be considered to obtain better results, also known as, *Proposed Future Works*.

B. STATE OF THE ART

B.1 SODIUM BOROHYDRIDE HYDROLYSIS

Among chemical hydrides, sodium borohydride ($NaBH_4$) is being studied as a potential hydrogen generation material proper to its high gravimetric hydrogen storage capacity (10.8 *wt.%*) [16, 17, 18, 19, 20], which makes it an attractive candidate for releasing and storing hydrogen. The main properties of $NaBH_4$ are displayed in the table below (*Table 3*). Arranged in a tetrahedral geometry, this compound is composed with a sodium cation (Na^+) and borohydride anion (BH_4^-), being relatively stable under dry air and with low toxicity compared to other chemical hydrides. Although, this chemical hydride is generally considered safe to handle, direct contact should be avoided, and protective equipment, such as gloves and lab coat, should be worn when working with this compound. When it reacts with water at room to moderate temperature, $NaBH_4$ produces hydrogen gas (H_2) as well as a by-product – sodium tetrahydroxyborate ($NaB(OH)_4$) – also, although this is an exothermic reaction, a catalyst is required to achieve an acceptable rate of hydrogen release. Without a catalyst, the reaction could last for hours and consequently with less effective results because may not achieve a complete reaction. Catalysts can be very expensive and may require specific conditions for an ideal performance, like *Co-W-B/Ni* catalyst [21], $Ru_{60}Co_{20}Fe_{20}$ catalyst [22], *PtRu-*$LiCoO_2$ catalyst [23], *Ni-Ru* catalyst [24], etc. Sodium borohydride is a synthesized inorganic compound due to its versatility and wide use in organic synthesis. Despite its stability under normal laboratory conditions, it is sensitive to moisture and prolonged exposure to air, which can lead to degradation of the compound [25].

Table 3 – *Properties of sodium borohydride ($NaBH_4$)* [26].

Molecular mass (*g/mol*)	37.83
Melting point (*K*)	673.15
Boiling point (*K*)	773.15
Density $_{@25ºC}$ (*g/mL*)	1.035
Water solubility $_{@25ºC}$ (*g/L*)	550

The catalytic hydrolysis reaction mechanism for hydrogen generation can be summarized as follows:

$$NaBH_4\,(aq) + 4H_2O\,(l) \rightarrow NaB(OH)_4\,(aq) + 4H_2\,(g) + heat \quad [18]$$

This exothermic reaction ($\Delta H < 0$) involves the collapse of alkaline $NaBH_4$ in the presence of water or an aqueous solution, whose x represents the hydration factor (usually with values of 2 or 4), i.e., the excess of water for the purity of limiting reactant (=$NaBH_4$). During the reaction, too much water leads to an hydrogen production decrease and consequently lower global performance. But limited water is also a problem because the by-product is characteristic of a propensity with water molecule bonds. Although sodium metaborate di-hydrate ($NaBO_2$) is the by-product described in literature (x = 2), some authors argue that the correct composition of the $NaBH_4$ hydrolysis reaction by-product is $NaB(OH)_4$ (also x = 2) where structural water is present instead of molecular water, favoring its recycling back to $NaBH_4$. This compound is also environmentally friendly, nontoxic, and can be recycled back to sodium borohydride, which is the main objective of this thesis. This alkaline salt can be found in various applications, including as a corrosion inhibitor and in the production of boron compounds. Moreover, the excess of water can influence the gravimetric hydrogen storage capacity (GHSC), as presented in figure below (*Figure 6*).

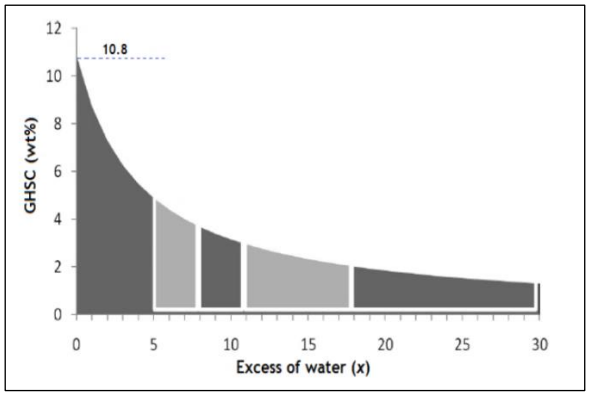

Figure 6 – *Evolution of GHSC over the excess of water [27].*

Based on this fact and the excessive cost of $NaBH_4$, the American Department of Energy (DOE), which regulates all H_2, declared several years ago a no-go recommendation for sodium borohydride as an on-board vehicular hydrogen storage due to associated costs and lack of conclusive interest value [27]. Being able to value it or recycle it (closing the $NaBH_4$ hydrolysis reaction cycle), is important for this technology to become viable. However, the DOE's targets for hydrogen's medium power portable equipment storage

can be achieved in case the excess of water is optimized, increasing the gravimetric and volumetric hydrogen storage capacities. To review the potential utility of hydrogen-containing materials for electricity generation purposes, it is crucial to make a clear distinction between the concepts of material and system gravimetric capacity. Material gravimetric capacity refers only to the amount of stored hydrogen, without any losses or inefficiencies that may occur during the storage and retrieval process. On the other hand, system gravimetric capacity refers to the amount of usable hydrogen that can be stored, including all reactants and system components [27].

Regarding the optimization of the reaction itself, specific studies are related to the geometry of the $NaBH_4$ hydrolysis reactor to obtain better results, i.e., better hydrogen yields and generation rates [28]. According to the open literature and a project the most common reactor geometries are cylindrical, with flat bottom, although it does not work in better results, like is shown in the next table (*Table 4*). Also, it is presented a study result developed by the research group with a different type of reactor, much smaller than the other reactors.

Table 4 – *Different reactors and their volumes with the H_2 yield* [28, 29].

Type of reactor	$V_{reactor}$ (cm^3)	H_2 yield (%)
Cylinder – flat bottom	646	78
Cylinder – conical bottom	369	86
Cylinder – conical bottom	229	98
Egg-shaped – conical bottom	9	90

The influence of a reactor with a conical bottom was previously studied by the research group. Better performances were observed, which are justified with an increase between the contact of reactants and catalyst, reducing the mass transfer and promoting hydrogen production.

