

Mestrado Integrado em Engenharia Química

Batch sodium-borohydride hydrolysis in the presence of nickel-ruthenium based catalyst: Addition of biopolymers to improve hydrogen storage in the liquid phase by solubility effects

Master Thesis

by

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Abstract

The present thesis aimed at studying the effects of small additions of cellulose based polymers on catalytic sodium borohydride hydrolysis, in order to improve hydrogen storage in the post-reaction liquid phase by solubility effects.

The carboxyl-methyl-cellulose (CMC), hydroxyl-ethyl-cellulose (HEC) and methyl-cellulose (MC) biopolymers were tested by their addition to the reactant solution.

Three studies were carried out: a reaction kinetics study, preliminary hydrogen solubility study and by-products analysis. The kinetics study enclosed a set of experiments of sodium borohydride hydrolysis in the presence of a reused Ni-Ru catalyst, in which the effects of temperature and biopolymers concentration on the hydrogen gas generation rate, yield and lag time were investigated.

The hydrolysis reactions were performed at two different temperatures (25 °C and 45 °C) in a batch reactor with an internal volume of 369 cm³, made of stainless-steel with a bottom conical shape, positioned vertically. The polymers were added to the reactant solution (15wt% NaBH₄ and 7wt%NaOH) in the two different mass concentrations: 0.05wt% and 0.25wt%.

A small addition of CMC and MC polymers gives a very rapid hydrogen generation (when comparing with classic hydrolysis) leading to a complete reaction for the CMC and MC cases at around half of the time. This result is of primordial importance bearing in mind the application of this concept to portable applications.

The preliminary solubility study comprised the measurement of conductivity solutions, after and post-reaction. Potential candidates to promote the store of hydrogen in the liquid phase are suggested according to this study. In a very near future, solubility tests will be performed in order to estimate the amount of hydrogen gas that solubilises in each solution and to compare the capability of the post-reactant solutions to store hydrogen in the liquid phase.

The crystal structure of the remaining solutions was analyzed by X-Ray Diffraction (XRD) analysis. The XRD analysis results of the crystals by-products structure, from the classic and with the addition of 0.05wt% HEC and 0.05wt% MC hydrolysis, reveals that both of them are a sodium metaborate dehydrate, NaBO₂·2H₂O. A crystal structure of sodium tetrahydroxoborate (NaB(OH)₄) for

hydrolysis with 0.05wt% and 0.25wt% of CMC and 0.25wt of HEC and MC polymers was found.

Key-words: hydrogen production, sodium borohydride hydrolysis, solubility effects, biopolymers, Ni-Ru based catalyst.

Resumo

A presente tese de mestrado investigou a influência da adição de pequenas quantidades de biopolímeros, à base de celulose, na hidrólise catalisada do borohidreto de sódio, realizada em reator por partidas, com o objetivo de possibilitar o armazenamento do hidrogénio produzido na fase líquida remanescente através de efeitos de solubilidade.

Através da sua adição à solução reagente foram testados os seguintes biopolímeros: carboxi-metilcelulose (CMC), hidroxi-etilcelulose (HEC) e metilcelulose (MC).

Durante o projeto de Tese foram realizados os seguintes estudos: estudo da cinética da reação de hidrólise, estudo preliminar de solubilidade de hidrogénio e análise dos sub-produtos da reação por cristalografia.

No estudo cinético foi executado um conjunto de experiências no qual os efeitos da temperatura reacional e da concentração de biopolímeros na taxa de produção de hidrogénio, no rendimento e no tempo de indução da reação de hidrólise do borohidreto de sódio na presença de um catalisador de Ni-Ru foram investigados. As reações de hidrólise ocorreram num reator por partidas posicionado verticalmente, feito de aço inoxidável, com um volume interno de 369 cm³ e uma geometria de fundo cónica, às temperaturas de 25°C e 45°C. Os diferentes biopolímeros foram adicionados à solução reagente (15wt% NaBH₄ e 7wt%NaOH) a duas concentrações mássicas diferentes: 0.05wt% e 0.25wt%. Verificou-se que uma pequena adição de CMC e MC tem um impacto elevado na cinética gerando hidrogénio a uma taxa bastante elevada quando comparada com a da hidrólise clássica atingindo-se o fim da reação num tempo significativamente menor. Este é um resultado de extrema importância quando se pensa na aplicação deste conceito (produção e contentorização de hidrogénio em aplicações portáteis).

O estudo preliminar de solubilidade de hidrogénio envolveu a determinação da condutividade das soluções antes e após a reação de hidrólise. São sugeridos alguns polímeros candidatos com potencial para promoverem um armazenamento de hidrogénio na fase líquida. Num futuro próximo irá ser realizado um estudo detalhado de solubilidade que permitirá determinar a quantidade de hidrogénio que é capaz de solubilizar em cada solução proposta e comparar a capacidade das soluções pós-reação para armazenar hidrogénio.

A estrutura química dos cristais, obtidos por evaporação da água das soluções sobrenadantes, foi determinada por difração de raios X. A análise dos cristais obtidos revelaram a existência de duas estruturas diferentes: metaborato de sódio di-hidratado ($\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$) e tetrahydroxoborato de sódio ($\text{NaB}(\text{OH})_4$).

Palavras-chave: produção de hidrogénio, hidrólise de borohidreto de sódio, solubilidade de hidrogénio, biopolímeros, catalisador à base de Ni-Ru.

Declaration

I declare, on oath, that this work is original and that all the not original contributions were appropriately referred with source identification.

Porto, 31st july 2013

(Joana Sofia Oliveira Madureira)

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Nomenclature/Glossary

dP/dt	linear region slope	bar.s ⁻¹
K_H	Henry's constant	MPa, bar ⁻¹
m_{cat}	catalyst mass	g
m_{NaBH_4}	mass of sodium borohydride in the reactant solution	g
MM_{H_2O}	molecular mass of water	g.mol ⁻¹
MM_{NaBH_4}	molecular mass of sodium borohydride	g.mol ⁻¹
$m_{solution}$	mass of reactant solution injected	g
n_{air}	number of moles of air produced	mol
$P(air + H_2)_{experimental}$	absolute pressure of the gas produced	bar
$P_{atmospheric}$	pressure inside of laboratory	bar
$P(air + H_2)_{relative}$	Relative pressure of the gas produced	bar
P_g	gas pressure	
Q	hydrogen flow rate	L(H ₂)min ⁻¹ gcat ⁻¹
R	Ideal gas constant	cm ³ .bar.mol ⁻¹ .K ⁻¹
T	temperature	°C, K
$V_{initial}$	available volume inside reactor for gas production	cm ³
V_{final}	volume occupied by the gas after reaction	cm ³
V_{free}	Volume occupied by the hydrogen injected	cm ³
V_m	the molar volume of an ideal gas at STP conditions	22,446 L.mol ⁻¹
V_r	reactor internal volume	cm ³
x	hydration factor	
y	gas concentration in liquid (molar ratio)	
ρ_{H_2O}	density of water	g.cm ⁻³
ρ_{cat}	catalyst density	g.cm ⁻³
$\rho_{solution}$	density of reactant solution injected	g.cm ⁻³

Acronyms

CMC	carboxyl-methyl-cellulose
FCs	fuel cells systems
HEC	hydroxyl-ethyl-cellulose
ILs	ionic liquids
LPOPS	Less polar organic polymeric solution
MC	methyl-cellulose
PEMFC	polymer electrolyte membrane fuel cell
XRD	X-Ray Diffraction

1 Introduction

The mankind's constant progress during the last three centuries drove progressively to an excessive and uncontrolled use of fossil fuels. The supply of fossil fuels is limited and the development of alternative and clean renewable energy carriers is of most importance [1]. Currently, the society still consumes large amounts of fossil fuels, although this large consumption is clearly a concern. The world's population has been focused on finding solutions for a secure energy future.

In this context, hydrogen arises as an alternative and clean renewable energy vector mainly for the transportation sector and other portable applications [1]. The hydrogen as an energy carrier is particularly interesting for Polymer Electrolyte Membrane Fuel Cell (PEMFC) technologies in which the chemical potential energy of the gas is directly converted into electric energy [2].

Unfortunately, molecular hydrogen is not available in large quantities, it must be synthesized from other energy sources before energy can be transferred to the end user. Moreover it has a very low volumetric energy density, so it is very difficult to store a sufficient amount of hydrogen in a small and light enough vessel [3]. This problem is the main impeditive for the establishment of a sustainable hydrogen-based energy especially for portable applications. Therefore, it is important to find and develop efficient and safe methods of hydrogen production and storage [1].

One of the promising hydrogen storage methods relies on liquid-phase chemical hydrogen storage materials.

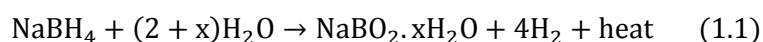
Chemical hydrogen storage, which involves storing of hydrogen in the form of chemical bonds, has received great attention and there are a number of materials with high hydrogen content that are being explored. For many years, solid-state hydrogen storage materials were considered as promising chemical hydrogen materials due to their appealing characteristics. However, their disadvantages, like the high temperature required to desorb hydrogen, slow hydrogen release kinetics as well as heat dissipation issues and the high system weight, led to a search for efficient and safe liquid phase hydrogen storage materials [4].

Aqueous sodium borohydride, ammonia borane, hydrazine, hydrazine borane and formic acid have been referred as promising liquid-phase chemical hydrogen storage materials. The use of these compounds provides high gravimetric and

volumetric densities, low potential risk and low capital investment in hydrogen storage [4].

The present project focuses on sodium borohydride as a material system for hydrogen production and storage and on its catalyzed hydrolysis reaction.

When sodium borohydride (NaBH_4) reacts with water (H_2O) at room temperature in presence of a catalyst, a theoretical hydrogen (H_2) content of 10.8wt% can be released and the by-product sodium metaborate is formed ($\text{Na}\cdot\text{BO}_2\cdot x\text{H}_2\text{O}$), through the following exothermic reaction [2]:



Ideal hydrolysis is attained for hydration factor $x = 0$, where two moles of water are required to react with one mole of solid sodium borohydride to release four moles of hydrogen. In practice, an excess of water is necessary but lowers the theoretical gravimetric hydrogen storage capacity of sodium borohydride [4].

The potential application of sodium borohydride as hydrogen carrier for portable applications is dependent not only on an easily controllable catalysed hydrolysis reaction at significant rates, to comply with fuel cell feeding, but also on the increase of the gravimetric density, which is of utmost importance [5]. Therefore, this technology of hydrogen production and storage is not yet economically feasible. One of the biggest challenges is to find a way to produce and simultaneously store molecular hydrogen in the liquid phase.

It is known that molecular hydrogen is a strongly non polar compound, not soluble in water and in almost all the liquid solvents at near ambient conditions. Due to this fact one possibility is to change the polarity of the reaction medium, in order to lowering the polarity/conductivity of the post-reaction solution, and make possible the storage of molecular hydrogen in the liquid phase by solubility effects.

A way to improve the affinity of hydrogen storage in the liquid phase is to increase the non-polar hydrogen-electrolyte interactions by adding small portions of compounds to the reactant solution. These compounds must be soluble in water and slightly polar.

For the first time, the addition of biopolymers to the reactant solution of sodium borohydride was explored through a study entitled "Effects of the addition of an organic polymer on the hydrolysis of sodium tetrahydroborate in batch reactors" [2]. The capability of storing hydrogen gas by its dissolution on the liquid by-product was investigated. That experimental study showed that at moderate pressures, up to

2.7 MPa, both the generation and storage of molecular hydrogen slightly increased by small additions of the organic polymer - carboxymethyl cellulose (CMC)[2].

It is important to continue the study of this new route to improve simultaneous hydrogen production and storage in the liquid phase, via batch hydrolysis of sodium borohydride. It is expected that other polymer compounds, also based on cellulose could change the polarity of the reaction medium and contribute to the hydrogen capture in their molecular cavities, increasing the yields and rates of sodium borohydride catalysed hydrolysis, with higher gravimetric and volumetric hydrogen densities.

In the present thesis, studies on the effects of small additions of cellulose based polymers on sodium borohydride hydrolysis, in the presence of a Ni-Ru based catalyst are reported. The biopolymers tested were: carboxyl-methyl-cellulose (CMC), hydroxyl-ethyl-cellulose (HEC) and methyl-cellulose (MC).

1.1 Project goals

The objective of the present research work was to investigate the influence of small additions of based cellulose polymers in the kinetics reaction of catalytic hydrolysis of stabilized aqueous solutions of sodium borohydride, in a batch reactor, bearing in mind the possibility of hydrogen storage in the liquid phase.

In order to achieve this goal, experiments of hydrolysis of sodium borohydride, in the presence of a reused nickel-ruthenium based catalyst, were carried out under pressure up to 2.5 MPa. Hydroxyl-ethyl-cellulose, carboxyl-methyl-cellulose and methyl-cellulose polymers, through small additions to the reactant solution were tested.

The influence of the biopolymer concentration and reaction temperature on the reaction rate and yield was investigated.

1.2 Thesis organization

The thesis is divided in 7 main chapters, next summarized.

Chapter 1, *Introduction*, introduces the reader to the research topic and presents the main objective.

In the Chapter 2, *State of the art*, the potential of hydrogen as an energy carrier and sodium borohydride as hydrogen carrier are described. A review of ruthenium based catalysts on sodium borohydride hydrolysis and a general introduction to polymer electrolyte membrane fuel cells are also reported. Finally, the concept of hydrogen solubility is introduced as well as the chemical compounds that may enhance its solubility on the hydrolysis liquid by-product.

Chapter 3, *Experimental Procedure and Technical Description* is focused on the methodology and materials used to produce hydrogen via batch sodium borohydride hydrolysis.

Chapter 4, *Results and Discussion* is devoted to presentation and discussion of the results, regarding the impact of the small additions of biopolymers on the kinetics reaction and on hydrogen solubility.

Chapter 5, *Conclusion*, presents the main conclusions of the developed work.

Chapter 6, *Project assessment*, gives an overall judgment about the work developed.

Chapter 7, *References*, is the list of the bibliographic references used.

2 State of the Art

This chapter presents firstly, the potential of the use of hydrogen and sodium borohydride as energy carriers. A review of ruthenium based catalysts used in sodium borohydride hydrolysis and a general introduction to polymer electrolyte membrane fuel cells are also reported. Finally, the concept of hydrogen solubility is recalled and some chemical compounds that may enhance its solubility on the hydrolysis by-products are proposed.

2.1 Hydrogen as a energy carrier

Hydrogen is an energy carrier, an indirect source of energy, not a resource itself. In spite of being the simplest and the most abundant atom both on the Universe and in Earth, it does not exist in its free form. It must be synthesized from other energy sources, and then used to transfer energy to another use [3].

As an energy carrier, hydrogen has high potential with an energy density of 142 MJ/kg, around three times higher than that of petroleum, 47 MJ/kg [6]. Moreover it presents minimal pollution characteristics, combustibility in internal combustion engines, feasibility of electrochemical combination with an oxidant in fuel cells and mass transportability comparable to that of petroleum [3]. On the other hand, hydrogen has a very low volumetric storage density which is not yet suitable for the establishment of a sustainable hydrogen-based energy future [3].

According to the U.S. Department of Energy, the current hydrogen storage technologies involve compressed hydrogen gas tanks, liquid hydrogen tanks, cryogenic compressed hydrogen, metal hydrides, high-surface-area adsorbents, and chemical hydrogen storage materials [7].

The most traditional storage system is the high-pressure gas cylinders. This type of storage operates at pressures between 300 and 700 bar. This higher pressure level requires material and design improvements in order to ensure tank integrity. Advances in compression technologies are also required to improve efficiencies and reduce the cost of producing high-pressure hydrogen [7].

Liquid hydrogen tanks can store more hydrogen in a given volume than compressed gas tanks. The volumetric capacity of liquid hydrogen is 0.070 kg/L,

compared to 0.030 kg/L for 700 bar gas tanks. However, this technology presents some drawbacks such as: hydrogen boil-off, the energy required for hydrogen liquefaction, volume, weight, and tank cost. New approaches able to lower these energy requirements and consequently the cost of liquefaction are needed [7].

The metal hydrides have higher volumetric density storage than pressurized hydrogen or liquid hydrogen. A further important feature of metal hydrides is the reversibility provided by almost all of the metal hydrides. As main limitations, they present low hydrogen gravimetric capacity, slow uptake, low stability and high cost [7].

Hydrogen adsorption on solids with large surface areas includes a range of carbon-based materials such as carbon nanotubes, aerogels, nanofibers, as well as metal-organic frameworks, conducting polymers, and clathrates. This is a new field on hydrogen storage that may be promising. For hydrogen storage capacity, a value of 4 wt% at 78K and of approximately 1 wt% at room temperature, via adsorptive mechanism has been reported. However, due to the highly porous nature of solids, volumetric capacity may still be an important issue to continuing exploring and improve [7].

Chemical storage materials have been investigated extensively as a primary hydrogen storage medium due their very high volumetric hydrogen storage density, ability to produce hydrogen on demand through hydrolysis reaction and stability during long periods of storage without usage [3]. Compared with other technologies, the chemical hydrides can store hydrogen at much milder ambient conditions and relatively low pressure. However, these hydrolysis reactions are not easily reversible on-board a vehicle. Hence, the by-products must be removed from the vehicle and regenerated off-board [7].

The present reached gravimetric and volumetric efficiencies for these six storage technologies are compared in Figure 1, as well as, the FreedomCAR targets for automotive hydrogen storage systems in 2010 and 2015, published by US Department Of Energy (DOE) [7].

