

A low cost and safe system of hydrogen production utilizing NaBH_4 and CoO catalysis.

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Abstract. *The objective of this study was to evaluate the hydrogen production through hydrolysis of sodium borohydride (NaBH_4) utilizing catalysts containing CoO . The reactant is safe and stable (when dry) at room temperature. Few works and studies have presented results of investigations utilizing catalysts containing cobalt; however utilizing catalysts containing CoO were not found yet. In this work simple and cheap hydrogen generation system was developed having reactions at normal conditions of temperature and pressure. A solution containing a gravimetric composition of 10% wt. NaOH , 10% wt. NaBH_4 and 80% wt. H_2O was utilized. The reaction was carried out at various times using the same catalyst to evaluate its performance. This catalyst presented high rates of hydrogen production, especially at its start-up (about 99% of the theoretical hydrogen volume was produced) at room temperature. After start-up, e.g., when more solution was put, rate of hydrogen production decreased having its production performance also decreased. Probably this fact occurred due to the formation of the solid phase products such as NaBO_2 which might fill the porous catalyst structure; decreasing the catalytic area. This catalyst is suggested in situations where high production rates are necessary such as start-up of fuel cells.*

Keywords: *hydrolysis, sodium borohydride, cobalt oxide, hydrogen production.*

1 INTRODUCTION

The use of hydrogen to energy supply, associated with use by fuel cells, become possible a more-efficient and environmentally friendly energy supply, beyond substituting toxic materials such as those encountered in batteries (nickel, cadmium, cobalt, and more) [1].

The sodium borohydride (NaBH_4) is widely utilized in some chemical, pharmaceutical, and pulp and paper industries. The melting point of this reactant (solid at room temperature, which facilitates its handling) is 36°C , and it is stable up to 300°C (if this material is maintained always dry). Additionally, it is soluble in cold water and reacts at hot water [1, 2].

The hydrolysis of NaBH_4 allows a high-purity hydrogen production, necessary to feed a fuel cell such as PEMFC (Proton Exchange Fuel Cell) [3, 4]. The hydrolysis could be performed at different reactants fractions and thermodynamic conditions. The hydrogen production rates vary considerably according to the utilized catalyst (and its characterization) [5].

Various advantages of use of NaBH_4 to hydrogen production are depicted below [6]:

- This material is not flammable and volatile;
- Its hydrolysis is safe and environmentally friendly (the NaBH_4 , if released into the environment, becomes a inert salt);
- The hydrogen generation is moderated if compared to reactions performed by other metallic hydrides;
- The products of this reaction could be recycled.

Monometallic hydrides (such as NaBH_4) are easier to be reduced than multimetallic hydrides (some of them must being reacted only at higher temperatures) [5].

Activated carbon, ruthenium, cobalt, platinum, nickel, rhodium, palladium, and other metals and their alloys, and salts, and even compounds that contain fluoride, chloride, and boron could be utilized as catalysts. Various supports to catalysts have been largely investigated such as carbon compounds, resins and some metallic alloys. The reactions could also be performed without catalysts; however in this case, acid or alkaline reactants could be suggested [7-9].

The hydrolysis of NaBH_4 is an exothermic reaction, that is, heat sources are not necessary to a reaction. This process is performed through a catalytic decomposition as follows:



This reaction has a theoretical efficiency equal to 10.8%. At 23°C , the saturation of NaBH_4 at aqueous solution occurs as soon as its proportion in the solution attains 35%wt. (56 g of NaBH_4 at 100 g of water), beyond to have a mass concentration of hydrogen higher than various metallic hydrides and hydrocarbons [7, 10, 11].

The obtained values of formation heat from previous reaction are different depending on the work. Table 1 compares these values. About this reaction, Table 2 compares the obtained values of the activation energy, also obtained from various works:

Table 1: Generated heat to hydrogen production by cited systems:

Authors:	Utilized catalysts:	Formation heat (kJ / mol H_2):
Zhang et al. [12]	RuCl_3	210 ± 11
Zhang et al. [12]	HCl	227 ± 8
Kojima et al. [13]	-	217
Suda et al. [14]	-	225
Wu et al. [15]	Pt - carbon	217
Zhang et al. [16]	Ru - carbon	210

Other reactions could occur as follows below [2, 5]:



Table 2: Activation energy to hydrolysis of NaBH₄:

Authors:	Utilized catalysts:	Activation energy (kJ/mol H ₂):
Amendola et al. [6]	Ru - IRA 400	47
Amendola et al. [17] ¹	Ru - IRA 400	56
Kaufman et al. [18]	Co	75
Kaufman et al. [18]	Ni	71
Kaufman et al. [18]	Ni	63
Hua et al. [10]	Ni _x B	38
Simagina et al. [19] ²	1% Rh/Al ₂ O ₃	50.6 ± 1.3
Simagina et al. [19] ³	1% Pt/Al ₂ O ₃	56.9 ± 0.9
Peña-Alonso et al. [20]	Pt/Pd-Si	19
Zhang et al. [21]	Ru-carbon	66.9

Pena-Alonso et al. [20] depicted a relationship among energy densities in various hydrogen sources, as shows Fig. 1:

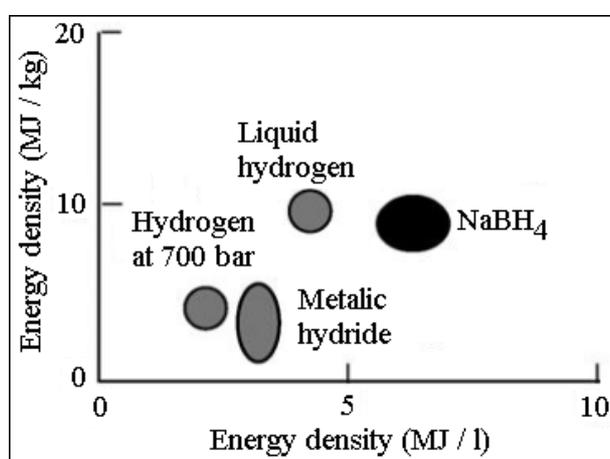


Figure 1 - Energy densities (mass and volume) of NaBH₄, and its comparison with various hydrogen sources (Pena-Alonso et al. [20])

The hydrolysis occurs in the presence of H⁻ ions, (from BH₄⁻ ions) which discharge electrons in the catalyst, reducing ion H⁺ from the water, occurring subsequently the hydrogen production. The availability of water near the catalyst facilitates this reaction [10]. The mechanism of this catalytic reaction is depicted in the Fig. 2:

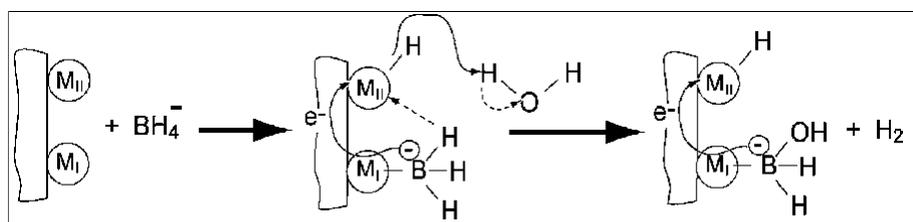


Figure 2 - Catalytic production mechanism of hydrogen from a aqueous solution of NaBH₄ (Pena-Alonso et al. [20])

The stabilization of this solution could be obtained with the inclusion of alkaline substances such as LiOH, KOH and NaOH, being the last one the most utilized due to its low cost [6, 13].

¹ Solution containing 5% Ru, 7.5% NaBH₄, 1% NaOH, and 91,5% H₂O.

² At 30, 40, and 50°C.

³ At 30, 40, and 50°C.

It is possible to obtain a major efficiency of hydrogen production through introduction of a small amount of NaOH and NaBH₄ in the utilized solution due to decrease of solution viscosity, allowing a major contact of reactants of solution with the catalyst surface, as describe Amendola et al. [6]. The hydroxide ions (OH⁻) from NaOH contribute to diminish the hydrolysis of ion BH₄⁻. With the increase of the concentration of NaOH in the solution, it occurs the reduction of performance of water in the hydrolysis process and reduction of solubility of NaBO₂, as cited in the work developed by Hua et al. [10]; however in the experiments described by Kojima et al. [22] the rate of hydrogen generation is not affected by variation of NaOH. Contradictory results about the influence of NaOH in the hydrogen production are found in various works and, according to some authors, this phenomenon is not possible to be explained, yet [10, 18].

Kim et al. [23] depicted an experiment where compounds of sodium, boron and potassium (after a hydrolysis process of NaBH₄) such as Na₂B₄O₇ · 10(H₂O), KB_xO_y and B₂O₃, were detected. In this case KOH was utilized to stabilize the solution. These compounds also contribute to reduce the area of catalyst. Hence, the depletion of catalyst occurs due its accumulation.

In works developed by Kojima et al. [13] and Simagina et al. [19], they were observed that the theoretical efficiencies of hydrogen generation without the use of catalysts is extremely low, which shows the need of use of catalysts.