Through the hydrolysis of $NaBH_4$, hydrogen can be simultaneously generated and stored. After that, it can be directly fed to a fuel cell and subsequently generate electrical energy. Fuel cells are formed with two electrodes (an anode and a cathode) and an electrolyte. In the anode is where oxidation reaction began, and the electrons are released to the exterior of the cell while the ions cross the cathode side. On the other hand, in the

cathode is where the reduction occurs, with the ions crossing from the electrolyte side. Oxidation-reduction reactions are typically promoted by catalysts [30]. The interest in PEM fuel cells is more passionate due to their application in transport and compact systems.

B.2 SODIUM TETRAHYDROXYBORATE RECYCLABILITY

As mentioned before, the hydrolysis reaction of $NaBH_4$ generates not only hydrogen, but also a by-product named sodium tetrahydroxyborate, a hydrated sodium metaborate commonly used in various industrial processes. This compound can be dissolved in water, which is difficult to recover from water solutions once it has been used. At laboratory level $NaB(OH)_4$ is consumed or transformed into other compounds during the manufacturing process, like recycle sodium borohydride again when in contact with an amine [31]. Through ball milling method it is possible to synthesize $NaBH_4$ using a reducing agent. According to the open literature, there are several reducing agents, predominantly *Mg*-based compounds, which enable the synthesis of $NaBH_4$ through ball milling. The main studied reducing agents are *Mg* and MgH_2, which chemical reactions are presented in the following equations.

$$NaB(OH)_4\,(s) + 4Mg\,(s) \rightarrow NaBH_4\,(s) + 4MgO\,(s)$$

$$NaB(OH)_4\,(s) + 4MgH_2\,(s) \rightarrow NaBH_4\,(s) + 4MgO\,(s) + 4H_2\,(g) \qquad [17]$$

To confirm if the main by-product can be recycled to sodium borohydride, it is necessary to perform several experiments with different compositions, i.e., different use of reducing agent, milling time, or number of zirconia balls. The products of the ball milling process were studied by XRD analysis with the aim of understanding the reaction mechanism.

For the XRD analysis it is necessary to understand the value and intensity of the peaks represented in the graphics obtained. This peaks shows the prevalence of the crystalline compounds, in percentage, and there is a proper pattern in angles for each studied compound. The diffraction peaks of $NaBH_4$ are at 2θ angle of 28.9°, 41.4°, 49.0°, and 51.3°. For the $NaB(OH)_4$ is characterized an intense diffraction peaks at 2θ angle of 17°, 23°, 30°, and 40°. To *MgO* the diffraction peaks is at 2θ angle of 36.9°, 42.8°, 62.2°, 74.5°, and 78.4°. The presence of MgH_2 is verified by the appearance of diffraction peaks at 2θ angle of 28°, 36°, 40°, and 55° [literature associated to the XRD program, 20].

According to *W. Chen* study case [17], when it is using MgH_2 as reducing agent, the diffraction peaks of by-product is gone when passes 30 minutes of reaction. The diffraction peaks of $NaBH_4$ and *MgO,* one of the reaction products, only appeared when 2 hours of ball milling its performed, concluding that is necessary at least this time to perform well the reaction, as can be seen in the first figure below (*Figure 7*).

On the other hand, according to *M. Huang* study case [20], the diffraction peaks of *MgO* appeared after one hour with ball milling, which means that the reaction of *Mg* and Mg_2Si had already occurred. As the ball milling time was prolonged to the next hour, the diffraction peaks of *Mg* completely disappeared, while the peaks of Mg_2Si were still present. This result indicates that the by-product reacts preferentially with *Mg* compared to Mg_2Si. That conclusion can be seen in the right figure below (*Figure 8*).

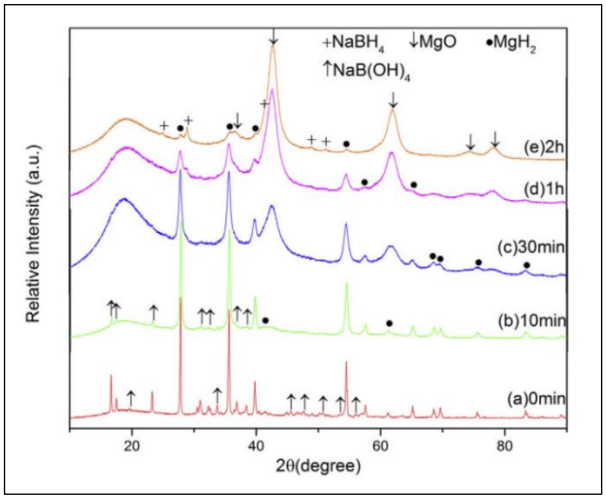

Figure 7 – *XRD analysis of samples with different milling times according to W. Chen study case [17].*

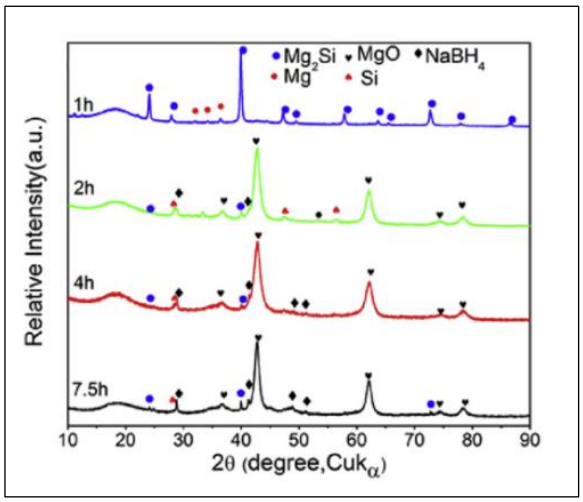

Figure 8 – *XRD analysis of samples with different milling times according to M. Huang study case [20].*

C. METHODS and EXPERIMENTAL PROCEDURE

C.1 METHODS

Medium Reactor with conical bottom (MRc)

To store the hydrogen and to control self-production on-demand, the hydrogen economy requires a simple and safe technology. In the present work, it was used a larger and well sealed stainless steel conical reactor (previously developed by research group [32]) to generate and store hydrogen. This particular reactor, presented in the next figure (*Figure 9*), has a volume of 368 cm^3, and is sealed using screws, and an o-ring to allow the crushing between the external and internal reator "cover", thus promoting the isolation of hydrogen throughout all reaction.