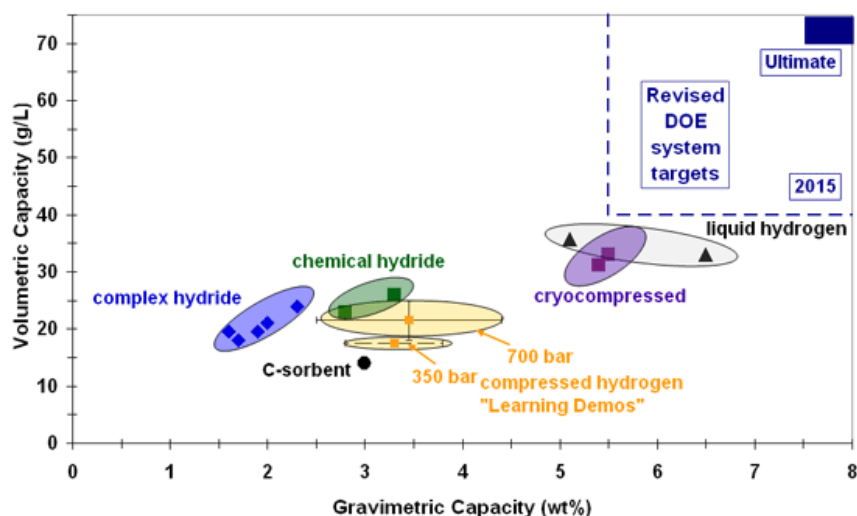


Figure 1 - Status of hydrogen storage technologies: gravimetric and volumetric efficiencies [7].

2.2 Sodium Borohydride as energy/hydrogen carrier

Sodium borohydride, also known as sodium tetrahydroborate is not a new compound: it has been discovered in 1940s by Prof. H.C. Brown, Nobel Laureate in Chemistry in 1979. It is especially known as a reducing agent and it is widely used in organic chemistry. In industry, it is mainly used as reducing agent in the manufacture of pharmaceuticals and a bleaching agent in the manufacture of paper [8].

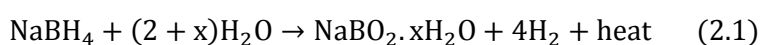
The year of 2000 marked a new beginning in the sodium borohydride history with the work of Amendola et al.: “a safe, portable, hydrogen gas generator using aqueous borohydride solution and Ru catalyst”. After that date, intensive research has been focused on sodium borohydride as a promising hydrogen carrier [2].

Nevertheless, the U.S. Department of Energy (U.S. DOE) recommended a no-go for sodium borohydride for vehicular applications due the non-compliance of the targets established for 2007 [9]. The U.S. DOE decision was based on the following observations: too low effective gravimetric hydrogen storage capacities, inefficiency of hydrolysis by-product recycling and cost [10].

Sodium borohydride did not meet the 2007 target from U.S. DOE but according to the intense published literature it has definitively potential for portable applications, or at least niche applications [9]. Hence, it is expected that sodium borohydride can meet the 2015 target: a gravimetric hydrogen storage capacity of 9

wt% [2]. In fact, sodium borohydride, for ideal hydrolysis ($x=0$) presents a high theoretical gravimetric storage capacity (10.8 wt%) [4].

When stored in aqueous solutions, sodium borohydride undergoes self-hydrolysis. Schlesinger et al. [11] discovered that it is possible to form a highly stable aqueous solution of sodium borohydride by dissolving it in basic solution. The hydrolysis reaction can then be initiated on demand by bringing the solution into contact with an heterogeneous catalyst, making the release of hydrogen very easy to control [6]. Hence, the catalytic hydrolysis of stabilized aqueous solutions of sodium borohydride occurs through the following exothermic reaction [2]:



The standard state enthalpy change of the above reaction at room temperature is -217 kJ/mol [3]. Ideal hydrolysis is attained for hydration factor $x = 0$, where two moles of water are required to react with one mole of solid NaBH_4 to release four moles of hydrogen. In practice, an excess of water is necessary due to the fact that the solid by-product sodium metaborate ($\text{NaBO}_2 \cdot x\text{H}_2\text{O}$), can exist with varying degrees of hydration; also the solubility of sodium borohydride and by-products in water are low: 55g NaBH_4 /100g H_2O at 25 °C and 28g NaBO_2 /100g H_2O at 25 °C, respectively [3][9]. However, excess of water lowers the theoretical gravimetric hydrogen storage capacity of sodium borohydride [4].

Some issues related to sodium borohydride hydrolysis have been intensively studied such as: concentration of inhibitor, usually sodium hydroxide, concentration of sodium borohydride, reaction temperature and suitable catalysts. In fact these parameters have a significant influence on the hydrolysis reaction [12].

Amendola and co-workers [13] investigated the influence of sodium hydroxide concentration in sodium borohydride solutions on the hydrogen generation rate, using a Ruthenium catalyst. They reported that for a given weight percent of sodium borohydride, hydrogen generation rates decreased with the increasing of the weight percent of sodium hydroxide (from 1wt% to 10 wt%).

Ingersoll et al. [14] reported similar results after their experiments with a (Ni-Co-B) catalyst: the hydrogen generation rate increased for lower sodium hydroxide concentrations and then decreased after reaching a maximum at 15wt% of sodium hydroxide. Minkina et al. [15] investigated the effects of temperature and sodium hydroxide concentration on the degradation of concentrated sodium borohydride

solutions. They suggest that above 30 °C, at least 5wt% of sodium hydroxide must be added to slow the hydrolysis.

Hence small amounts of sodium hydroxide must always be added to the reactant solution during its preparation. A possible explanation was given by Amendola et al. [13]: at higher sodium hydroxide concentrations, water presents a reduced activity. This occurs primarily because the ions, especially hydroxide (OH⁻), strongly complex water, decreasing the available free water necessary for the hydrolysis. It was stated that, also in sodium borohydride solutions having low weight percent of sodium hydroxide, not only will hydrogen generation rates will be faster, but more of the by-products will remain in solution.

Regarding to the sodium borohydride reactant, Amendola et al.[13] studied the variation of its concentration (1wt%, 5wt% and 10wt%) on aqueous solution, maintaining sodium hydroxide concentration and catalyst quantity constants. The authors reported that, as the weight percent of sodium borohydride is increased, initial hydrogen generation rates increase and reach a maximum in the range of 7.5-12.5 wt% of sodium borohydride (depending on weight percent of sodium hydroxide). At higher values of the weight percent of sodium borohydride, the initial hydrogen generation rates decrease. Then the authors stated that greater hydrogen generation rates at lower weight percent of sodium borohydride are possibly due to reduced solution viscosity, i.e. reduced mass transport allows more sodium borohydride and water to contact catalyst surfaces.

Also Zhang et al. [16] published similar results. They mentioned that sodium borohydride concentration should be as high as possible in order to improve the fuel energy density, however, when the concentration was high enough, the concentration of the reaction product metaborate would exceed its solubility limit and precipitate out of solution, blocking catalyst active sites.

According to Amendola et al. [13] and Pinto et al. [17], the hydrogen generation rates are very sensitive to the reaction temperature. Between 0°C and 55°C these different studies show, as expected, that the hydrogen rates rise with the increase of temperature.

In the last few years both noble and non-noble metal catalysts have been investigated. While noble metal catalysts are superior in terms of specific activity, in the last years non-noble metals have been developed with similar activities [6].

The catalyst used in the present project was a Ni-Ru based powdered catalyst, in which the main active component is the noble metal ruthenium.

Appendix A summarises the results obtained in some selected works using ruthenium based catalyst for sodium borohydride hydrolysis since the year 2000 [6].

Despite these intensive studies, there are some problems that still need to be solved. The sodium borohydride production cost is the biggest limitation for an early adoption of this technology to premium power applications. This technology will not be economically feasible until the production cost of sodium borohydride become significantly reduced. A considerable decrease in its cost might be achieved by finding an effective method of recycling by-products back to sodium borohydride. The electrochemical method have been appointed with favourable results to convert sodium metaborate into sodium borohydride [4].

2.3 Polymer Electrolyte Membrane Fuel Cell

Fuel cells systems (FCs) are nowadays seen as belonging to the portfolio of solutions to solve the world energetic problem. FCs convert the chemical energy of hydrogen and oxygen into electricity and heat by electrochemical redox reactions. FCs are an advanced power system that is sustainable, clean and environmental friendly, which produces water as the only by-product [18].

Fuel cell systems could use pure hydrogen fuel or a variety of primary fuels such as natural gas and methanol that could be used directly or used to produce the hydrogen fuel instead [18].

The first working fuel cell was invented by Sir William Grove in 1843, by reacting oxygen and hydrogen on separate platinum electrodes that were immersed in dilute sulphuric acid inside five cells of a gas voltaic battery and using the current produced to electrolyze water in another similar cell [18].

Currently, six types of fuel cells are receiving attention for energy production in stationary or transportation applications: Solid Oxide Fuel Cells (SOFC), Alkaline Fuel Cells (AFC), Phosphoric Acid Fuel Cells (PAFC), Molten Carbonate Fuel Cells (MCFC), Direct methanol Fuel Cells (DMFC) and Polymer Electrolyte Membrane Fuel Cells (PEMFC) [7].

In the last decade, most of research has been focused primarily on using PEMFCs also called Proton Exchange Membrane fuel cells for transportation purposes. They deliver high-power density and offer the advantages of low weight and volume, compared with other fuel cells [7].

This type of fuel cells was developed, for the first time, by General Electric in the USA in the 1960's to be incorporated by NASA on their first manned space vehicles [19].

The key part of a PEM fuel cell is the membrane electrode assembly (MEA) consisting in a polymer electrolyte with catalyst layer, in each side. Usually the catalyst layers are composed by platinum (or platinum-ruthenium) particles loaded into a carbon cloth support [19][20].

A typical PEMFC and the reactions [20] that occur to the electrodes are shown below:

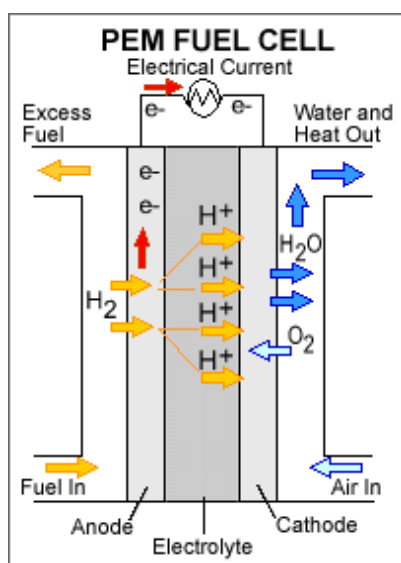
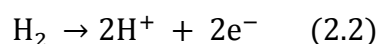


Figure 2 - Schematic view of a typical PEMFC [7].

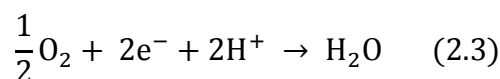
The main role of the membrane is to enable the transport of protons from the anode to the cathode; the most used membrane polymers have sulfonic groups which facilitate the proton transport. Different types of membrane have been tested and developed, being the most widely used the Nafion membrane, created by the DuPont Company [19][20].

The PEM fuel cells operate at relatively low temperatures, around 353 K. Low-temperature operation allows a quick start (less warm-up time) and results in simple system designs, resulting in enhanced durability [7].

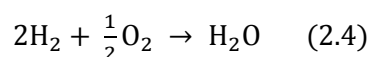
Anode reaction:



Cathode reaction:



Overall cell reaction:



2.4 Hydrogen gas solubility

The solubility of gases in a liquid medium is an important parameter required for the interpretation of rate data in gas-liquid, gas-liquid-liquid and gas-liquid-solid reactions [21].

The concentration of a gas in a liquid, up to a certain pressure range, is a linear function of the external gas partial pressure - Henry's law. According to Henry's law, the gas solubility in a liquid is proportional to the gas pressure on solution [22]:

$$y = k_H p_g \quad (2.5)$$

where y is the gas concentration in liquid, in the form of a molar ratio, p_g is the gas pressure and k_H is the Henry's constant.

Several methods have been used to measure the solubility of gases in liquids. Detailed reviews of experimental techniques and methods and their applications have been published in the literature [23-26].

There are two types of methods for the measurement of gases solubility in liquids: chemical methods and physical methods. The first one type depends on the chemical properties of the gas, so it is a specific method for a given gas. On the other hand, the physical methods do not depend on the gas properties and are based on the quantification of the amount of gas that solubilises in a liquid by measuring properties such as pressure, volume, temperature, composition and volume system [23].

Among the physical methods the most common are the saturation or the volumetric method, in which the degassed liquid is saturated with a volume of gas that can be determined at a given pressure and temperature [23].

There have been many designs of volumetric apparatus. The main differences between them involve: the pre-saturation of the gas in liquid's vapours; the method used to measure pressure and temperature; the promotion of a good gas-liquid contact; the method used to determine the volume of liquid and gas dissolved [23][24].

It is known that hydrogen gas is a strongly non polar compound, not soluble in water and in almost all the liquid solvents. Figure 3 shows the values of solubility in water for different gases at atmospheric pressure as a function of temperature. As can be seen, the hydrogen, at 25 °C, presents a solubility of 0.00155 gram of gas per kilogram of water.

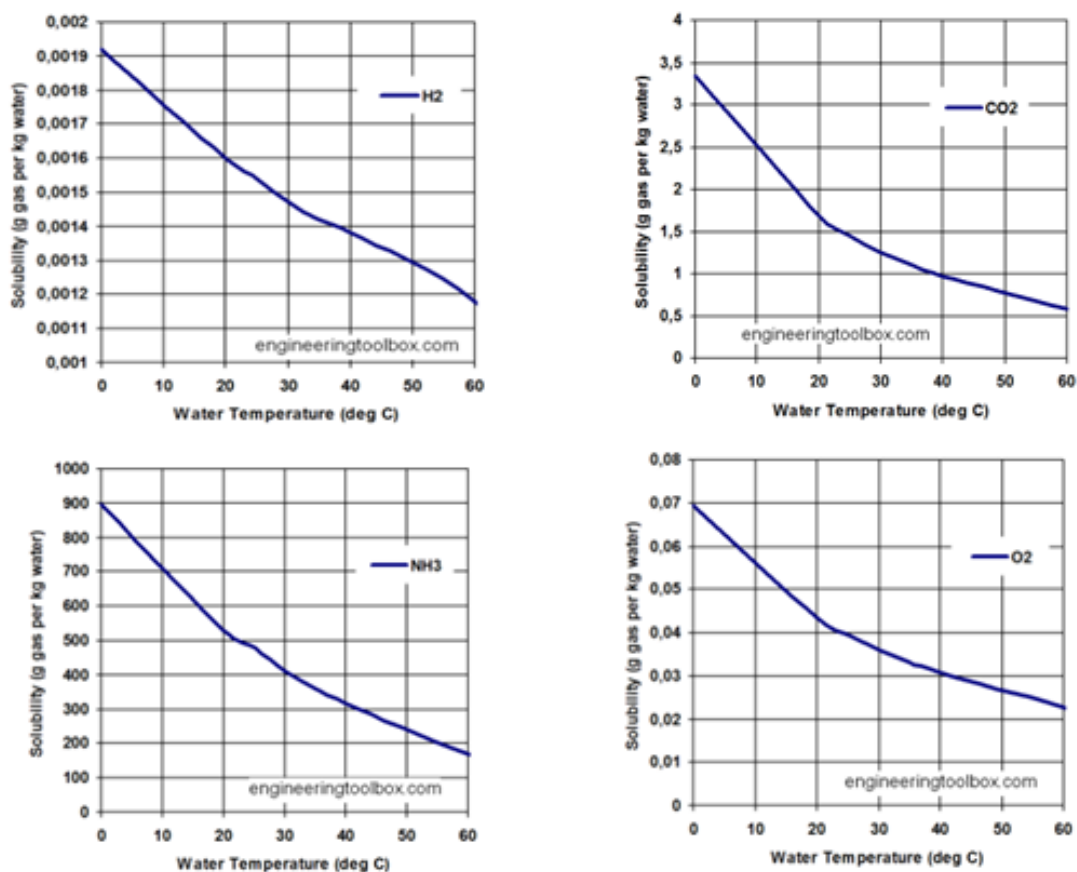


Figure 3 - Solubility of hydrogen, carbon dioxide, ammonia and oxygen in water [27].

Findlay and Shen [28], in 1912, studied the hydrogen solubility in pure water and in presence of colloids such as dextrin, gelatin, starch, ferric hydroxide and metallic silver suspension. The results obtained through this investigation were not very inspiring. As they reported, in presence of ferric hydroxide and in the metallic silver suspension, the solubility of hydrogen was not appreciably different from the one in pure water. For the other compounds tested, the solubility decreased with the increase of solution concentration. However, the solubility of hydrogen in these solutions was, with the possible exception of the solutions of gelatin, in accordance with Henry's law.

These results, about the influence of colloids on the solubility of gases in pure water, coupled with the possibility of enhancing their influence, when increasing the operating pressure according to Henry's law, were the main inspiration for the present work thesis, which is in line with the previous work of Ferreira et al. [2].

The authors tested an organic polymer based on cellulose: carboxymethyl cellulose (CMC). The sodium borohydride hydrolysis was carried out from stabilized reactant solutions in the presence of a reused Ni-Ru based catalyst. The obtained

results have shown that working at moderate pressures, up to 2.7 MPa, increases slightly the gas dissolution in the liquid phase, enhanced by the changing of the polarity of the remained solution. A value of 0.182 for dimensionless hydrogen solubility in the liquid phase with 0.25wt% of polymer was found, at 45 °C, based on Henry's law. Also it was shown that both hydrogen generation rates and yields and hydrogen storage capacities can be increased by adding small amounts of this organic polymer to the reactant solution [2].

Carboxymethyl cellulose is a derivative of cellulose, which is among the most important renewable resources in the world. It is commonly used in food science as a viscosity modifier. Carboxymethyl cellulose is water soluble with a degree of substitution of 0.4-1.2 in common applications. The average chain length and the degree of substitution are of great importance since it scripts the possible hydrophobic character of the polymer (affecting the number of non polar -CH₂-groups). Moreover, this polymer dissolves rapidly in cold water and its viscosity drops during heating, which in the presence of gas formation improves the gas volume yield by 'encouraging' gas bubble generation [2][29].

To continue this novel route of sodium borohydride hydrolysis, in order to produce and simultaneously store molecular hydrogen in the remaining liquid phase, the present work is focused on other based cellulose polymers, with less polar driven force: hydroxyethyl cellulose (HEC) and methyl cellulose (MC), respectively.

Hydroxyethyl cellulose with a molar substitution value greater than 1.6 is soluble in hot or cold water. HEC forms oil and grease resistant films that retain clarity over time. It is used as an adhesive in billboards, corrugated board, plywood, and wallpaper, and as a sizing and binding agent in paper products [29].

Methyl cellulose with a low degree of substitution (0.4-0.6) is soluble in dilute aqueous sodium hydroxide. As substitution is increased, the methyl cellulose becomes soluble in water (1.3-2.6), then in organic solvents (2.4-2.6). The most commonly used derivatives have a degree of substitution of 1.2-2.0, which results in cold-water solubility and solution stability for pH 2-12. Methyl cellulose is used for paper coating and sizing to impart grease resistance, in ceramics as a binder, as a no staining paste for wallpaper, and in adhesives for leather drying. An important fact is that upon heating, methyl cellulose thickens reversibly [29]. Figure 4 illustrates the chemical structure of the studied biopolymers.

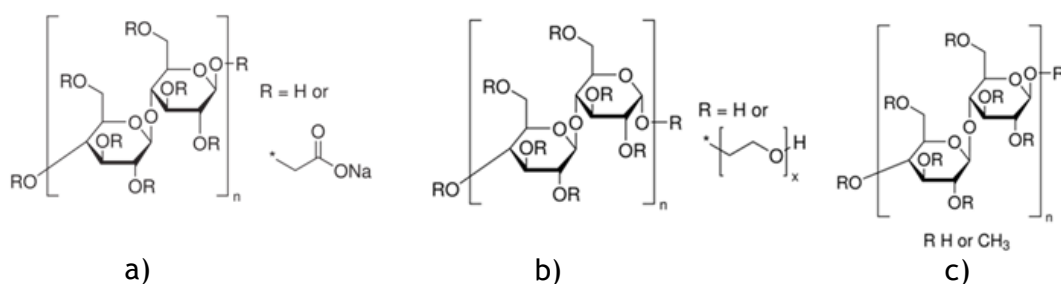


Figure 4 - Chemical structures: a) Carboxymethyl cellulose b) hydroxyethyl cellulose; c) methyl cellulose [48]

Other chemical compounds, such as cyclodextrins and ionic liquids, due to their particular properties have become interesting for different application fields, namely for hydrogen.

Cyclodextrins are a family of cyclic oligosaccharides formed by glucopyranose units linked by α -(1,4) bonds. They are also known as cycloamyloses, cyclomaltooses and Schardinger dextrins. These polymers were first discovered by Villiers in 1891 and are produced through the intramolecular transglycosylation reaction from degradation of starch by an enzyme named glucanotransferase (CGTase) [30][31]. The most common are α -, β -, and γ -Cyclodextrins, which are formed by six, seven, and eight glucose units, respectively [30].

The major interest in cyclodextrins lies in their capability to form inclusion complexes (host-guest complexes) with several compounds by a molecular complexation. Due to this ability, cyclodextrins can modify significantly the properties of the materials. They actually enhance the solubility of highly insoluble guests [30][31].

Because of the presence of a lipophilic cavity that provides a microenvironment into which appropriately sized non-polar moieties can enter to form reversible inclusion complexes [30].

In aqueous solution, water molecules from the cavity are displaced by more hydrophobic guest molecules present in the solution. A non polar-non polar association is formed as well as a more stable lower energy state [30]. No covalent bonds are broken or formed during formation of the complex. Complex formation is a dimensional fit between host cavity and guest molecule [30][31].

Figure 5 and table 1 show the chemical structure of the three types of cyclodextrins and some of their properties, respectively.

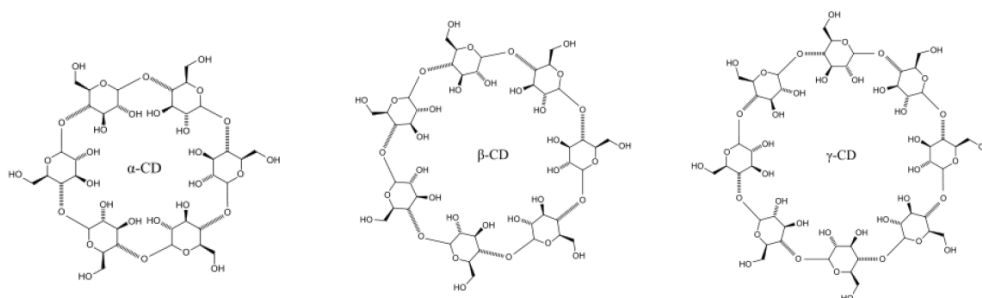


Figure 5 - Cyclodextrins chemical structures [32].

Table 1 - Cyclodextrins properties [30].

Property	α-Cyclodextrin	β-Cyclodextrin	γ-Cyclodextrin
Number of glucopyranose units	6	7	8
Molecular weight (g/mol)	972	1135	1297
Solubility in water at 25 °C (%,w/v)	14.5	1.85	23.2
Outer diameter (Å)	14.6	15.4	17.5
Cavity diameter (Å)	4.7-5.3	6.0-6.5	7.5-8.3
Height of torus (Å)	7.9	7.9	7.9
Cavity volume (Å ³)	174	262	427

Ionic liquids (ILs) are salts with organic ions that are liquids at room temperature. Their properties could be tailored for specific applications by adjusting the structure and species of cations and/or anions. In fact, the number of possible combinations of cations and anions is uncountable with vast and still unexplored possibilities [33].

The ionic liquids are of interest because they are considered environmentally friendly or green media due to their favourable properties such as chemical and thermal stability, negligible vapour pressure, non-flammability and high ionic conductivity [34]. Moreover, their ionic bonds induce a miscibility in a large concentration range with polar compounds, and the cations chains determine their solubility in less polar compounds [34].

Currently ILs are under intensive investigation as alternative solvents for biphasic catalysis and a number of reviews on this subject are available [35].

Catalytic applications involving gaseous substrates, in particular hydroformylation and hydrogenation, have been well developed. The solubility of

gases in ionic liquids is an important factor in catalytic reactions, where the gas is the substrate. It has been suggested that increased reaction rates, in biphasic hydrogenation reactions in ionic liquids, could be due to high solubility of hydrogen in the ionic liquid [35].

The most used techniques to measure the solubility of gases in ILs are the same to measure the solubility of gases in conventional liquids (for example the volumetric or saturation method). Due to ILs negligible vapour pressure it is also possible to determine the gas solubility through the methods used in solubility of gases in solids, such as gravimetric and oscillation method. Other methods such as spectroscopic and chromatographic methods have been occasionally used.

Table 2 shows the Henry's constant for the solubility of hydrogen in some of the most studied ionic liquids: 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf₂N]). Figure 6 puts in evidence their ions chemical structure.

Table 2 - Values of Henry's constant for the hydrogen solubility in ionic liquids.

Ionic Liquid	Henry's constant K _H / MPa	Temperature °C	Pressure MPa	Method	Authors
[bmim][PF ₆]	118	40	<9	Static	Kumelan et al. [36]
	104	60			
[hmim][Tf ₂ N]	86,3	20	<10	Isochoric saturation	Kumelan et al. [37]
[bmim][BF ₄]	203,6	25	<0,1		Jacquemin et al. [38]
	239,1	40			
[bmim][PF ₆]	244,5	20	<0,1	Jacquemin et al. [39]	
	187,8	45			

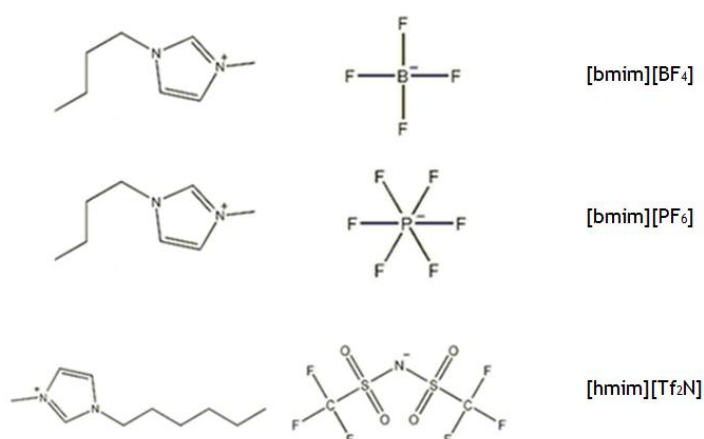


Figure 6 - Cations and anions chemical structures [40].

Taking into account the expected impact of polymers addition on sodium borohydride hydrolysis, it is expected that the ionic liquids listed in Table 2, when added to the reactant solution also enhance the solubilisation of hydrogen in the liquid phase. It is suggested that the most electronegative elements such as fluorine and nitrogen, present in the ILs chemical structures may establish chemical bonds with the produced hydrogen.

Some ILs have been already investigated and tested as solvents in reactions of ammonia borane dehydrogenation and as catalysts in the sodium borohydride hydrolysis for hydrogen production [41][34].

Himmelberger et al. [41], reported that imidazolium based ionic liquids tested provide advantageous media for ammonia borane dehydrogenation in which both the extent and rate of hydrogen release are significantly increased. Their low solvent volatility, the high extent of their hydrogen release, the tunability of both their hydrogen materials-weight-percent and release rates, and their product control attained by either trapping or suppressing unwanted volatile side products, make ammonia borane/ionic liquid based systems appealing candidates for hydrogen storage applications.

On the other hand, Chinnappan et al. [34], demonstrated that 1,1'-hexane-1,6-diylbis (3-methylpyridinium) tetrachloronickelate (II) is an efficient catalyst for the hydrogen generation from sodium borohydride showed by its excellent catalytic activity results.

To conclude the above considerations, and bear in mind the particular properties of cyclodextrins and some ILs, it can be stated that those compounds have strong capabilities of contributing to hydrogen storage in post-reaction solutions by solubility effects at moderate pressures (up to 2.5 MPa).

3 Experimental Procedure and Technical Description

The materials, experimental setup and experimental procedure used in the kinetic study of the catalytic hydrolysis of sodium borohydride solutions are thoroughly described in this section. The techniques used for the analysis of the reaction by-products are also presented.

3.1 Reaction kinetics study

The kinetics reaction study involved a set of experimental work allowing the analysis of the effect of biopolymer (CMC, HEC and MC) concentration, reaction temperature and catalyst activity, on hydrogen generation rates, yields, the reaction induction time and on the gravimetric and volumetric hydrogen storage capacities.

3.1.1 Materials

The materials used for the preparation of the reactant solutions are mentioned below:

- Sodium borohydride white powder was provided by Panreac (123314.1608) and stored in a dessicator until use. In all the experiments it was used dissolved in water forming aqueous solutions.

- Sodium hydroxide pellets (98% purity) was supplied by EKA (No.: 1310.73.2) and it was used as a hydrolysis inhibitor.

- Methyl-cellulose microgranular powder was provided by SIGMA-ALDRICH (CAS 9000-11-7).

- Hydroxyethyl cellulose and Methyl cellulose powders were already available in the laboratory.

- Nickel based bimetallic unsupported catalyst, in the form of a finely divided black powder was synthesized at LNEG - Laboratório Nacional de Energia e Geologia, Fuel Cells and Hydrogen Unit, Lisbon - Portugal, in November 2012.

3.1.2 Experimental setup

The experimental setup for the reaction kinetics study comprised a batch reactor where hydrogen was produced, a demonstration prototype with a PEM fuel cell and a data acquisition system.

The batch reactor made of stainless steel AISI 316L, with wall width equal to 10 mm, has a conical bottom geometry with an internal volume of 369 cm³. The reactor bottom configuration - conical - enables non dispersible effects between the contacting powdered catalyst and the injected reactant solution [3].

The reactor design allows the possibility of following the reaction temperature at two different locations inside it by using two thermocouples. One of the thermocouples is used to monitor the increase of temperature in the core of the catalyzed exothermic hydrolysis reaction, and the second one, measures the temperature of molecular hydrogen in the free volume of the container opened for the generated gas. The temperature of the reactor medium and the rate of hydrogen generation were recorded with a data acquisition system using Labview software. The gas pressure inside the reactor was followed with an adequate pressure transducer calibrated from 0-40 bar gauge and also by a Bourdon manometer (from 0-60 bar gauge), until attaining a constant pressure inside the reactor.

The hydrogen generated was supplied to a PEMFC single cell placed inside of a didactic demonstration prototype named "MicroBoro Bus", which is a bus like shaped mobile platform [42].

The developed low power PEM fuel cell uses an air breathing cathode and humidified hydrogen produced by the borohydride reactor. Natural convection to air feed the cathode is used when the platform is located on a stand and the energy conversion required is just the one needed to make the wheels of the platform bus turn [3][42]. In figures 7 and 8 it is possible to see a photograph of the experimental rig as well as the reactor bottom configuration.

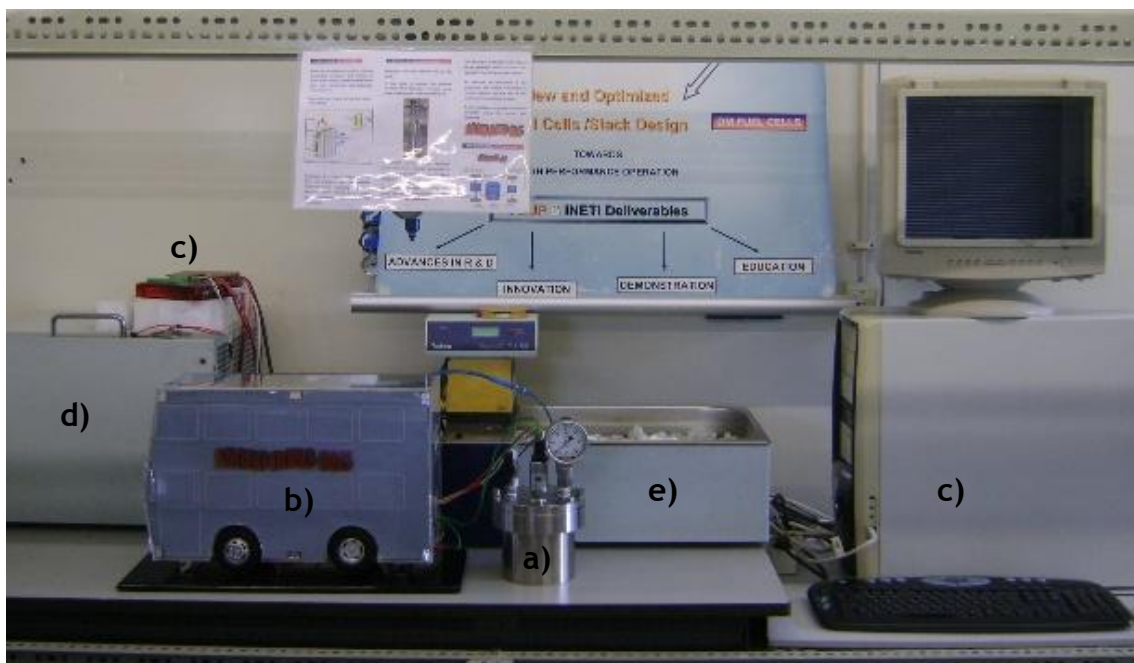


Figure 7 -Photograph of the experimental rig: a) batch reactor; b) “MicroBoro Bus” with a PEM fuel cell inside; c) data acquisition system; d) refrigeration unit; e) thermostatic bath.

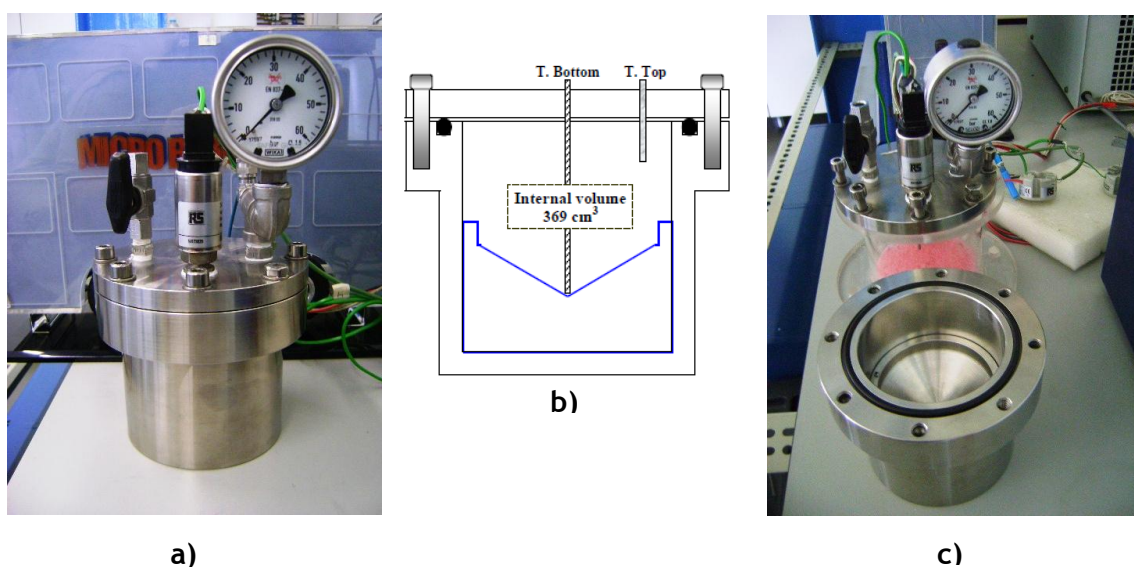


Figure 8 - Reactor batch design: a) external view of the batch reactor closed; b) schematic view of the batch reactor inside with mention of the internal available free volume [3]; c) view of the batch reactor inside.

3.1.3 Experimental procedure

Two different types of reactant solutions were prepared to study the kinetics of catalysed sodium borohydride hydrolysis for simultaneous hydrogen generation and storage: classic solutions of sodium borohydride and Less Polar Organic Polymeric Solutions. The first solutions were prepared by adding the appropriate amount of sodium borohydride to a certain volume of aqueous solution of the inhibitor sodium hydroxide. The second type of solutions was prepared by adding the appropriate amount of sodium borohydride to a certain volume of aqueous solution of the inhibitor sodium hydroxide plus small portions of cellulose based polymers.

In order to achieve a high energy density and pressures up 2.5 MPa, which would be advantageous for hydrogen storage in the liquid phase by solubility effects, a sodium borohydride constant concentration of 15wt% by weight was found suitable for all the experiments and all of them occurred in excess of water as required. This value was chosen based on previous studies briefly referred in the Chapter 2.