Figure 9 – *Open cross-section of MRc with an o-ring placed.*

RETSCH MM200 mixer mill

After the hydrolysis reaction is over, it is necessary to consider a laboratory device capable to grind, blend, and homogenize all the amounts of reactants that was prepared. For this purpose, the mixer mill (*Figure 10*) is ideal to promote a mechano-chemical reaction, i.e., reducing the particle size and mixing all the compounds. A ball milling vessel (*Figure 11*) it is required to carry out the reaction, with 2 or 3 milling balls to achieve the pretended product through the collision and friction between them and the reactants. The vessel has a cylindrical geometry and is built with zirconia (ZrO_2) coated with stainless steel, responsible for the thread locking system, and an internal diameter of 9 *mm* (internal volume of 15 cm^3). However, during the experiments the screw thread of vessel was damaged and, therefore, the original vessel provided together with RETSCH MM200 was used. This vessel is similar to the previous one although does not have a screw closure, so it is prone to hydrogen leak. In order to overcome the leaks, all the grooves were covered with cientific parafilm, as represented in the figure below.

Figure 10 – *RETSCH MM200 mixer mill with 2 ball milling vessels.*

Figure 11 – *Ball milling vessel ready to go to the mixer mill with zirconia balls and reactants inside.*

X-ray Diffraction (XRD)

When the reaction ends, i.e., taking into account the necessary time at the mixer mill, the product of the ball milling was stored and then analysed by x-ray diffraction (XRD). It is note worthy that this technique only reads the presence of crystalline compounds on the surface of the compound that are being used. The x-ray beam scattered by the different arrangements of atoms at the level of the crystal sctructure will induce in a diffraction in different directions and intensities, depending on its size and shape, with a possibly pattern detectable by an x-ray detector [33]. This analysis is used to identify unknown crystalline compounds, which for better analysis must be homogeneous and single phased, i.e., all the atoms or molecules are arranged in a uniform and consistent well-defined structure [34]. One of the main components of the diffractometer, major part of XRD (*Figure 12*), is the detector whose is responsible for the detection of each x-ray, generating a current pulse when absorbing it [35].

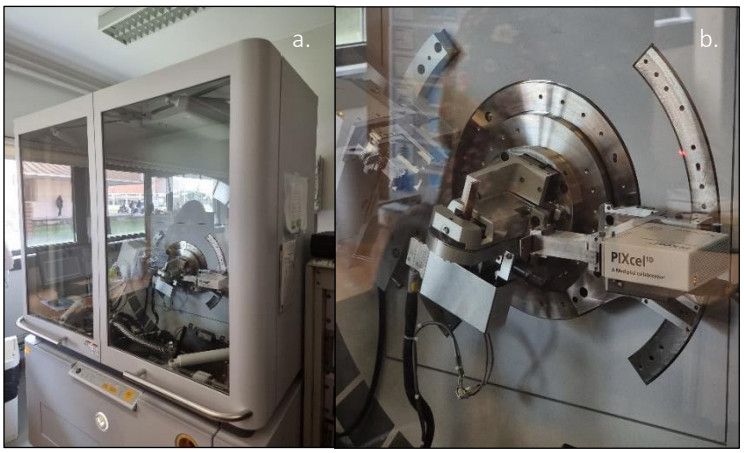

Figure 12 – *a: XRD. b: X-ray diffractometer.*

C.2 EXPERIMENTAL PROCEDURE

To study and evaluate the regeneration of $NaBH_4$ (Merck 452882, ≥ 98% purity) (*Figure 13*) under hydrogen production, it was made a catalytic hydrolysis performed 9 times in a reactor with conical bottom in order to obtain the by-product $NaB(OH)_4$. In general, for each hydrolysis, considering not adding any additives, were prepared according to the mass percentage of reactants to be added, such as 83% of distilled water, 7% of *NaOH* (Merck 221465, ≥ 97% purity), and the remaining 10% of $NaBH_4$ [25]. These were the conditions previously optimized by the research group in order to assure maximum $NaB(OH)_4$ purity – the by-product of most interest to recycle back to $NaBH_4$. It is important to refer that the preparation of the solution involves an initial dissolution of *NaOH* in water, during agitation, before adding $NaBH_4$ since *NaOH* works as an inhibitor, i.e., by increasing the pH of the solution it inhibits the H_2 formation, favored by lower pHs. To speed up the reaction a *Ni-Ru* catalyst (*Figure 14*) was previously added to the reactor. The density of each solution and consequent mass of catalyst to be added was determined using a 10 mL pycnometer.

Figure 13 – *Sodium borohydride packed.*

Figure 14 – *Ni-Ru catalyst drying.*

Therefore, with the catalyst placed in the bottom and the reactor properly closed, the reaction began with the proper injection of the $NaBH_4$ solution through an on-off valve to assure enough $NaB(OH)_4$ formation to study its recycling in the ball milling. The pressure and the temperature inside the reactor were measured with a pressure sensor and two thermocouples (one in the top and the other in the bottom, close to where the reaction takes place). The experiment was concluded when the pressure inside the reactor stabilized, indicating maximum H_2 has been formed. In the end of each reaction, hydrogen was carefully release to the atmosphere and the *Ni-Ru* catalyst was recovered for reutilization by washing it three times with distilled water and then dried in an oven

to become a dried powder again. The by-product was dried for at least 5 days in a proper vacuum desiccator (*Figure 15*).

Figure 15 – *Samples in a vacuum desiccator after hydrolysis reaction.*

Then, the sample was placed in the ball milling vessel, together with an identified reducing agent, to perform the ball milling experiments in the mixer mill. The amount of $NaB(OH)_4$ added to the vessel was 0.65 *g* in each experiment. By stoichiometry, the amount of reducing agent added was calculated (0.74 *g* to magnesium (*Mg*), and 0.80 *g* to magnesium hydride (MgH_2)). The calculations are presented in the appendices (*Appendix A*). Also, it is need to take account the 2 or 3 balls to put in the vessel together with the rest of reactants, in order to vary the BPR. Usually, the ratio of the internal volume occupied by the reactants, occupied with the zirconia balls, and the empty space (air) are equal, i.e., 1/3 filled between them. From here, everything is prepared to take the sample to the mixer mill, and studies of 3 or 6 hours were carried out. Given the difficulty to optimize the available space in the vessel, the time of milling was increased up to 6 hours (the maximum stipulated for each experiment) to compensate.