The concentration of sodium hydroxide and mass ratio catalyst/sodium borohydride (g/g) were also held constant. In all the experiments, the selected values of these two parameters were defined after the performance of preliminary studies (section 3.1.4).

The preparation of test solutions involved a continuous magnetic stirring. Firstly, sodium hydroxide pellets were added to the distilled water. After complete dissolution, the specific biopolymer was added and lastly, sodium borohydride was completely dissolved in the solution. Due to the fact that methyl cellulose polymer is not soluble in water at room temperature, special care was given on its dissolution. A dissolving method of Sigma-Aldrich product information sheet of methyl cellulose was followed [43]:

- Heat about 1/3 of the required volume of water to at least 80 °C;
- Add the methyl cellulose powder to the hot water with agitation;
- Agitate the mixture until the particles are thoroughly wetted and evenly dispersed;
- For complete solubilisation, the remainder of the water is then added as cold water or ice to lower the temperature of the dispersion. Solution should be cooled to 0-5 °C for 20-40 minutes;
- Continuous agitation for at least 30 minutes after the proper temperature is reached [43].

For each experiment, a proper quantity of catalyst measured in an analytical balance, was previously stored in the bottom of the reactor (approximately 0.6 g).

After perfectly sealing the batch reactor, 20 cm³ of reactant solution were rapidly injected into the reactor by using a syringe with a long needle to guarantee that the reactant solution is delivered very close to the catalyst powder.

All the experiments were done with one single injection of reactant solution and with reaction temperature control, by using a thermostatic bath, coupled with a refrigeration unit.

After each reaction, the remaining solution in the reactor was treated in two centrifuges, firstly at 4000 rpm and then after at 14000 rpm, for the complete separation of the liquid by-product from the solid Ni-Ru based catalyst. The by-product was collected for posterior hydrogen solubility tests and X-Ray Diffraction studies.

The catalyst, after each experiment, was recovered for reutilization. It was washed four times with distilled water, before the complete physical separation from distilled water by gravitational sedimentation. Thereafter it was dried in an oven at 80 °C for one hour.

The calculus involved in the determination of hydrogen rate, yield and gravimetric and volumetric hydrogen density for each reaction is described in the appendix B.

3.1.4 Preliminary studies

Preliminary studies were carried out to select the most appropriate sodium hydroxide concentration and a suitable mass ratio catalyst/sodium borohydride.

Firstly, for the selection of the most appropriate inhibitor concentration, two classic hydrolysis with 15wt% of sodium borohydride, were performed at room temperature, for two different sodium hydroxide concentrations, 3wt% and 7wt%. These two values of concentration were chosen according to the previous studies mentioned in Chapter 2.

For each reaction, 20 cm³ of reactant solution was injected into the batch reactor and a ratio catalyst/sodium borohydride of 0,2 g/g was used. Based on the results obtained, presented in Appendix C, the value of 7wt% for the inhibitor concentration was chosen and was used in all the experiments described in the following sections.

The most suitable ratio catalyst/sodium borohydride was selected through the execution of three classic hydrolysis reactions, with different mass ratio catalyst/sodium borohydride: 0.1 g/g, 0.2 g/g and 0.4 g/g. In this preliminary study, 5 cm³ of reactant solution, with 10wt% of sodium borohydride and 7wt% of inhibitor,

was injected into the batch reactor (instead of 20 cm³ of a reactant solution of 15wt% sodium borohydride, justified by economical purposes). The reactions were performed at 45 °C which is the optimal operation temperature for the synthesis of the Ni-Ru catalyst. A mass ratio catalyst/sodium borohydride of 0.2 g/g was found suitable (Appendix C) and was used in all the experimental tests described in the following sections.

3.1.5 Effect of biopolymers concentration and reaction temperature

The effect of small additions of polymers on hydrogen generation rates and yields were investigated by performing the following experiments:

- Classic hydrolysis: 15wt% NaBH₄, 7wt% NaOH, 78wt% H₂O;
- Less Polar Organic Polymeric Solutions Hydrolysis: 15wt% NaBH₄, 7wt% NaOH, with the range of polymer concentrations shown in the Table 3, and remaining percentage of H₂O.

Table 3 - Polymers concentration (weight percent)

	HEC	CMC	MC
Weight		0.25	
percent (wt %)		0.05	

To explore the effect of reaction the temperature on hydrogen generation rate and yields, the experiments described above, were carried out at two different temperatures: 25 °C and 45 °C. The first one, close to room temperature, is the ideal temperature for the sodium borohydride hydrolysis to become a real option for producing hydrogen for PEMFC. The second one is referred as the optimal operation temperature for the synthesis of the Ni-Ru catalyst.

In these experiments the Ni-Ru based powdered catalyst was reused between 14 and 35 times.

3.2 Catalyst activity study

The catalyst activity was studied by determination of its activation energy, performing a set of experiments for constant concentration of sodium hydroxide (7wt%) and sodium borohydride (15wt%), at different five temperatures: 15°C, 25°C, 35°C, 45°C and 55°C. These experiments were performed following the same procedure as presented in section 3.1.3, where 5 cm³ of reactant solution were injected into the batch reactor (instead of 20 cm³, justified by economical purposes). With the results obtained for each temperature, the activation energy was estimated using the Arrhenius plot (ln of reaction rate as function of ln(1/T)).

3.3 Preliminary hydrogen solubility study

Bearing in mind that the polymers addition to the reactant solution makes it a less Polar Organic Polymeric Solution (LPOPS) and causes a change in the overall conductivity of the remaining solution inside the reactor, a preliminary hydrogen solubility study was performed by the measurement of conductivity and pH of the reactants solutions and also of the correspondent by-products.

The pH and the electrolytic conductivity of some solutions were measured using a pH meter and a conductivity meter. The pH was measured at 20°C and the conductivity at 25°C. All the solutions were diluted with distilled water, in a proportion 1:5, for the conductivity measurements due to the detection limit of the conductivity meter.

3.4 Reaction products analysis

Through the different performed hydrolysis reactions, various by-products were produced along with the hydrogen gas. These by-products are sodium borates. A small volume (around 1ml) of each aqueous by-product solution was dried by slow evaporation of water content at environmental uncontrolled conditions. Hence

suitable crystals were obtained and subsequently analyzed using the X-Ray Diffraction technique (XRD).

The X-ray diffraction is a non-destructive analytical technique, which reveals information about the crystallographic structure, chemical composition and physical properties of materials. The diffraction data was collected at 293 K with a Gemini PX Ultra equipped with CuK_α radiation ($\lambda=1.54184\text{\AA}$) (facility of IBMC - Instituto de Biologia Molecular e Celular, University of Porto, Portugal).

4 Results and Discussion

This chapter is focused on the presentation of the results obtained in the performed hydrolysis experiments, regarding the kinetics and hydrogen solubility studies. The effect of addition of polymers, temperature and catalyst activity on the hydrogen generation rates and yields are investigated and discussed. The analysis of the reaction by-products is also presented. The results enable the suggestion of different capability of several polymers to store hydrogen in the liquid by-products solution.

4.1 Reaction kinetics study

4.1.1 Effect of biopolymers concentration and reaction temperature

The effect of 0.05wt% and 0.25wt% of biopolymers concentrations in the reactant solutions, at two different temperatures is presented in Figures 9 to 12. The course of hydrogen generation in terms of hydrogen pressure as a function of time is shown up to 400 seconds. Results obtained in classic hydrolysis are also shown as well as the theoretical pressure predicted by the ideal gas law. The Appendix D presents the complete evolution of hydrogen generation and the temperatures profiles. Table 4 shows the values of yield, lag time, reaction rates and gravimetric and volumetric hydrogen densities obtained. The volume of hydrogen produced is also presented.

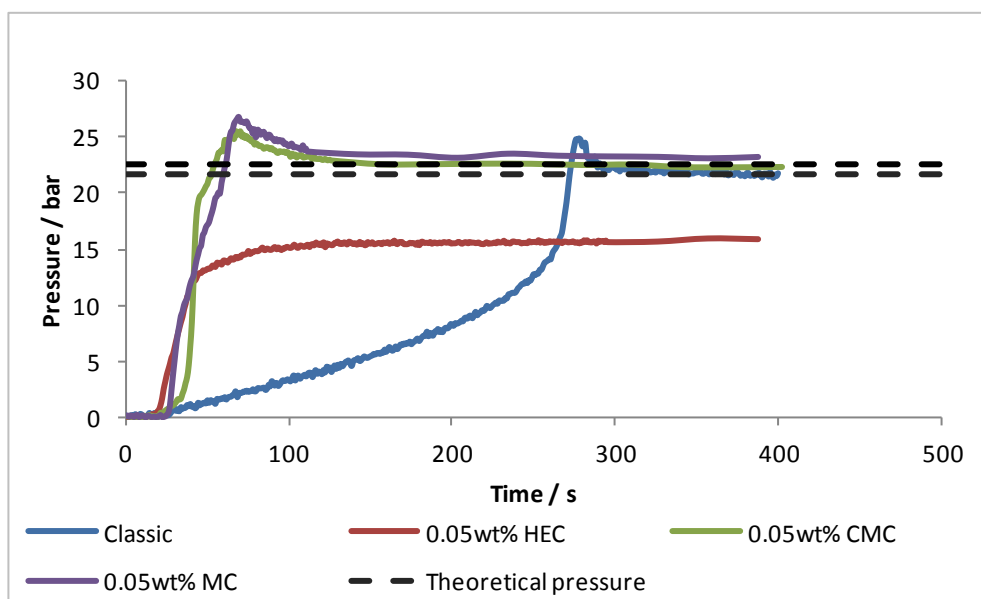


Figure 9 - Effect of 0.05wt% polymers concentration on the hydrogen generation rate via hydrolysis of sodium borohydride (20cm^3 of reactant solution with 15wt% NaBH_4 and 7wt% NaOH) at 25°C . The catalyst, in the proportion Ni-Ru catalyst/ NaBH_4 : 0.2 g/g was reused between 11 and 34 times.

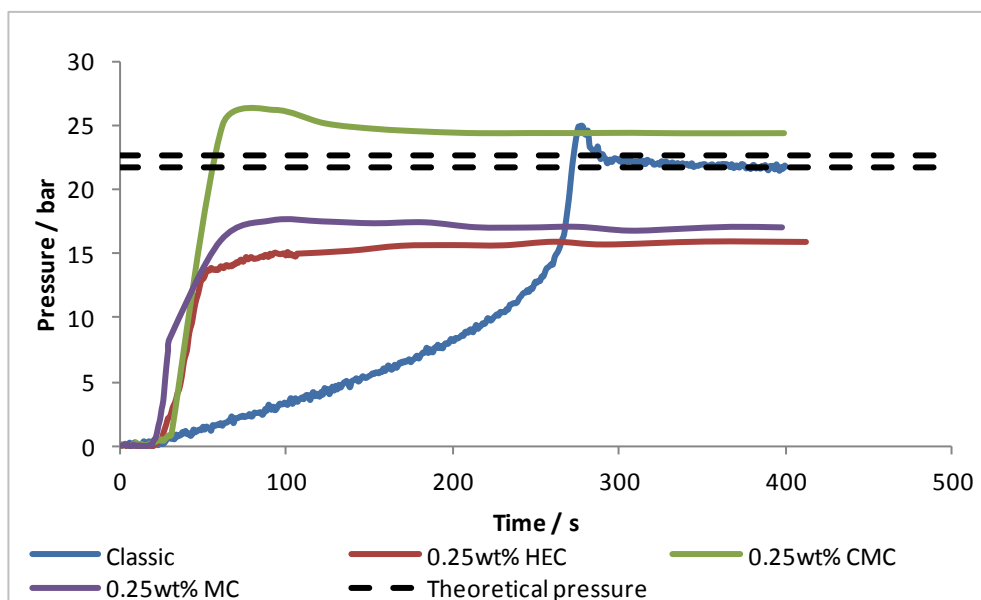


Figure 10 - Effect of 0.25wt% polymers concentration on the hydrogen generation rate via hydrolysis of sodium borohydride (20cm^3 of reactant solution with 15wt% NaBH_4 and 7wt% NaOH) at 25°C . The catalyst, in the proportion Ni-Ru catalyst/ NaBH_4 : 0.2 g/g was reused between 11 and 21 times.

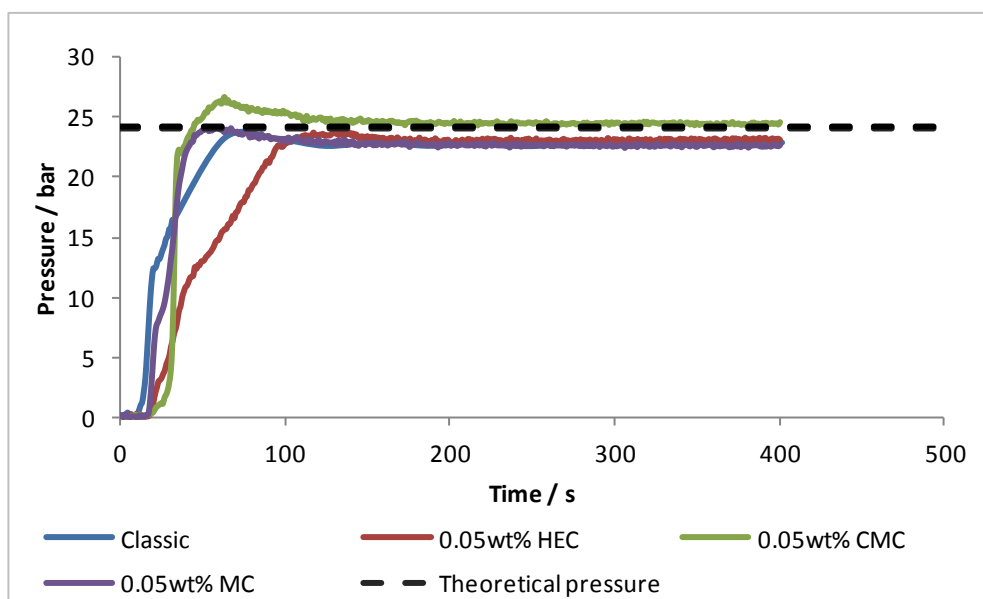


Figure 11 - Effect of 0.05wt% polymers concentration on the hydrogen generation rate via hydrolysis of sodium borohydride (20cm^3 of reactant solution with 15wt% NaBH_4 and 7wt% NaOH) at 45°C . The catalyst, in the proportion Ni-Ru catalyst/ NaBH_4 : 0.2 g/g was reused between 26 and 35 times.

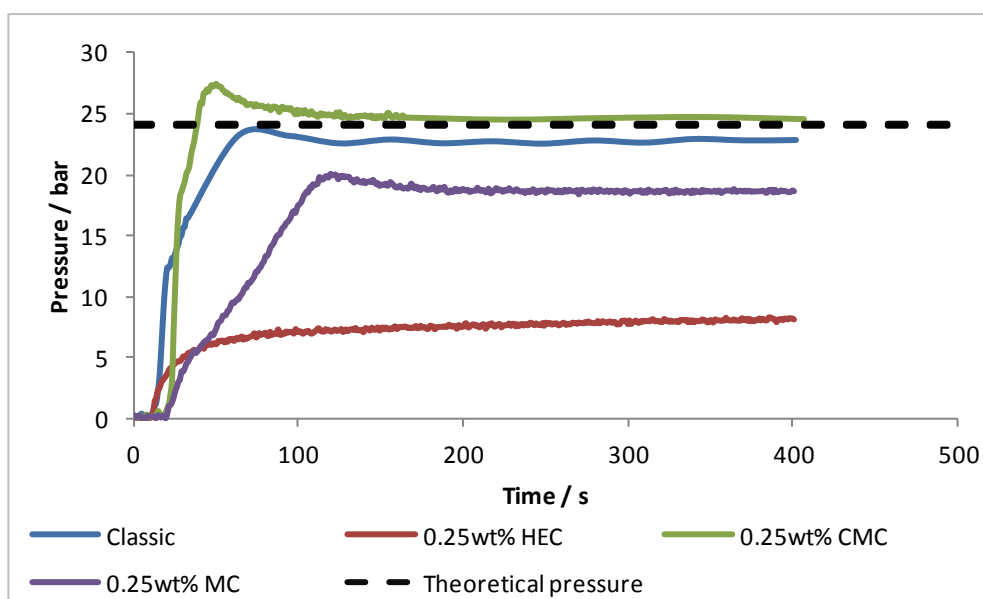


Figure 12 - Effect of 0.25wt% polymers concentration on the hydrogen generation rate via hydrolysis of sodium borohydride (20cm^3 of reactant solution with 15wt% NaBH_4 and 7wt% NaOH) at 45°C . The catalyst, in the proportion Ni-Ru catalyst/ NaBH_4 : 0.2 g/g was reused between 27 and 35 times.

Table 4 - Values of yield, reaction rate, lag time and gravimetric and volumetric densities obtained.

	Yield up to 400 s (%)	dP/dt slope (bar/s)	Hydrogen rate (L(H ₂) min ⁻¹ gcat ⁻¹)	Lag time (s)	Gravimetric H ₂ density (wt%)	Volumetric H ₂ density (kg H ₂ /m ³)	Volume (H ₂) at STP (L)	
25 °C	Classic	100	0.05 1.02	1.6 35	29	3.0	33	7.58
	0.05wt%							
	HEC	69	0,55	20	21	2.8	31	7.48
	CMC	100	3.17	111	25	3.0	33	7.83
	MC	100	0.51	18	25	3.1	34	8.14
	0.25wt%							
	HEC	71	0.62	22	25	3.1	34	8.15
	CMC	>100	0.76	30	25	3.2	35	8.45
	MC	76	1.12	39	22	3.0	33	7.97
	45 °C	Classic	94	2.02 0.22	66 7.5	12	3.0	33
0.05wt%								
HEC		96	0.48 0.21	16 7.0	19	3.0	33	7.98
CMC		>100	6.21	203	22	3.1	34	8.07
MC		95	1.14	37	19	2.8	31	7.48
0.25wt%								
HEC		33	-----	-----	13	-----	-----	-----
CMC		>100	3.57	117	21	3.1	34	8.10
MC		79	0.19	6.3	22	2.5	27	6.52

The plots from Figures 9 - 12 reveal quite interesting results. From Figure 9, it is evident that at a temperature close to room temperature, a small addition of the three polymers (0.05%) has a significant impact on the reaction kinetics. The abnormal two stage hydrogen evolution of the classic hydrolysis disappears and a very rapid hydrogen generation leads to a complete hydrolysis for the CMC and MC cases at around half of the time. This result is of primordial importance bearing in mind hydrogen-PEMFC portable applications. For the HEC curve, a strong impact with a high H₂ generation rate occurs but is interrupted before reaching the theoretical pressure plateau. The values of the gas generation rates displayed in Table 4 further confirm these findings. For the curves plotted in Figure 10, corresponding to a higher polymer concentration (0.25%) the same effect is observed but now both the MC and HEC curves while showing initially high generation rates, exhibit a very slow hydrogen

evolution. For this polymer concentration, the CMC polymer enhances strongly the reaction rate reaching a yield above 100%. It seems that for this condition the catalyst is active enough to break the CH bonds in polymers chains, which allows the generation of additional hydrogen gas.

At 45°C, the results are surprising. The kinetics of the classic hydrolysis is, as expected, enhanced by the higher temperature, but the evolution curve still has two rate stages. The experiments with the smaller concentration of polymers (Figure 11) show a positive impact of the addition of polymer in the generation rates. One should note the remarkable value of 203 L(H₂) min⁻¹ gcat⁻¹ for the CMC case. The curves obtained with the higher polymer concentration show a poorer performance namely for the MC and HEC cases showing a very slow gas evolution after an initial relatively high generation rate. The CMC polymer seems to be the better choice for a higher generation rate and a rapid complete hydrolysis but, as is evident when comparing the curves in Figures 9 to 12, a very small addition of this polymer at room temperature is sufficient to achieve good hydrolysis performances.

The hydrogen generation with 0.25wt% of HEC polymer is very slow: at 25°C the gas pressure attained the theoretical predicted value after only approximately 8 hours (30000 seconds), (Figure D.4, Appendix D); at 45°C, the final plateau was reached only after 50 hours (180000 seconds), (Figure D.6, Appendix D). The remaining solution, inside the reactor, after these reactions, has the appearance shown in Figures 13 and 14:



Figure 13 - Remaining solution after hydrolysis reaction with 0.25wt% HEC polymer (15wt% NaBH₄ and 7wt% NaOH) at 25°C. The catalyst, in the proportion Ni-Ru catalyst/NaBH₄: 0.2 g/g was reused 15 times.



Figure 14 - Remaining solution after hydrolysis reaction with 0.25wt% HEC polymer (15wt% NaBH₄ and 7wt% NaOH) at 45°C. The catalyst, in the proportion Ni-Ru catalyst/NaBH₄: 0.2 g/g was reused 27 times.

It seems that the HEC polymer addition to the reactant solution in a concentration of 0.25wt% forms a “sponge” that may act as a barrier for the hydrogen liberation from solution. On the other hand, the reaction with 0.05wt% of HEC at 45°C presents a better performance than the reaction at 25°C (Figures D.3 and D.5 in Appendix D). Apparently, the increase of temperature for lower concentrations of HEC polymers enhances the reaction performance.

The reaction lag time, which is defined as the time required to observe the hydrogen formation, is similar for all the performed experiments. This means that the catalyst reutilization does not affect the lag time (it should be noted that the catalyst was reused among each experiment, between eleven and thirty five times).

Curiously, the reactions with HEC polymers present the lower lag time values. It seems that the addition of this polymer is favourable for the beginning of reaction. However, as referred above, probably while the reactants are consumed the solution forms a sponge that slows the hydrogen production rate.

The gravimetric and volumetric hydrogen densities obtained in the present work are much lower than the FreedomCAR requirements for hydrogen storage systems established by the US Department of Energy (DOE) - see Table 5, next presented:

Table 5 - The gravimetric and volumetric hydrogen densities values publish by US Department Of Energy (DOE) and the values obtained in the present work.

	The FreedomCAR targets			Present work
	2007	2010	2015	
Gravimetric H ₂ density (wt%)	4.5	6.0	9.0	2.5-3.2
Volumetric H ₂ density (kg H ₂ /m ³)	36	45	81	27-35

However these specifications are based on system mass and volume, i.e., not only the storage material itself but also the reactors, tanks, valves, and all auxiliary equipment (which usually are call *hardware*) and the predicted values for gravimetric hydrogen density and volumetric hydrogen density achieved in the present work are based only on the storage *material* itself. The Appendix B presents the calculus involved in the determination of gravimetric and volumetric hydrogen densities.

Table 6 shows the gravimetric and volumetric hydrogen densities and reaction rate obtained in the hydrolysis with addition of 0.25wt% and 0.05wt% CMC polymer performed in the present work and the values published by Ferreira et al. [2].

Table 6 - Comparison between the results obtained from the hydrolysis with CMC addition in the work published by Ferreira et al. [2] and in the present work.

	Ferreira et al.	Present work	
NaBH ₄ (wt%)	10	15	
NaOH (wt%)		7	
CMC polymer (wt%)	0.25	0.25	0.05
Temperature (°C)		45	
Catalyst reutilization	280	30	28
mass ratio catalyst/sodium borohydride (g/g)	0.25	0.20	
Hydration factor (x)	16	10	
Gravimetric H ₂ density (wt%)	2.0	3.1	
Volumetric H ₂ density (kg H ₂ /m ³)	22	34	
dP/dt slope (bar/s)	0.11	3.57	6.21
Hydrogen rate (L(H ₂) min ⁻¹ gcat ⁻¹)	2.34	117	203

As can be seen in the Table 6, the results obtained for the hydrolysis carried out in the present work are much higher than the values published by Ferreira et al. [2]. However, it is important to note that although the catalyst used in both works has the same chemical properties (Ni-Ru), the number of reutilizations is much different, which has an important role in the performance of the hydrolysis. Also the sodium borohydride concentration presents a great contribution. In fact the increase of its concentration value enhanced the hydrolysis reaction hydrodynamics as stated in Chapter 2.

On the other hand, the gravimetric and volumetric energy densities achievable from hydrolysis of chemical hydrides depend in large measure on the amount of water required for the process. Experimental studies revealed that if the excess hydration factor (x) is less than 2 ($x < 2$), unreacted hydride remains in solution, but if $x > 2$ there is enough water for complete reaction and hydration of the borate [3]. However, chemical hydrides have the potential to meet the hydrogen storage targets only if the water consumption is minimized. In fact, the reduction of the excess hydration factor (x) from 16 to 10 leads to an increase of gravimetric and volumetric densities, as can be checked in Table 6.

The Table A.1 (Appendix A) shows a review of Ruthenium based catalyst for sodium borohydride hydrolysis since the year 2000. Comparing the values of hydrogen rate obtained in the present work with other values published elsewhere, it is possible to say that, in general, Ni-Ru based catalyst presents a great performance. All the present values of hydrogen rate ($L(H_2) \text{ min}^{-1} \text{ gcat}^{-1}$) are higher than the published by the authors referred in the Table A.1. However it is worth to mention that the experimental conditions are not the same.

4.2 Catalytic activity study

A set of classic hydrolysis experiments was performed, at different temperatures, using fixed concentrations of sodium borohydride and sodium hydroxide as well as a constant ratio catalyst/sodium borohydride (15wt%, 7wt% and 0.2 g/g). Those experiments allowed the study of the Ni-Ru catalyst activity by the determination of its activation energy.

Figure 15 shows the rate of hydrogen generation, in terms of hydrogen pressure as a function of time, for a range temperature between 15°C and 65°C.

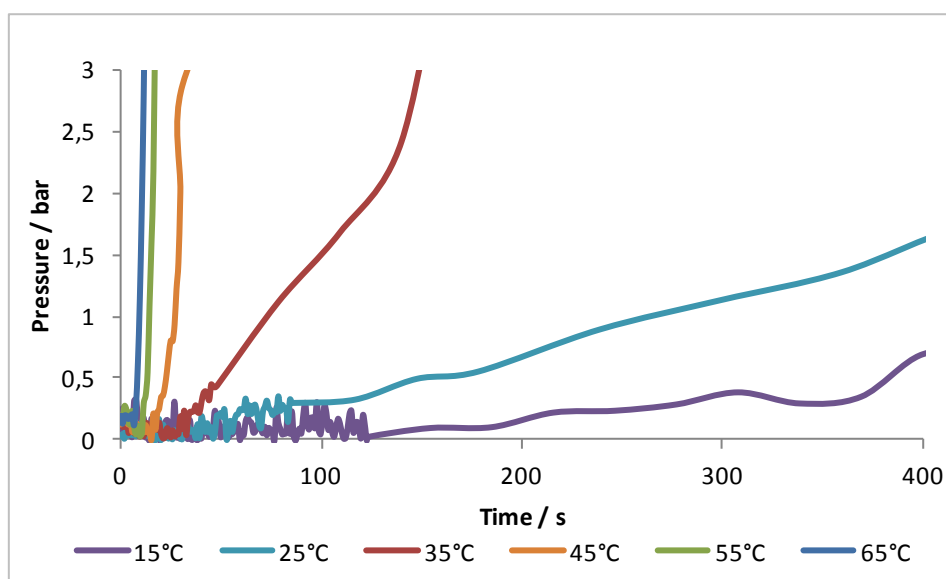


Figure 15 - Hydrogen generation rate as a function of time for catalyzed hydrolysis of sodium borohydride (5cm^3 of reactant solution with 15wt% NaBH_4 and 7wt% NaOH) at different temperatures. The catalyst, in the proportion Ni-Ru catalyst/ NaBH_4 : 0.2 g/g was reused between 38 and 43 times.

In Figure 15, it is possible to verify the increasing slope values on the linear region of the plots, for increasing values of the reaction temperature. In fact the reaction rate is strongly influenced by the reaction temperature.

During the course of hydrolysis reaction, the reaction rate remains approximately constant while sodium borohydride and water are consumed. The reaction rate follows a linear variation with time until the pressure plateau is reached, indicating the end of reaction. These results allow to confirm that the studied sodium borohydride hydrolysis presents a zero-order kinetics related to the temperature as stated by Liu et al. [12].

In order to estimate the catalyst activation energy of the used Ni-Ru catalyst, the results were represented in an Arrhenius plot, as shown in Figure 16. An activation energy of 104 kJ/mol was determined by the slope of Arrhenius plot.

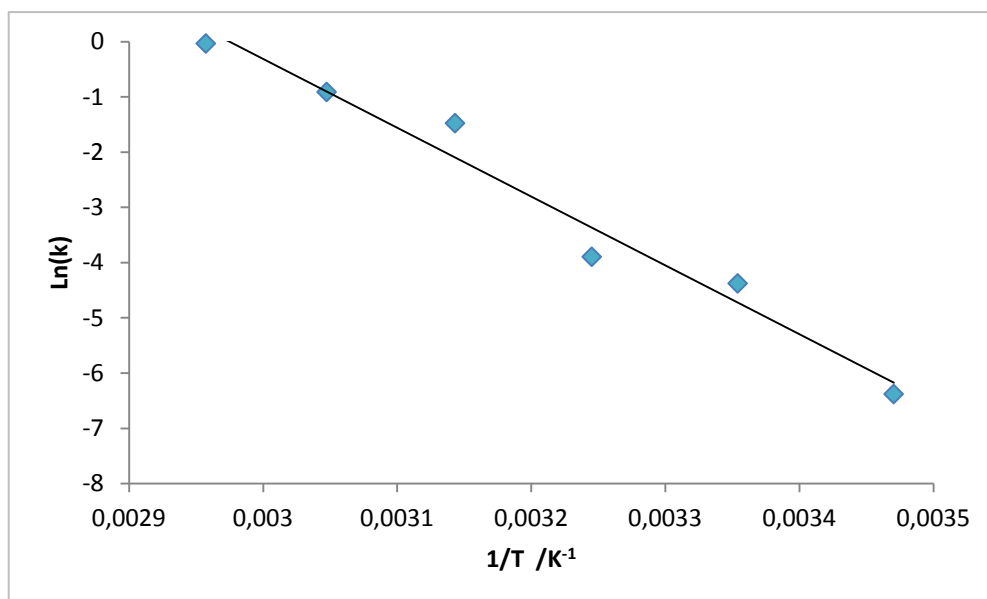


Figure 16 - Arrhenius plot obtained from the kinetic data of hydrolysis reaction performed at temperatures from 15 °C to 65 °C.

Regarding to the information about the optimal sodium borohydride hydrolysis operation temperature for the used Ni-Ru based catalyst, which is 45 °C and the highest slope value for 45 °C, it was also determined the catalyst activation energy for the temperature range between 45 °C and 65 °C. In fact, for this latter temperatures interval, the catalyst presents an activation energy of 65 kJ/mol, which is considerable lower than the determined for all the studied temperature range, patent in Figure 16.

The Table 7 shows a comparison between the activation energy value obtained in the present work thesis and the values available in the open literature for ruthenium based catalyst.

Table 7 - Comparison of the activation energy between the catalyst used in the present work with data published on literature.

Authors /Year	Catalyst	Temperature °C	Energy activation (kJ/mol)
Amendola et al. 2000	Ru/Resin	25-55	47
	Ru/IRA400	0-40	56
Shang et al. / 2006	Ru/C	26-60	37
This work	Ni-Ru	15-65	104
This work	Ni-Ru	45-65	65

4.3 Preliminary Hydrogen solubility study

The polymers addition to the reactant solution makes it a less Polar Organic Polymeric Solution (IPOPS) and causes a change in the overall conductivity of the remaining solution inside the reactor. In the Table 8, the pH and conductivity values for all the solutions tested, measured before and after the reaction completion are listed.

Table 8 - Values of pH and conductivity of the reactant solutions before and after reaction completion

	Before reaction		After reaction	
	pH	Conductivity (mS/cm)	pH	Conductivity (mS/cm)
Classic Hydrolysis 45 °C	11.37	96.8	11.88	86.1
0.05wt% HEC 45 °C	11.63	117.5	11.73	54.9
0.25wt% HEC 25 °C	11.63	124.8	11.58	85.2
0.05wt% CMC 45 °C	11.47	145.1	11.67	53.2
0.25wt% CMC 45 °C	11.45	-----	11.60	112.4
0.05wt% MC 45 °C	11.58	109.1	11.71	105.9
0.25wt% MC 25 °C	11.75	-----	-----	96.4

It is well known that the conductivity of an aqueous solution measures its ability to conduct an electric current and is highly dependent on the concentration of dissolved salts. As can be seen from the values conductivity displayed, the use of the small addition of only 0.05 wt% of HEC and CMC at the higher temperature reveals a strong decrease on the conductivity after reaction making these two polymers as good candidates for the storage of H₂ (a non polar molecule) in the liquid phase. The

presence of the polymers probably changes the polarity of the final solution due to the presence of the C-H groups.

In a very near future and after solving some experimental difficulties, solubility tests will be performed, in which the remaining solutions after sodium borohydride hydrolysis will contact with pure hydrogen, pressurized at different pressures, up to 2.5 MPa. This study will allow to estimate the amount of hydrogen gas that solubilises in each solution and to compare the capability of the post-reactant solutions to store hydrogen in the liquid phase.

From the experiments reported and recalling the reaction yields showed in Table 4 and the complete generation curves presented in Appendix D, the following remaining solutions should be also tested: at 25 °C HEC 0.05wt% and MC 0.25wt%; at 45 °C HEC 0.25wt% and MC 0.25wt%.

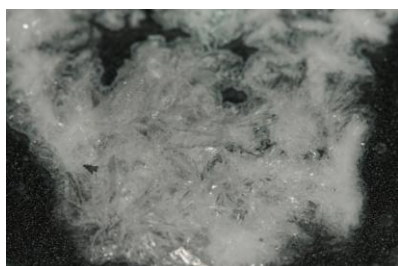
It should be noted that in these experiments the gas generation was very slow after an initial rapid generation rate, suggesting that the H₂ formed and dissolved in the solution was slowly released.

4.4 Reaction products analysis

The by-products crystals of all the reactions performed at 25°C were obtained by slow evaporation of a water solution at environmental conditions in the laboratory. The crystals (pictures shown in Figure 17) were analyzed by X-Ray Diffractometry.



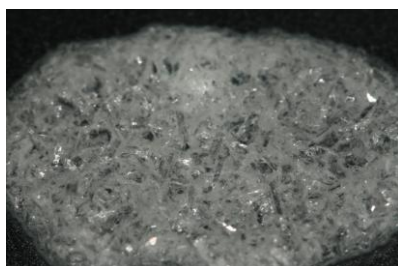
Classic hydrolysis



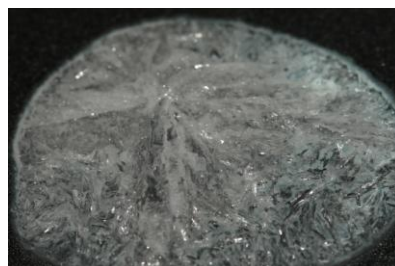
0.05wt% CMC



0.25wt% CMC



0.05wt% HEC



0.25wt% HEC



0.05wt% MC



0.25wt% MC

Figure 17 - By-products crystals pictures of the reactions performed at 25°C, obtained by slow evaporation of a water solution at environmental conditions in the laboratory.

The XRD analysis of the crystals by-products structure, from the classic and with the addition of 0.05wt% HEC and 0.05wt% MC hydrolysis, reveals that both of them are a sodium metaborate dehydrate, $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$. The boron atoms are in a triangular configuration with three oxygen atoms, with B-O bond lengths between 1.27 and 1.29 Å. The BO_3 triangular arrangement was already found in the crystal structure of orthorhombic [44] and monoclinic [45] metaboric acid although in the title crystal structure the oxygen atoms are bound to just one B atom. The BO_3 triangles form layers 3.238 Å apart that sandwich a layer of sodium and water molecules. For each boron atom there are three bound oxygen atoms and one oxygen of water.

Half of the sodium atoms have their valence strength distributed between six Na-O bonds and the other half between seven Na-O bonds (as already determined in other sodium metaborate structures [46]). The water molecules are involved in a net of interactions with the sodium atoms. Figure 18 shows two different views of the crystal structure of sodium metaborate dehydrate.