The extraction of the ball milling products is an important part of this project to predict the amount of primary compound, sodium borohydride. XRD analysis depicts theoretically the amount of each product, but the extraction shows the remain quantity of sodium borohydride. Whence it is used an organic compound typically of the alkylamine class to extract the by-product without any contamination, such as isopropylamine. This amine is a colorless substance that provokes irritation to the skin, eyes, and respiratory system and because of that should be used in a chemical hotte. Despite this, an hotte environment also helps to minimize eventual air contaminations due to by-product characteristics.

D. RESULTS and DISCUSSION

D.1 HYDROLYSIS

Taking into account the objective of the work, experiments of hydrogen production were performed through the $NaBH_4$ hydrolysis in order to obtain the by-product $NaB(OH)_4$. This by-product, which is the main raw material for the studies over this thesis, was then extracted and ball milling reactions were carried out in order to study its recycling. The performance of the several hydrolysis experiments realized as described in subchapter C.2 can be seen in following table (*Table 5*). Moreover, the experimental studies are plotted as a function of continuing part of pressure over time in the following figure (*Figure 16*).

Table 5 – *Results obtained from all the hydrolysis reaction performed.*

No	η (%)	dP/dT	HGR ($L/min.g_{cat}$)	Lag time (s)	Storage capacities	
					GHSC ($wt.\%$)	VHSC (kg/m^3)
1	98.46	1.25×10^{-2}	0.77	125	1.97	22.00
2	84.40	3.32×10^{-2}	1.01	83	1.67	18.64
3	99.21	4.23×10^{-2}	1.70	77	1.99	22.23
4	82.69	3.39×10^{-2}	1.03	94	1.63	18.24
5	72.79	4.21×10^{-2}	1.29	92	1.41	15.83
6	85.05	5.17×10^{-2}	1.70	54	1.68	18.77
7	100	5.11×10^{-2}	1.68	49	2.08	23.17
8	8.99	3.10×10^{-2}	0.60	48	0.09	0.95
9	92.55	7.32×10^{-2}	2.36	34	1.84	20.59

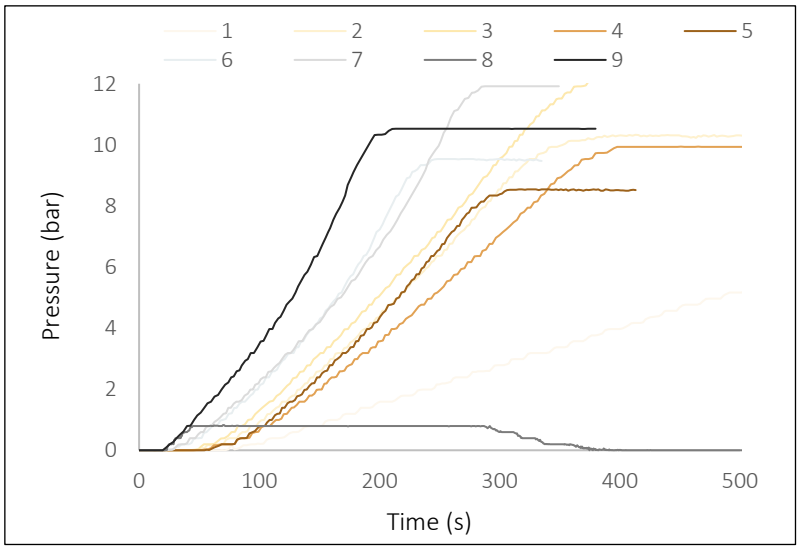

Figure 16 – *Continuing part of pressure over time for all hydrolysis analysis.*

As it can see from the table, the majority of the experiments had a good performance, i.e., considerably high yield and low lag times, as expected. This means that hydrogen production was done almost rightly, whose yield shows that the closer to 100% the less hydrogen left to react with the solution after the hydrolysis takes end. This was proven when the reactor was opened at the end of each reaction, seeing the solution "bubbling", concluding that the lower related yield, the higher "bubbling". So, in the case of no 9 with the minimum yield associated, this was due to an high hydrogen leak caused by an inappropriate closure of the reactor. As well, attention is also needed when injecting the solution into the reactor, making sure that the entire solution is being well injected, and the valve is subsequently well closed.

Relatively to the hydrogen generation rate (HGR), the greater the slope of the straight line equation of pressure-time graphic (dP/dT) the greater the amount of hydrogen produced. This indicates that for low lag times and typically higher yields the HGR will be much more significant.

For the storage capacities, both are relatable so gravimetric and volumetric hydrogen system capacity means the reactor weight or volume needed to store a given amount of H_2. So, a wider reaction yield will increase the GHSC or VHSC.

D.2 RECYCLABILITY: BALL MILLING

Due to low availability and accessibility of the mixer mill, a limited number of experiments were performed. However, some of them were immediately decided not to perform due to the previous conclusions of the XRD analysis. So, from the reactions performed, it was possible to reach some important conclusions as will later explained about using new reducing agents or more milling time. What is already known is that the ball milling reaction is strongly influenced by the reactant's molar fraction, the time of milling and the ball to powder ratio (BPR), this one represented in the next table (*Table 6*). BPR can be exemplified as a ratio between the mass of the milling balls (assuming each one has a 3.75 *g* of mass) and the summatory of the measured masses of the by-product and the reducing agent (their theoretical masses are present in the subchapter C.2).

Table 6 – *BPR for each sample.*

Reducing agent	No of balls	BPR
Mg	2	5
	3	8
MgH_2	2	5
	3	8

Initially, ball milling was only performed reactions with 2 balls, but due to its lower BPR, it was decided to increase it to one more ball in order to raise the BPR and thus promote more contact inside the ball milling vessel to a better heterogenized solution.

In the next page, the tables presented consist in all ball milling reactions performed with the proper reducing agent, number of balls and different hours elapsed (*Tables 7 and 8*). It were done replicas to confirm if the sample was performed relatively well and thus minimize possible errors in the discussion of the results.