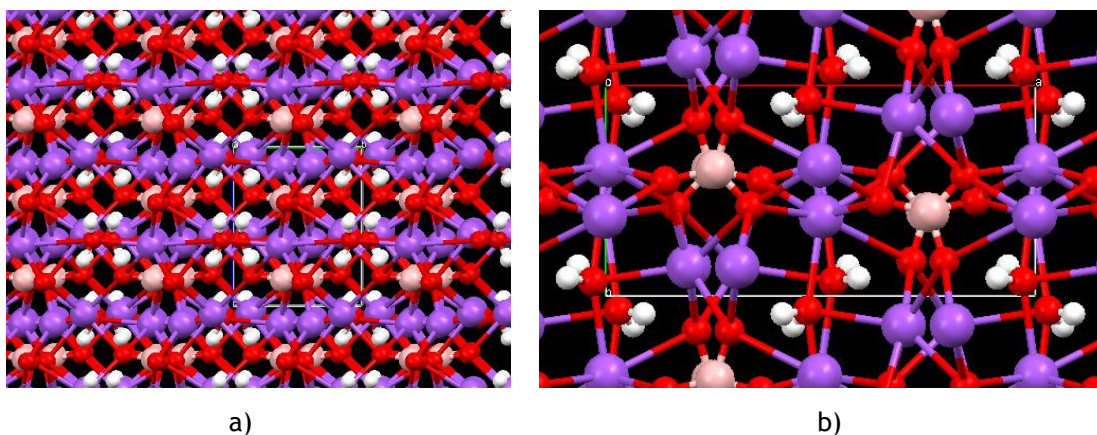


Figure 18 Views of crystal structure of sodium metaborate dehydrate (obtained from the classic hydrolysis and hydrolysis with addition of 0.05wt% HEC and 0.05wt% MC, at 25°C). Na in violet, O in red, B in pink and H in white: a) view along the a-axis of the crystal structure showing stacking layers formed by BO_3 triangles and by Na and water molecules; b) view along the c-axis of the crystal structure showing the BO_3 triangular arrangement and the Na bound network.

The crystal structure of by-products resultant from the sodium borohydride hydrolysis reactions with addition of 0.25wt% of all the tested polymers and of 0.05wt% of CMC reveals that the by-product is a sodium tetrahydroxoborate $\text{NaB}(\text{OH})_4$. The boron atoms are in a tetrahedral configuration with four oxygen atoms, with B-O bond lengths within the interval 1.465 and 1.487 Å. The B-O interatomic distances are around the expected value for a tetrahedral configuration 1.475 Å, which is appreciable higher than observed for triangular configurations

(1.365 Å) [45].

The sodium atoms are hexacoordinated with Na-O bonds within 2.294 and 2.592 Å. The mean length of the Na-O bonds is 2.512 Å when the Na coordination number is seven and it is 2.450 Å when the coordination number is six [46]. It is reasonable to assume that the bond length and the Na coordination number decrease as the bond strength increases. Each oxygen atom connects one boron and one sodium atom producing endless zigzag sheets. Figure 19 shows two different views of the crystal structure.

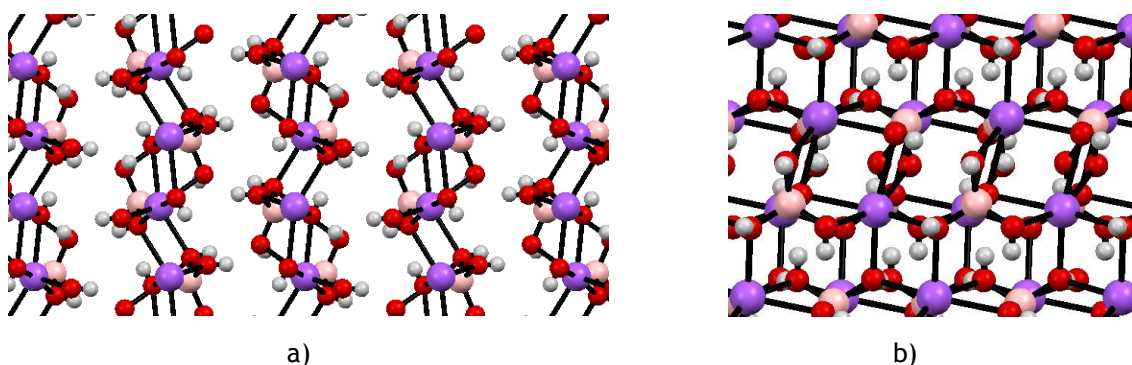


Figure 19 - Views of crystal structure of sodium tetrahydroxoborate (obtained from the hydrolysis with 0.25wt% of all the polymers tested and from the hydrolysis with addition of 0.05wt% CMC, both at 25°C. Na in violet, O in red, B in pink and H in white: a) view along the a-axis; b) view along the b-axis.

Table 9 resumes the crystal structures obtained for the different by-products analysed.

Table 9 - Crystal structures

Crystal structure	Hydrolysis reaction
NaBO ₂ ·2H ₂ O	Classic hydrolysis
	0.05wt% HEC
	0.05wt% MC
NaB(OH) ₄	0.05wt% CMC
	0.25wt CMC, HEC and MC

The crystal structure of the classic hydrolysis by products was in some way expected since the sodium metaborate dehydrate (NaBO₂·2H₂O) appears to be a preferential product at temperatures up to 105°C, according to Marrero-Alfonso et al. [47].

The obtained result for the crystal structure of the 0.25wt% CMC polymer

hydrolysis (NaB(OH)_4) was also expected. Ferreira et al. [2] had already found this crystal structure. The by-products of 0.05wt% CMC polymer hydrolysis present the same structure. As those authors reported, in the sodium borohydride hydrolysis with 0.25wt% of CMC polymer, there is no crystalline water in the crystal structure of sodium tetrahydroxoborate (NaB(OH)_4). It seems to be due to the presence of CMC molecules which have the particularity of holding water. These most extended molecules probably difficult groups -OH from linking the metaborate to form crystalline water during the crystallization process. It was formed structural water instead of crystalline water, as the boron atoms are linked to four hydroxyl groups.

According to the results obtained in the present work, the CMC polymer even at low concentration (0.05wt%) has the same potential in difficult the crystalline water formation.

On the other hand, the by-products from HEC and MC polymers hydrolysis present different crystal structures for the two studied polymers concentrations. For 0.25wt% polymers concentration, the crystal structure is NaB(OH)_4 . At low biopolymer concentration (0.05wt%), the crystal structure obtained is the same as for the classic hydrolysis, $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$. Hence, it seems that, at the lower biopolymer concentration, these cellulose based polymers do not interfere in the formation of crystalline water during the crystallization process.

According to Ferreira et al. [2] the finding of sodium tetrahydroxoborate (NaB(OH)_4) as the main by-product of sodium borohydride hydrolysis with addition of these specific polymers has a major impact in sodium borohydride by-products hydrolysis recyclability. In fact the recycling of sodium metaborate ($\text{NaBO}_2 \cdot x\text{H}_2\text{O}$) back to sodium borohydride is one the most important issues related to the cost reduction of sodium borohydride as hydrogen/energy carrier. It is also stated [2] that the sodium tetrahydroxoborate (NaB(OH)_4) as by-product, reduces the steps needed to obtain anhydrous metaborate comparing the process with the traditional $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$.

In this context, it is not only the CMC polymer addition to the reactant solution, but also, the HEC and MC polymers at a value of 0.25wt% mass concentration, to have an important contribution to the process of recycling the sodium borates back to sodium borohydride.

5 Conclusions

This chapter summarizes the most relevant conclusions of the work.

In the present thesis the effect of small additions of cellulose based polymers on the sodium borohydride catalyzed hydrolysis was investigated through the following studies: kinetics reaction study, preliminary hydrogen solubility study and by-products analysis.

The kinetic study reveals quite interesting results:

- At a temperature close to room temperature, a small addition of the three polymers (0.05wt%) has a significant impact on the reaction kinetics. The reactions with CMC and MC polymers attain the completion with rapid hydrogen generation at around half of the time when compared with classic hydrolysis.
- The CMC polymer is the better choice for a higher generation rate and a rapid complete hydrolysis, even a very small addition of this polymer at room temperature is sufficient to achieve good hydrolysis performances.
- The increase of temperature and polymer concentration in HEC and MC cases demonstrated a poorer reaction performance, showing a very slow gas evolution after an initial relatively high generation rate. These results suggesting that the hydrogen formed remains in the solution and is slowly released.

In the preliminary hydrogen solubility study:

From this study, several candidates to store hydrogen in the liquid post reaction solution were selected. The post-reaction solutions with 0.05 wt% of HEC and CMC at the higher temperature reveal a strong decrease on the conductivity. This is thought to be due the capability of these polymers to store hydrogen in the liquid phase. The presence of the polymers probably changes the polarity of the final solution due to the presence of the C-H groups. From the experiments reported the following remaining solutions should be also tested: at 25 °C HEC 0.05wt% and MC 0.25wt%; at 45 °C HEC 0.25wt% and MC 0.25wt%.

The by-products analysis by XRD revealed:

- A sodium metaborate dehydrated, $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$, as the by-product of classic hydrolysis as expected.
- A crystal structure of sodium tetrahydroxoborate ($\text{NaB}(\text{OH})_4$) for hydrolysis with 0.05wt% and 0.25wt% of CMC and 0.25wt% of HEC and MC polymers. It was formed structural water instead crystalline water, which has a great impact in sodium borohydride by-products hydrolysis recyclability. In fact the recycling of metaborate (NaBO_2) back to sodium borohydride is one the most important issues related to the cost reduction of sodium borohydride.
- A sodium metaborate dehydrated, $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$, as the by-product of hydrolysis with addition of 0.05wt% of HEC and MC polymers. At the lower biopolymer concentration, these cellulose based polymers do not interfere in the formation of crystalline water during the crystallization process.

6 Project assessment

This chapter intends to give an overall judgment about the performed work. It is divided in 3 sections: Accomplished Objectives, Limitations and future work and at last Final assessment.

6.1 Accomplished objectives

The objective of the present research was to investigate the influence of small additions of based cellulose polymers in the kinetics reaction of catalytic hydrolysis of stabilized aqueous solutions of sodium borohydride, in a batch reactor, bearing in mind the possibility of hydrogen storage in the liquid phase.

This objective was accomplished, three different polymers were tested and their contribution to improve the kinetics reaction was investigated. Other compounds are suggested as possible materials to host hydrogen gas, are suggested to be tested in future works.

6.2 Limitations and future work

The issues related with the method for hydrogen solubility measurements was the major limitation on the present work. Due to the particular hydrogen properties (strong non polar gas) it was difficult to find a suitable method that could measure with accuracy values of hydrogen solubility in the studied post-reaction solutions. In fact, hydrogen presents values of solubility below the detection limit of the common methods used for gas absorption in liquid phase. For a future work, the gravimetric method seems to be an efficient method for the measurement of hydrogen solubility in liquids. However it is necessary to find suitable equipment, with a higher precision and accuracy, for the measurements of hydrogen solubility in aqueous solutions at moderate pressures. The recent developments in magnetic suspension balances could be a pathway to adopt.

As other future work and developments it would be also interesting to continue the study of the influence of other polymers addition (such as cyclodextrins) on the sodium borohydride hydrolysis for the improvement of hydrogen gas solubility

in liquid phase. A deeper understanding on the chemical bonds between the different compounds involved is needed.

Also other chemical compounds should be tested on the sodium borohydride hydrolysis as referred in the Chapter 2. For example, the study of the influence of ionic liquids on sodium borohydride hydrolysis for hydrogen generation is suggested as future work. Moreover, data on hydrogen solubility in aqueous borate systems is in fact necessary to deeply understand the mechanisms of hydrogen storage in the liquid phase.

Bearing in mind the catalyst activity, it would be important determine the catalyst activation energy in the hydrolysis reaction with addition of the biopolymers studied in the present work.

6.3 Final assessment

As a final assessment I want to say that it was a privilege to have developed my Master Thesis on such interesting subject. In fact, working in this field of research was a motivation for me that provided me a better understanding of different topics leading to an overall increase in my knowledge. It is great to think that the work accomplished will somehow contribute to the development of a new energetic paradigm based on the hydrogen compound and sodium borohydride as a hydrogen carrier.

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Appendix A - Review of ruthenium based catalyst

Table A.1 - Data on Ruthenium based catalyst for sodium borohydride hydrolysis since the year 2000[6].

Year	Authors	Catalyst	Activity (L(H ₂)/min/ g _{cat})	Activity (L(H ₂)/min/ g _{metal})	NaBH ₄ wt%	NaOH wt%	T (°C)
2000	Amendola et al.	Ru/IRA-400	0.189	3.80	20	10	25
2005	Krishnan et al.	Pt- Ru/LiCoO ₂	2.400	24.0	5	5	25
2005	Ozkar et al.	Ru nanoclusters	96.80	96.8	0.75	0	25
2006	Zahmakiran et al.	Ru nanoclusters	0.004	0.004	0.57	10	25
2007	J. Zhang et al.	Ru/C	0.770	12.9	1	3.75	25
2008	Dermici et al.	Ru-Pt/TiO ₂	0.150	15.2	2	4	20
2008	Park et al.	Ru-Fe-Co/AC	5.030	41.7	10	4	25
2008	Z. Liu et al.	Ru/LiCoO ₂	2.700	270	10	5	25
2008	Hsueh et al.	Ru/IR-120	0.132	13.2	5	1	25
2009	Zahmakiran et al.	Ru nanoclusters / zeolite	0.130	16.1	1.1	5	25
2009	Chen et al.	Ru/PS	0.216	5.40	1	1	Not state d
2010	Liang et al.	Ru/C (graphite)	0.969	32.3	10	5	30

Appendix B - Hydrogen rate, yield and gravimetric and volumetric hydrogen densities determination

1) Hydrogen Reaction rate determination

The hydrogen generation rate Q ($L(H_2)\text{min}^{-1}\text{gcat}^{-1}$) was determined taking into account the ideal gas Law:

$$Q = \frac{dP}{dt} \cdot \frac{V_{final}}{RT} \cdot \frac{V_m}{m_{cat}} \quad (B.1)$$

Where:

$$V_{final} = V_{initial} + \left((2 + x) \cdot \frac{m_{NaBH_4}}{MM_{NaBH_4}} \cdot \frac{MM_{H_2O}}{\rho_{H_2O}} \right) \quad (B.2)$$

$$V_{initial} = V_r - \frac{m_{solution}}{\rho_{solution}} - \frac{m_{cat}}{\rho_{cat}} \quad (B.3)$$

2) Reaction yield determination

The hydrogen yield in all the reactions was determined by the following equation:

$$yield(H_2) = \frac{n(H_2)_{experimental}}{n(H_2)_{theoretical}} \cdot 100\% \quad (B.4)$$

Where $n(H_2)_{experimental}$ corresponds to the number of moles of hydrogen produced and $n(H_2)_{theoretical}$ is the theoretical amount of hydrogen produced assuming 100 % conversion of sodium borohydride by applying the ideal gas law to the final volume of gas inside the batch reactor. The reactor was not initially evacuated, so the air is taken into account in the calculations.

$$n(H_2)_{experimental} = \frac{P(\text{air} + H_2)_{experimental} \cdot V_{final}}{RT} - n_{air} \quad (B.5)$$

$$n_{air} = \frac{P_{atmospheric} \cdot V_{initial}}{RT} \quad (B.6)$$

$$P(\text{air} + H_2)_{experimental} = P_{atmospheric} + P(\text{air} + H_2)_{relative} \quad (B.7)$$

3) Gravimetric and volumetric hydrogen densities determination

The gravimetric capacity or specific energy is a measure of the usable energy per kilogram of system mass. In practical terms, this quantity is usually expressed as a weight percentage of hydrogen. Volumetric capacity or energy density is the useful energy per litre of system volume.

The gravimetric and volumetric hydrogen densities were determined by the following equations:

$$\text{gravimetric } H_2 \text{ density} = \frac{m_{H_2}}{m_{solution} + m_{cat}} \cdot 100 \quad (B.8)$$

$$\text{volumetric } H_2 \text{ density} = \frac{m_{H_2}}{\frac{m_{solution}}{\rho_{solution}} + \frac{m_{cat}}{\rho_{cat}}} \quad (B.9)$$

Appendix C - Preliminary studies

In order to select the most adequate sodium hydroxide concentration for all the hydrolysis experiments of the present project, two experiments were made at constant temperature, 25°C, for two sodium hydroxide concentrations, 3wt% and 7wt%. The influence of sodium hydroxide concentration on the classic hydrolysis is put in evidence in Figure C.1.

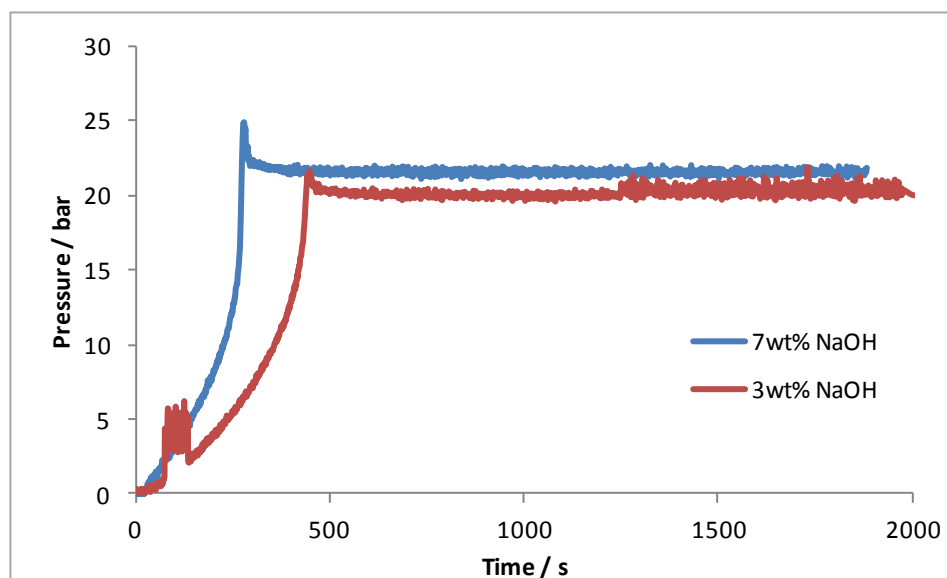


Figure C.1 - Hydrogen generation rate as a function of time for classic hydrolysis of sodium borohydride (15wt%) at two different sodium hydroxide concentrations, with a ratio catalyst/sodium borohydride of 0.2g/g. The reactions, for 20 cm³ of reactant solution were performed at 25°C. The catalyst was reused 11 and 12 times.