Table 7 – *Constitution of each Mg sample with the right no of balls and ball milling time.*

Reducing agent	No	No of balls		Time (*h*)	
		2	3	3	6
A. Mg	1	✓	-	✓	-
	1’	✓	-	✓	-
	2	-	✓	✓	-
	2’	-	✓	✓	-
	3	-	✓	-	✓
	3’	-	✓	-	✓

Table 8 – *Constitution of each MgH_2 sample with the right no of balls and ball milling time.*

Reducing agent	No	No of balls		Time (*h*)	
		2	3	3	6
B. MgH_2	4	-	✓	✓	-
	4’	-	✓	✓	-
	5	✓	-	-	✓
	5’	✓	-	-	✓
	6	-	✓	-	✓
	6’	-	✓	-	✓

The two previous tables make it easier to identify some of the samples performed at ball milling. Each sample has a replica with the same prepared properties, i.e., same number of balls and milling time. As the results by the XRD analysis were not very conclusive, it was decided to, in addition to reactions with a milling time of 3 hours, also carry out reactions of 6 hours to result in possible better conclusions.

The tables beneath show the composition of the samples after ball milling reactions, identifying all the predictable crystalline compounds as mass percentage recorded by the diffractometer (*Tables 9 and 10*).

Table 9 – *Percentage of each crystalline compound in the Mg samples through XRD analysis*

Crystalline compound	Reducing agent					
	A. Mg					
	1	1’	2	2’	3	3’
$NaB(OH)_4$	64%	x	73%	68%	x	63%
Mg	25%	-	25%	27%	x	28%
$NaBH_4$	-	-	-	-	-	-
MgO	-	-	-	-	-	-
$Na_2B_6O_{10}(H_2O)$	5%	-	-	-	-	-
$Mg(OH)_2$	6%	x	2%	5%	x	9%
MgH_2	-	x	-	-	x	-

Table 10 – Percentage of each crystalline compound in the MgH_2 samples through XRD analysis.

Crystalline compound	Reducing agent					
	B. MgH_2					
	4	4'	5	5'	6	6'
$NaB(OH)_4$	42%	42%	-	-	58%	41%
MgH_2	-	-	26%	x	35%	53%
$NaBH_4$	-	-	-	-	-	-
MgO	-	-	26%	x	-	-
Na_2CO_3	-	-	48%	x	-	-
$Mg(OH)_2$	6%	6%	-	-	6%	5%
Mg	52%	52%	-	-	1%	2%

Like it can be seen, the achieved results through XRD analysis are divided into each type of reducing agent, firstly to magnesium (*Mg*) samples and secondly to magnesium hydride (MgH_2) samples. Each sample was replicated to obtain more concise and objective results. This results are presented in crystalline compounds percentage, where is quickly noticed the default of $NaBH_4$ in all performed reactions. Although $NaBH_4$ are not presented in its original form, *MgO* is present as expected according to the chemical equation written in subchapter B2. Also but in bigger evidence due to the presence in almost every reactions, $Mg(OH)_2$ might prove that the reactions were initiated by this compound being a reaction intermediate, according to the following equation.

$$NaB(OH)_4\,(s) + 2MgH_4\,(s) \rightarrow NaBH_4\,(s) + 2Mg(OH)_2\,(s)$$

The presence of Na_2CO_3 could be another form to prove its recyclability due to probable air contamination where CO_2 are prevailing. The x result represented in the table means the quantities that were not possible to quantify by XRD. Although XRD technique only detects the compounds presented at the surface of the samples this method is sufficient to use because the main objective of this project is only to identify if there has been any formation of sodium borohydride after the reaction takes end. If additionally, it was

necessary to know the (exact) amount of $NaBH_4$ formed, the results would have to be complemented with other type of analysis, like Nuclear Magnetic Resonance (NMR) or Fourier Transform Infrared Spectroscopy (FT-IR).

The below figures present the XRD analysis of ball milling experiments with selected samples prepared with the same characteristics in the same graphs, i.e., with the respective replicas (*Figures 17 to 22*). These graphics have the function to prove whether the regeneration of any samples was achieved, representing different and evident peaks across all samples. These peaks means the strength of the compounds diffracted by the x-ray and recorded by the diffractometer, i.e., more facility in identifying the compound. More than one peak can represent the same compound and without necessarily being present in a larger amount. Given that, this analysis only identifies crystalline compounds, we can only assume the presence of amorphous compounds if the background of the graphics is above the horizontal axis (with a minimal intensity higher than 0).

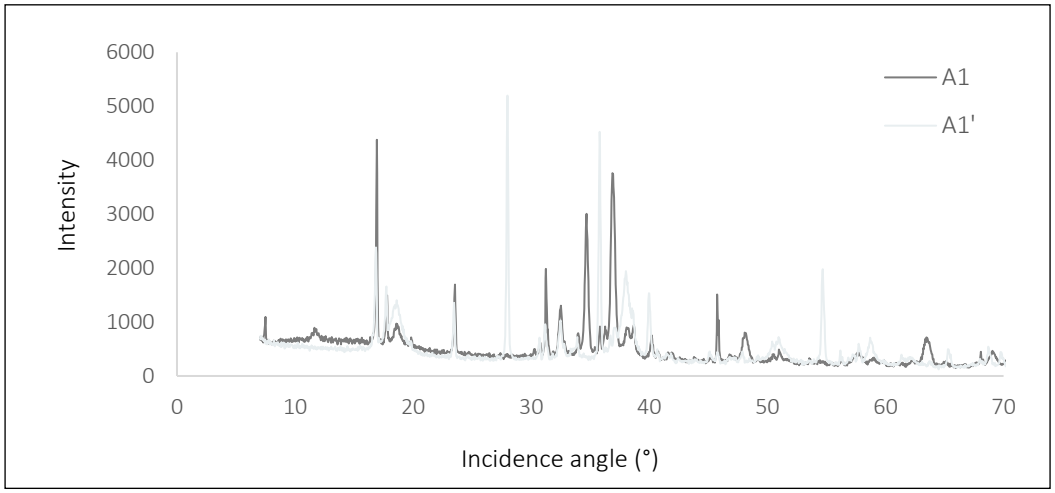

Figure 17 – *XRD graphic for samples A1 and its replica A1'.*

This first graphic shows that every peaks are mainly of $NaB(OH)_4$ for the two samples, corresponding to diffraction peaks at 2θ angle of 17°, 23°, 30°, and 40°. It is worth to mention that the by-product obtained by a patented method developed by the research group is 100% of $NaB(OH)_4$. However, it can also easily predict the existence of MgH_2 in A1's sample comparing the peaks at 2θ angle of 28°, 36°, 40° and 55°. These are the two main crystalline compounds read by the program, which indicates a very low reaction.

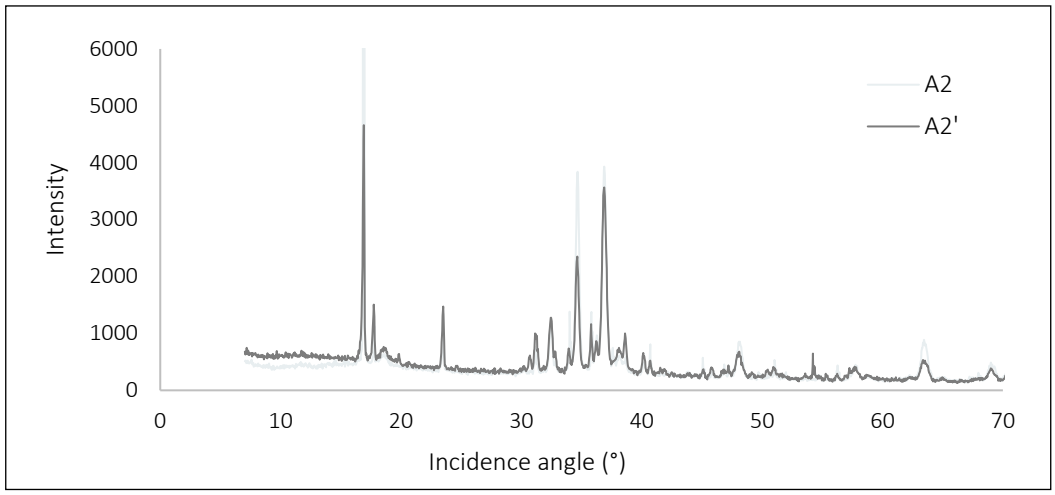

Figure 18 – *XRD graphic for samples A2 and its replica A2'.*

Same as the previous reactions, despite a higher BPR these two reactions proved once again that *Mg* is not the best reducing agent to promote better results, based on the XRD representations of the ball milling experiments.

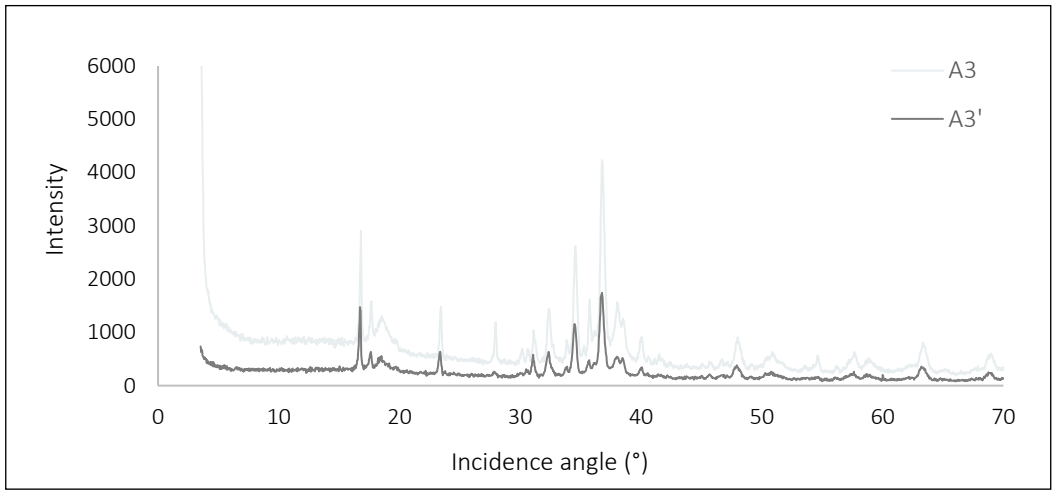

Figure 19 – *XRD graphic for samples A3 and its replica A3'.*

For the last two samples using *Mg* as reducing agent, despite the increase of milling time, identical results and conclusions were made, and that is why had to choose one more (at least) reducing agent to possible result in better results.

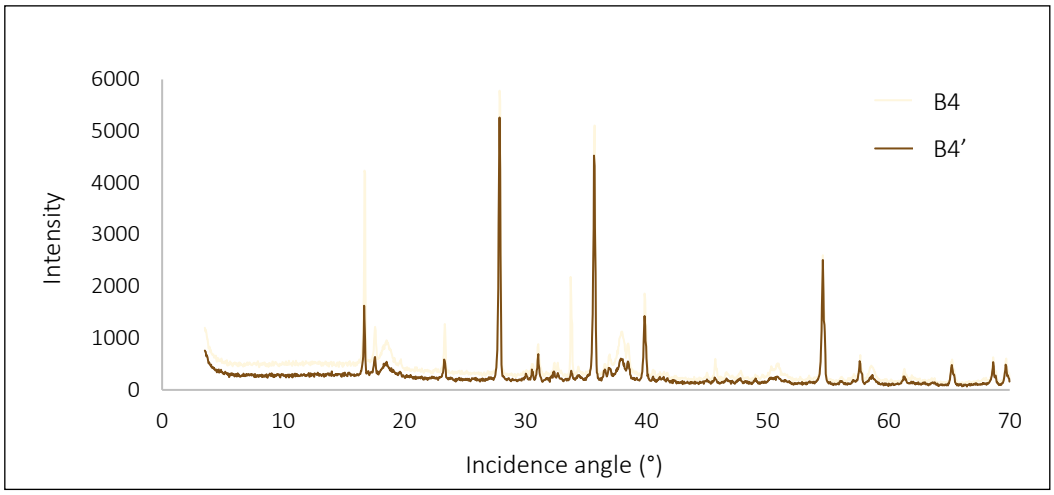

Figure 20 – *XRD graphic for samples B4 and its replica B4'.*

On the other hand, using MgH_2 as reducing agent bring better results, however, for these conditions were not as much results as expected. It is easy to predict that, according to the graphic above, both reactions were not complete with less milling time, i.e., still with a partial composition of $NaB(OH)_4$ and *Mg*.