As can be seen in the Figure C.1, for the higher value of sodium hydroxide concentration, the reaction rate is significantly enhanced. This result is according to the previous studies mentioned in the Chapter 2. The reaction with 3wt% of sodium hydroxide attained completion after 500 seconds and a yield of 97% was found. On the other hand the reaction, with 7wt% of sodium hydroxide, attained completion after 400 seconds and a yield of 100% was found. Hence, the value of 7wt% sodium hydroxide was chosen for all the experiments carried out.

The most suitable ratio catalyst/sodium borohydride was defined after the execution of three classic hydrolysis reactions at 45 °C with different mass ratio catalyst/sodium borohydride: 0.1 g/g, 0.2 g/g and 0.4 g/g. Figure C.2 shows the plot of the reaction rate with different ratios catalyst/sodium borohydride.

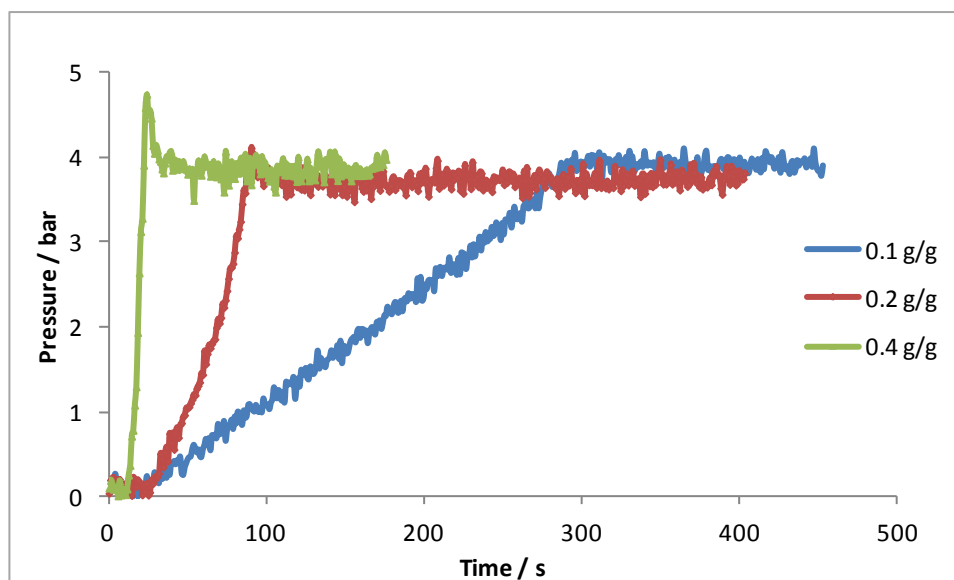


Figure C.2 - Effect of ratio catalyst/sodium borohydride on the hydrogen generation rate via classic hydrolysis of sodium borohydride (10wt% NaBH₄ and 7wt% NaOH). The reactions, for 5 cm³ of reactant solution were performed at 45 °C and stabilized with 7wt% of sodium hydroxide. The catalyst was reused 8, 9 and 10 times.

According to the Figure C.2, the hydrolysis reaction under study presents a better performance with the increasing of ratio catalyst/sodium borohydride. However, the value of 0.2 g/g was defined as suitable for the experiments, according to the total amount of catalyst available for present work.

Appendix D - Hydrogen generation and temperatures profiles

➤ Classic hydrolysis:

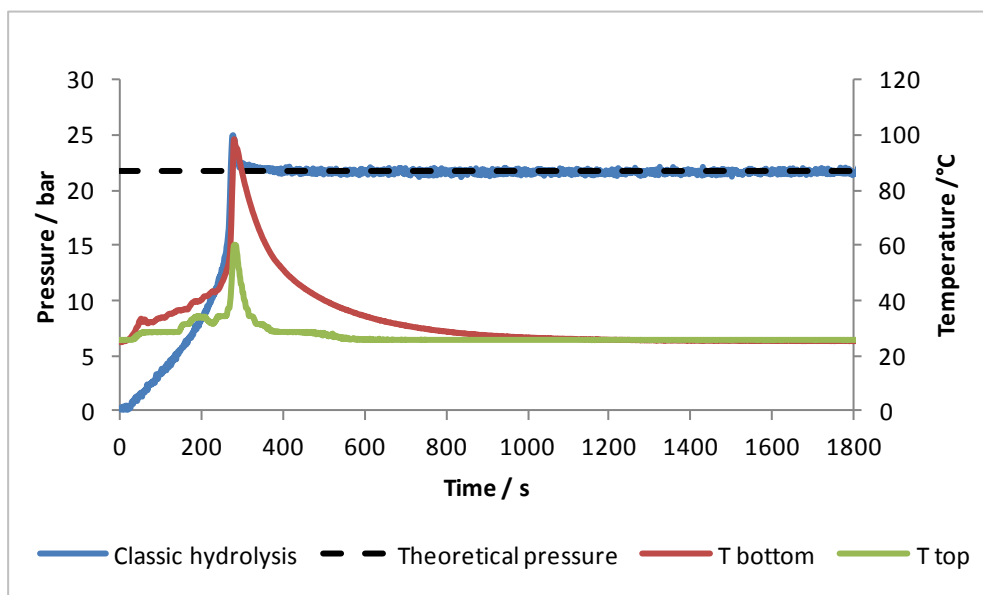


Figure D.1 - Hydrogen generation rate as a function of time and temperatures profile for classic hydrolysis of sodium borohydride (20cm^3 of reactant solution with 15wt% NaBH_4 and 7wt% NaOH) at 25°C . The catalyst, in the proportion $\text{Ni-Ru catalyst}/\text{NaBH}_4$: 0.2 g/g was reused 11 times.

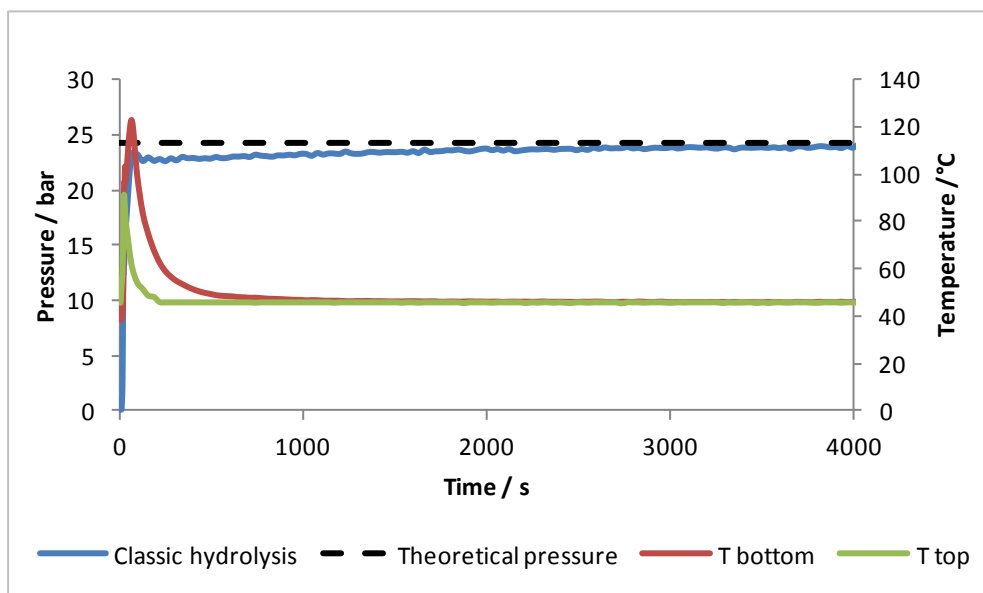


Figure D.2 - Hydrogen generation rate as a function of time and temperatures profile for classic hydrolysis of sodium borohydride (20cm^3 of reactant solution with 15wt% NaBH_4 and 7wt% NaOH) at 45°C . The catalyst, in the proportion $\text{Ni-Ru catalyst}/\text{NaBH}_4$: 0.2 g/g was reused 35 times.

➤ Hydrolysis with addition of HEC polymer at 25 °C:

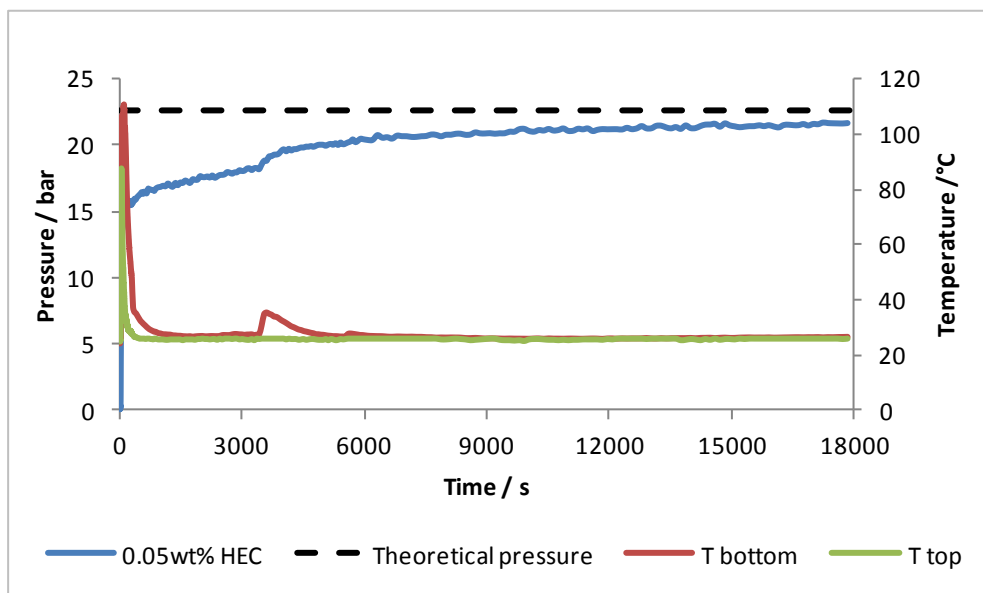


Figure D.3 - Hydrogen generation rate as a function of time and temperatures profile for hydrolysis of sodium borohydride with addition of 0.05wt% of HEC polymer (20cm³ of reactant solution with 15wt% NaBH₄ and 7wt% NaOH) at 25 °C. The catalyst, in the proportion Ni-Ru catalyst/NaBH₄: 0.2 g/g was reused 34 times.

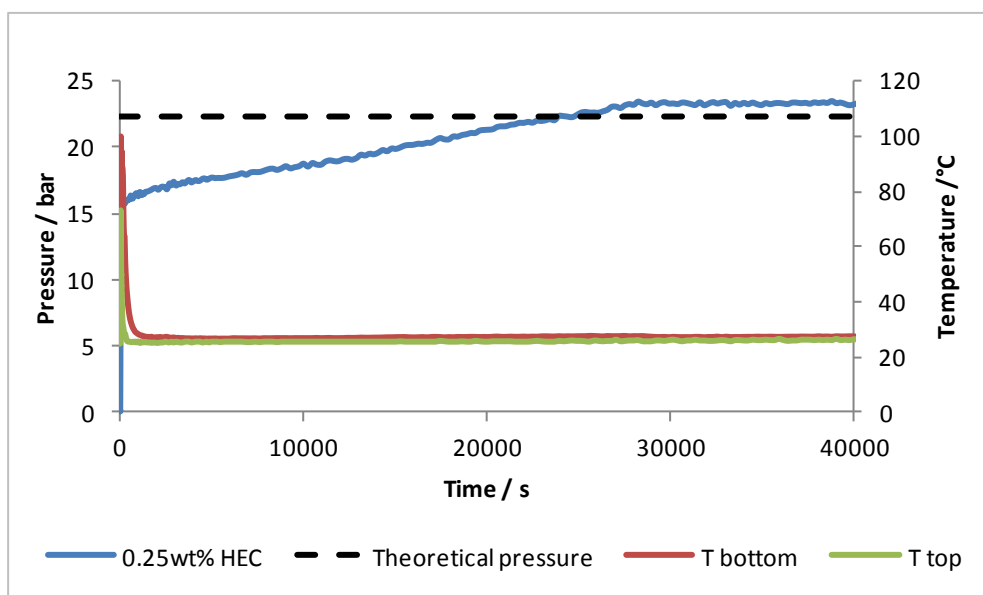


Figure D.4 - Hydrogen generation rate as a function of time and temperatures profile for hydrolysis of sodium borohydride with addition of 0.25wt% of HEC polymer (20cm³ of reactant solution with 15wt% NaBH₄ and 7wt% NaOH) at 25 °C. The catalyst, in the proportion Ni-Ru catalyst/NaBH₄: 0.2 g/g was reused 15 times.

➤ Hydrolysis with addition of HEC polymer at 45 °C:

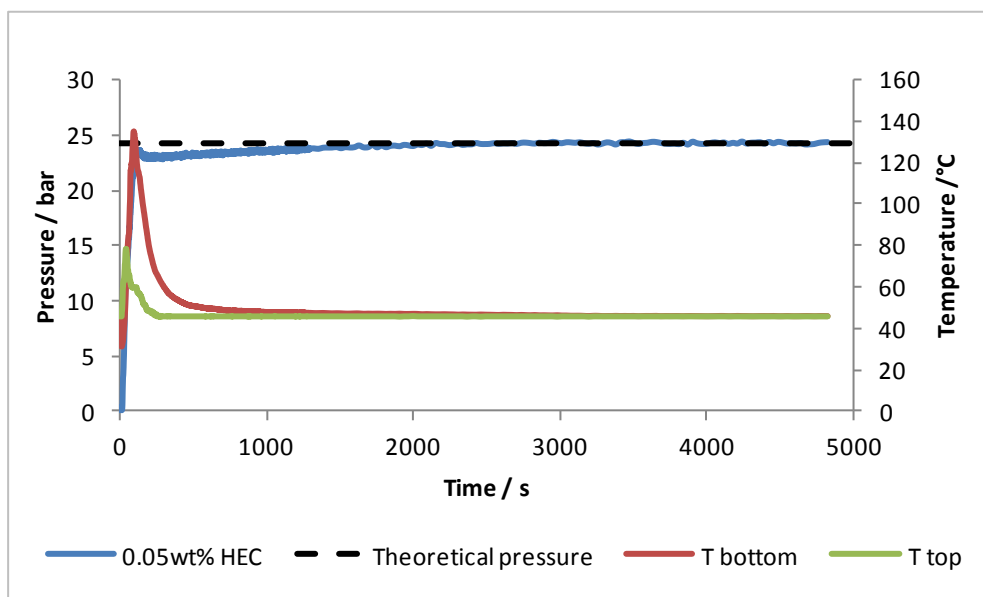


Figure D.5 - Hydrogen generation rate as a function of time and temperatures profile for hydrolysis of sodium borohydride with addition of 0.05wt% of HEC polymer (20cm^3 of reactant solution with 15wt% NaBH_4 and 7wt% NaOH) at 45°C . The catalyst, in the proportion Ni-Ru catalyst/ NaBH_4 : 0.2 g/g was reused 26 times.

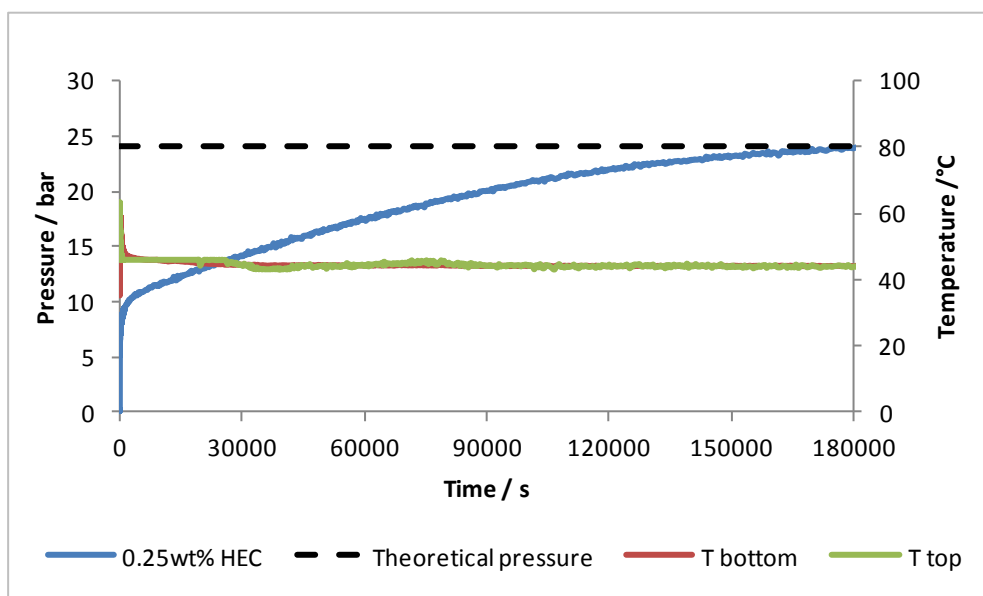


Figure D.6 - Hydrogen generation rate as a function of time and temperatures profile for hydrolysis of sodium borohydride with addition of 0.25wt% of HEC polymer (20cm^3 of reactant solution with 15wt% NaBH_4 and 7wt% NaOH) at 45°C . The catalyst, in the proportion Ni-Ru catalyst/ NaBH_4 : 0.2 g/g was reused 27 times.