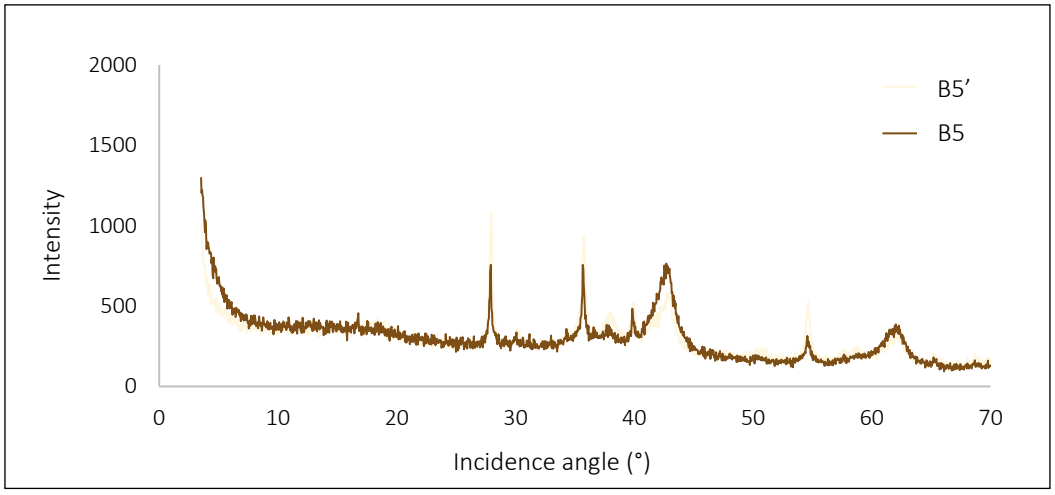

Figure 21 – *XRD graphic for samples B5 and its replica B5'.*

Moving on to the 6 hours reactions, the results were particularly good because XRD analysis did not indicate any presence of the by-product, contrasting with the rest of *Mg* and MgH_2 reactions. Despite not surging any percentage of $NaBH_4$, it appeared a small but significant percentage of *MgO* (with corresponding peaks at 2θ angle of 28°, 36°, 40° and 55°) and Na_2CO_3.

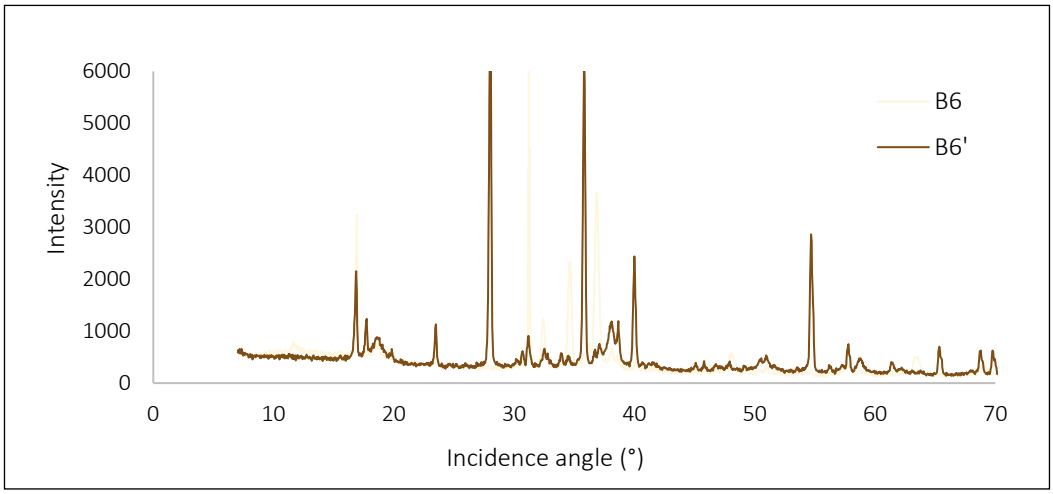

Figure 22 – *XRD graphic for samples B6 and its replica B6'.*

Finally but contrary to the expected, these last results was not as good confirming that a bigger BPR, when its assume this type (volume) of vessel and MgH_2 as reducing agent, indicates a poor reaction inside the vessel and, consequently, still remain a high presence of by-product.

E. MAIN CONCLUSIONS and PROPOSED FUTURE WORKS

Fossil fuels have been the primary source of energy worldwide for a long time, powering such areas as industrial processes, electricity generation, and transportation facilities. However, the use of fossil fuels contributes to environmental issues, including air pollution, greenhouse gas emissions, climate change, etc. As result of that, there is a growing necessity to explore alternative energy vectors that are not harmful for the environment and, if possible, with renewable facilities towards a more sustainable future. H_2 production from $NaBH_4$ can be a possible concept to a better and cleaner world due to its high hydrogen content and purity when released. Thus, a by-product is formed from the $NaBH_4$ regeneration, who can through a mechano-chemical process transform into its original hydride form.

For this purpose, the ball milling method was used to promote the recyclability of this by-product, $NaB(OH)_4$, always taking into account the available space of vessel due to the low internal volume. When this one is replete with zirconia balls, would lead to less space inside it and more clashes between the zirconia balls, bringing fewer effective results because of the lower interaction with the balls and the inner compound. If we want the same number of balls, to have more empty space inside the vessel, the amount of reagents should decrease, however what is pretended is to obtain the largest amount of solution and therefore this option is inappropriate.

According to the results obtained, in general none of the reactions was completed, i.e., none of them got $NaBH_4$ as a product. However, it can be assumed that the reactions using MgH_2 and 2 zirconia balls and 6 hours milling got MgO, the main by-product of the ball milling reaction. Also well, these experiments showed the formation of Na_2CO_3 in their composition, indicating the formation of $NaBH_4$ due to probable prolonged air exposure by the uncontrolled ambience that exist in the laboratory where CO_2 are prevailing. To face it, would be necessary to perform in a controlled and closed glove box which always has an inert ambience inside.

Despite of Mg as reducing agent has a great innovation used by practically the most of research articles due to its easier recover/recycle with less costs., it influence was not good as projected because, no matter the number of balls or milling time, $NaB(OH)_4$ was still largely present in the samples. If the intention is to obtain the most correct and

concise results with this reducing agent, increase the milling time is an hypothesis to retain for the future projects, however, could bring significantly logistical difficulties and greater dependence on the mixer mill.

In addition, MgH_2 as reducing agent also showed that it was not needed to perform a shorter milling time (i.e., 3 hours of analysis) despite the number of balls. Since with 6 hours analysis there was a smaller indicator of reaction, with 3 hours analysis the reaction would be less reacted.

As proposed future works, the main one would be improve the whole ball milling process, such as increase the BPR, increase the milling time, and consider using a mixer mill to perform ball milling reactions with higher amount of reactants. Also, new reducing agents might be a suggestion for the future to better recover this chemical hydride, e.g., magnesium silicide (Mg_2Si), lithium hydride (LiH), although it reacts strongly with water, Portugal has significant source of lithium, contrarily to Mg (extracted mostly in China). Perform other characterization analysis to complement the XRD analysis is another suggestion for the future works because, as already mentioned, this program only reads the surface layer of the samples and to achieve more concise results would be necessary to analyze it further.

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G. APPENDICES

G.1 APPENDIX A

Magnesium (Mg)

$NaB(OH)_4\,(s) + 4Mg\,(s) \rightarrow NaBH_4\,(s) + 4MgO\,(s)$

- v [Mg / $NaB(OH)_4$] = 4
- e (Mg +20%) = 1.2
- m [$NaB(OH)_4$] = 0.65 g
- M [$NaB(OH)_4$] = 101.83 g/mol
- M [Mg] = 24.305 g/mol
- $m\,[Mg] = \frac{m\,[NaB(OH)_4]}{M\,[NaB(OH)_4]} \times v\,[Mg\,/\,NaB(OH)_4] \times M\,[Mg] \times e = 0.7447\ g$

Magnesium hydride (MgH_2)

$NaB(OH)_4\,(s) + 4MgH_2\,(s) \rightarrow NaBH_4\,(s) + 4MgO\,(s) + 8H_2\,(s)$

- v [MgH_2 / $NaB(OH)_4$] = 4
- e (MgH_2 +20%) = 1.2
- m [$NaB(OH)_4$] = 0.65 g
- M [$NaB(OH)_4$] = 101.83 g/mol
- M [MgH_2] = 26.32 g/mol
- $m\,[MgH_2] = \frac{m\,[NaB(OH)_4]}{M\,[NaB(OH)_4]} \times v\,[MgH_2\,/\,NaB(OH)_4] \times M\,[MgH_2] \times e = 0.8064\ g$

G.2 APPENDIX B

Alkali hydrolysis reaction (example for one of performed reactions, No 1)

- Yield (η) – calculated by gas pressure, i.e., equation of state of hypothetical ideal gas (Gas = Air + H_2): $\eta = \frac{P_{Gas,\ Exp\ Abs}}{P_{Gas,\ Theo}} \times 100 = \frac{6.79}{6.89} \times 100 \approx 98\%$, where $P_{Gas,\ Exp\ Abs}$ means the average of the final experimental stabilized pressure of the gas inside the reactor in *bar* plus the relative air pressure (= 1.01325 *bar*), and $P_{Gas,\ Theo}$ the theoretical pressure of gas that appears on the literature in *bar* too.
- dP/dT – slope of straight line equation of pressure-time graphic.
- Hydrogen Generation Rate (HGR) – firstly determined in *mol/s*: $HGR = \frac{V_{R,\ Fin}}{R \times T} \times dP/dT = \frac{225.11}{83.14472 \times (21 + 273.15)} \times 1.25{\times}10^{-2} \approx 1.20{\times}10^{-4}\ mol/s$, where $V_{R,\ Fin}$ is the volume of reactor after the reaction takes end in cm^3, R is the ideal gas constant in $cm^3.bar$/K.mol and T is the local temperature of the room in kelvin. Then to pass to $L/min.g_{cat}$: $HGR = 1.20{\times}10^{-4} \times 60 \times \frac{V_{molar,\ STP}}{m_{cat}} = 1.20{\times}10^{-4} \times 60 \times \frac{24.466}{0.2187} \approx 0.77\ L/min.g_{cat}$, where $V_{molar,\ STP}$ is the molar volume in *L/mol* at STP conditions, i.e., temperature at 25ºC and pressure at 101.325 *kPa*, and m_{cat} is the measured mass of catalyst used in the reaction in *g*.
- Lag time – is the time in seconds it takes for the reaction to react with the catalyst, typically up to 0.5 bar.
- Gravimetric Hydrogen System Capacity (GHSC) – the amount of hydrogen able to be stored in weight: $GHSC = \frac{m_{H_2,\ Exp}}{m_{cat} + m_{sol}} \times 100 = \frac{0.1072}{0.2187 + 5.2267} \times 100 \approx 1.97\ wt.\%$, where m_{sol} is the measured mass of $NaBH_4$ solution, and $m_{H_2,\ Exp}$ is the experimental mass of hydrogen that is calculated using the experimental number of moles multiplied by the molar mass of H_2 (=2.016 *g/mol*). The number of moles has the following expression: $n_{H_2,\ Exp} = \frac{P_{Gas,\ Exp\ Abs} \times V_{R,\ Fin}}{R \times T} - V_{R,\ In} = \frac{6.79 \times 225.11}{83.14472 \times (21 + 273.15)} - 224.13 \approx 0.0532$ mol, where the only missing factor to be explained is the $V_{R,\ In}$ that represents the volume of reactor before the reaction takes action in cm^3.

- Volumetric Hydrogen System Capacity (VHSC) – the amount of hydrogen able to be stored in volume: $VHSC = \frac{m_{H_2,\,Exp}}{V_{cat} + V_{sol}} \times 100 = \frac{0.1072}{0.0690 + 48026} \times 1000 \approx 22\ kg/m^3$, where it just need to understand the represent of V_{cat} and V_{sol}, whose formula is the same for both: $V_{cat} = \frac{m_{cat}}{\rho_{cat}} = \frac{0.2187}{3.17} = 0.0690\ cm^3$ and $V_{sol} = \frac{m_{sol}}{\rho_{sol}} = \frac{5.2267}{1.0883} = 4.8026\ cm^3$, where ρ is the density of the compound in g/cm^3.