➤ Hydrolysis with addition of CMC polymer at 25 °C:

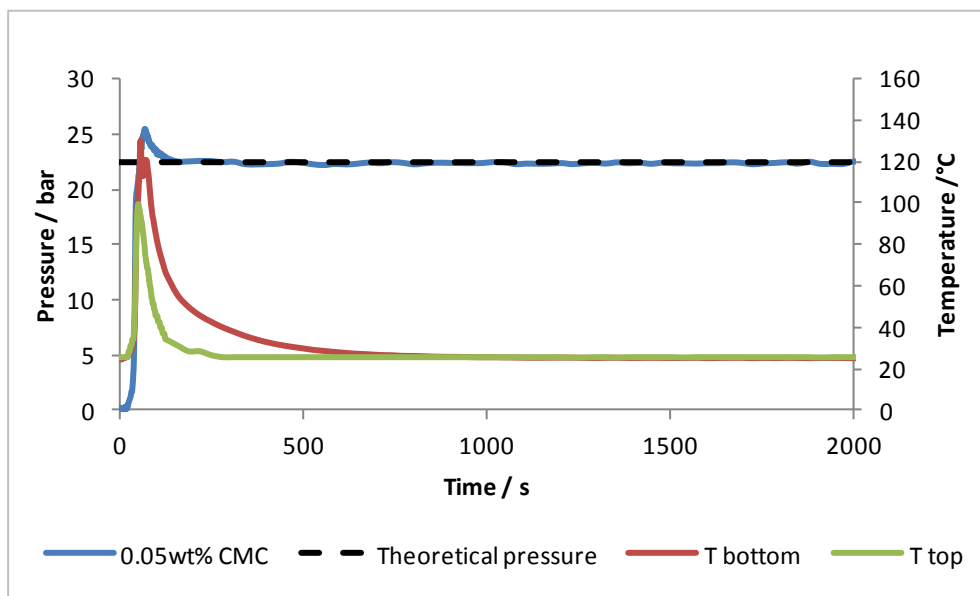


Figure D.7 - Hydrogen generation rate as a function of time and temperatures profile for hydrolysis of sodium borohydride with addition of 0.05wt% of CMC polymer (20cm³ of reactant solution with 15wt% NaBH₄ and 7wt% NaOH) at 25°C. The catalyst, in the proportion Ni-Ru catalyst/NaBH₄: 0.2 g/g was reused 19 times.

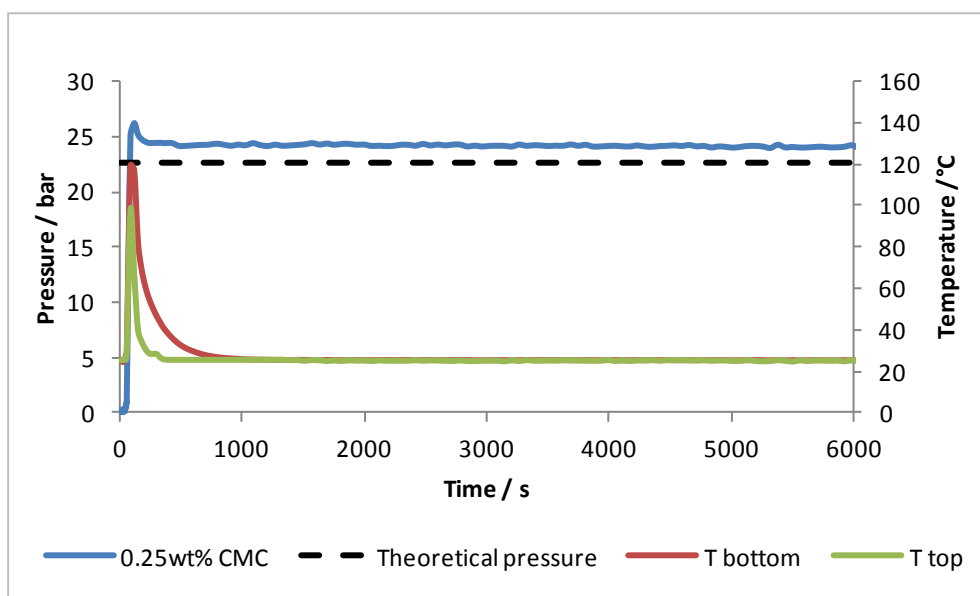


Figure D.8 - Hydrogen generation rate as a function of time and temperatures profile for hydrolysis of sodium borohydride with addition of 0.25wt% of CMC polymer (20cm³ of reactant solution with 15wt% NaBH₄ and 7wt% NaOH) at 25°C. The catalyst, in the proportion Ni-Ru catalyst/NaBH₄: 0.2 g/g was reused 18 times.

➤ Hydrolysis with addition of CMC polymer at 45 °C:

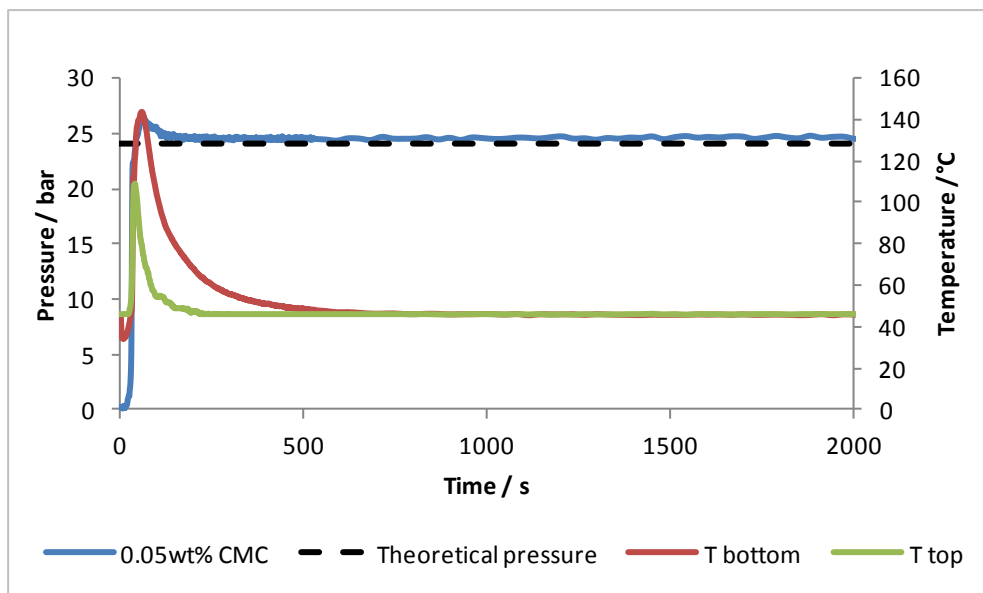


Figure D.9 - Hydrogen generation rate as a function of time and temperatures profile for hydrolysis of sodium borohydride with addition of 0.05wt% of CMC polymer (20cm^3 of reactant solution with 15wt% NaBH_4 and 7wt% NaOH) at 45°C. The catalyst, in the proportion Ni-Ru catalyst/ NaBH_4 : 0.2 g/g was reused 28 times.

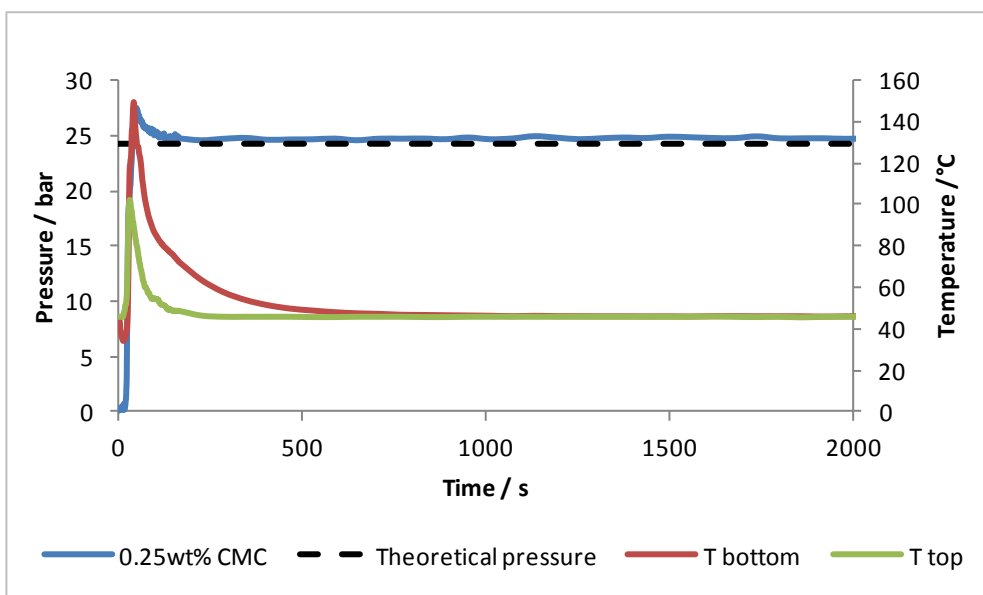


Figure D.10 - Hydrogen generation rate as a function of time and temperatures profile for hydrolysis of sodium borohydride with addition of 0.25wt% of CMC polymer (20cm^3 of reactant solution with 15wt% NaBH_4 and 7wt% NaOH) at 45°C. The catalyst, in the proportion Ni-Ru catalyst/ NaBH_4 : 0.2 g/g was reused 30 times.

➤ Hydrolysis with addition of MC polymer at 25 °C:

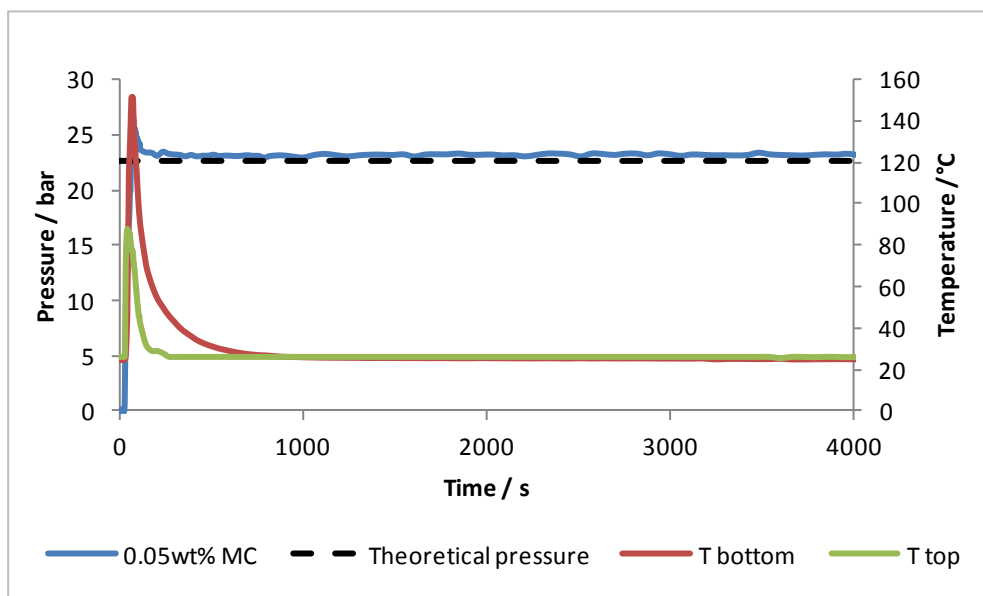


Figure D.11 - Hydrogen generation rate as a function of time and temperatures profile for hydrolysis of sodium borohydride with addition of 0.05wt% of MC polymer (20cm³ of reactant solution with 15wt% NaBH₄ and 7wt% NaOH) at 25°C. The catalyst, in the proportion Ni-Ru catalyst/NaBH₄: 0.2 g/g was reused 20 times.

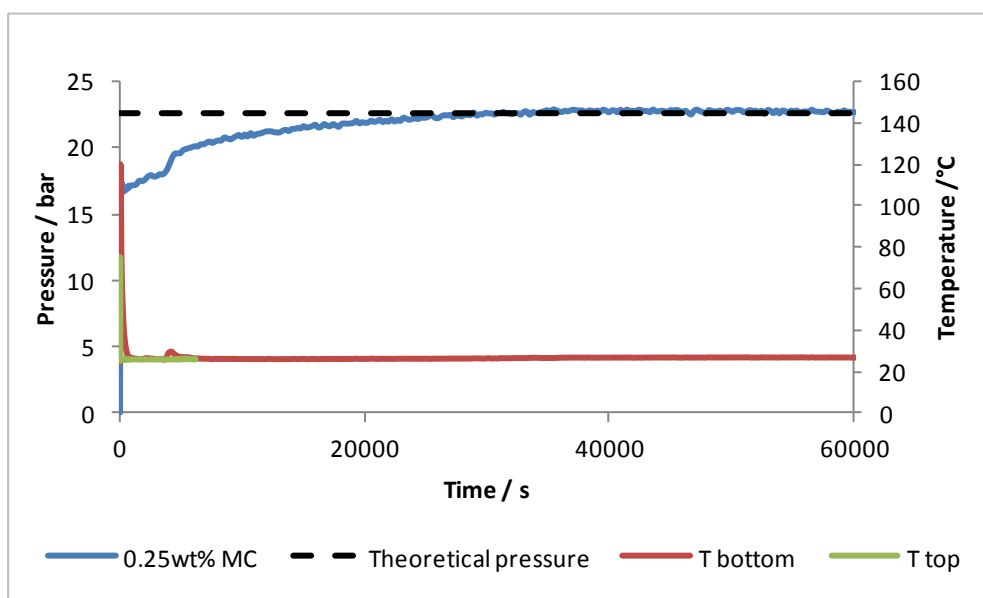


Figure D.12 - Hydrogen generation rate as a function of time and temperatures profile for hydrolysis of sodium borohydride with addition of 0.25wt% of MC polymer (20cm³ of reactant solution with 15wt% NaBH₄ and 7wt% NaOH) at 25°C. The catalyst, in the proportion Ni-Ru catalyst/NaBH₄: 0.2 g/g was reused 21 times.

➤ Hydrolysis with addition of MC polymer at 45 °C:

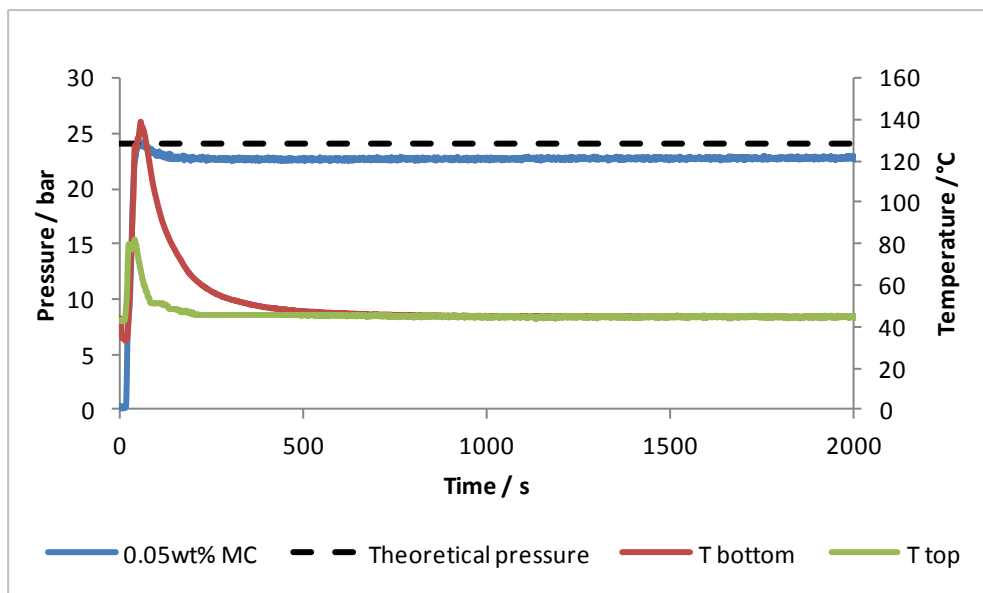


Figure D.13 - Hydrogen generation rate as a function of time and temperatures profile for hydrolysis of sodium borohydride with addition of 0.05wt% of MC polymer (20cm³ of reactant solution with 15wt% NaBH₄ and 7wt% NaOH) at 45°C. The catalyst, in the proportion Ni-Ru catalyst/NaBH₄: 0.2 g/g was reused 29 times.

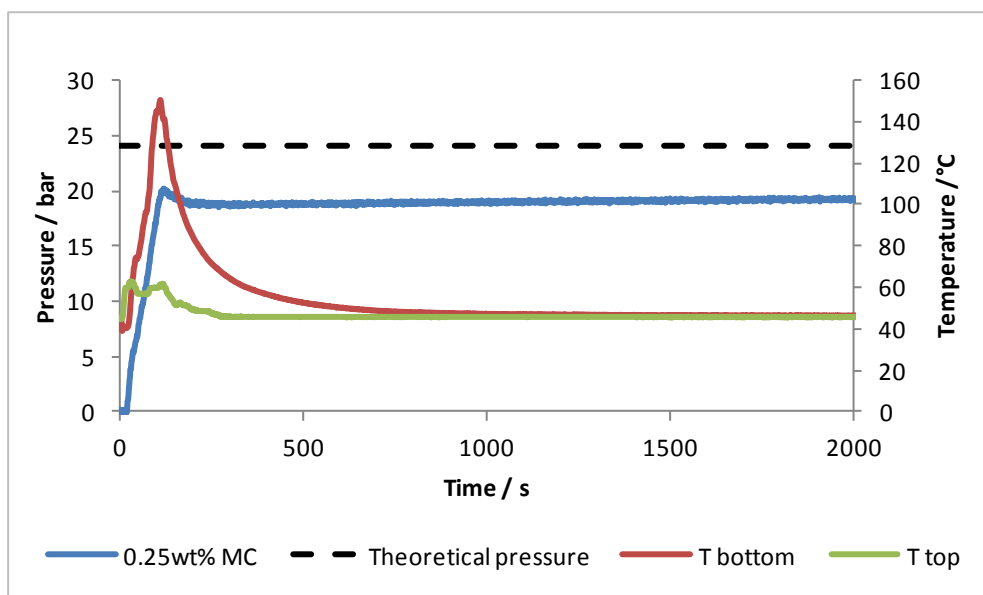


Figure D.14 - Hydrogen generation rate as a function of time and temperatures profile for hydrolysis of sodium borohydride with addition of 0.25wt% of MC polymer (20cm³ of reactant solution with 15wt% NaBH₄ and 7wt% NaOH) at 45°C. The catalyst, in the proportion Ni-Ru catalyst/NaBH₄: 0.2 g/g was reused 31 times.