2 EXPERIMENT DESCRIPTION

The experiments were performed in the laboratories of Chemical Engineering and Technology Department - Division of Chemical Reactions Engineering - Royal Institute of Technology (KTH) in Stockholm (Sweden).

A Cobalt Oxide (CoO) catalyst, whose amount utilized in this work was 270 mg, was prepared. Subsequently, a system to perform the experiment was developed. This system, which is simple and low-cost, is showed in the Fig. 3:



Figure 3 - System of hydrogen production

An aqueous solution containing 10%wt. of NaOH and 10%wt. of NaBH₄ was produced to this reaction. Firstly the NaOH was diluted into the water, being subsequently added into the solution the NaBH₄. An additional attention must to be paid to the increase of the solution temperature during the solution preparation with the application of NaOH and NaBH₄. The increase of temperature could result in an uncontrolled hydrogen production.

In works developed by Xia et al. [24] and Krishnan et al. [25], it was detected that the major rate and also a major hydrogen production occurred for solutions containing 10% of NaBH₄, comparing to solutions containing 5, 15, or 20% of NaBH₄; however the hydrogen production at two last amounts is more stable than utilizing other proportions.

In the work developed by Pinto et al. [26], it was also cited that hydrogen production rate was higher in the solution containing 10% of NaBH₄ than in the solution containing 20% of this reactant. This fact is due to a major production of NaBO₂, which could exceed its solubility, precipitating in the solution and accumulating in the pores of catalyst.

Spite of stability of solution, its use immediately after its production is recommended. The assessment of pH of solution and pH of reaction product were performed. Utilizing indicator materials (as showed in the Fig. 4), the values of pH of the produced solution were detected. The detected pH of solution (immediately after its preparation) was equal to 13. And pH of reaction product was 11.5. At following day, the pH of solution was only 12, in contrary to some works which cited that solution containing NaBH_4 would be stable for months, such as cited works by Amendola et al. [6]. This instability indicates a small amount of hydrogen produced.

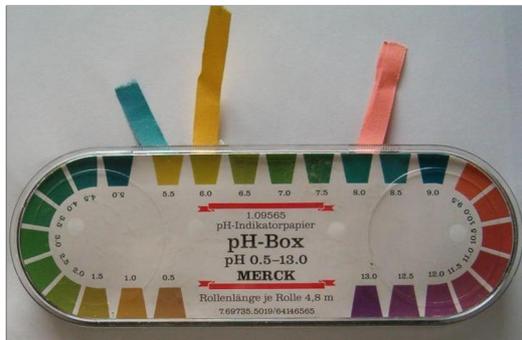


Figure 4 - pH indicator

A formula was developed to evaluate the half-life of this solution:

$$\log t_{1/2} = \text{pH} - (0.034 T - 1,92) \quad (4)$$

Where $t_{1/2}$ is the half-life of solution (in minutes), which depends on its pH and its temperature (measurement in K) [6].

Some works were developed utilizing solutions whose pH was near 14. The controlled production of hydrogen must being performed utilizing solutions that contains high pH [20].

Works developed by Amendola et al. [17] and Suda et al. [14] showed the influence of temperature in the hydrogen production rate, having the greatest production rate as soon as the process of hydrolysis is developed at a major temperature. This phenomenon also occurs in other processes of hydrogen production such as steam reforming [27].

As cited Hua et al. [10], the hydrolysis of NaBH_4 , if submitted at temperatures higher than 25°C , the efficiency of reaction could attains values over 90%. However, the efficiency of hydrolysis attains only about 78% if the solution temperature is about 15°C . As follows Richardson et al. [11], increasing 5°C in the reaction temperature an increase of about 50% in the hydrogen production rate could occur.

The increase of pressure results a major resistance in the solution transport in the reactor. As follows Zhang at al. [16], the increase of pressure contributes to put the reaction equilibrium in the side of reactants, resulting in a minor conversion.

Figure 5 shows the temperature variation during the preparation of solution and in the catalytic reaction. During preparation of solution, the greatest temperatures were encountered in the first minute immediately after the insertion of NaOH in the water and five minutes after inserting NaBH_4 in the mixture. This figure also shows the temperature variation during catalytic reaction utilizing catalyst CoO . It was verified that the greatest temperature utilizing this catalyst after 4 minutes of reaction, having subsequently a rough decrease of temperature, beyond to be attained its stability about 30 minutes after initiating the reaction.

The occurrence of major temperatures in the first minutes of catalytic reaction is present phenomenon in various works [18, 19].

These findings contribute to conclude that the presented reactions are exothermic.

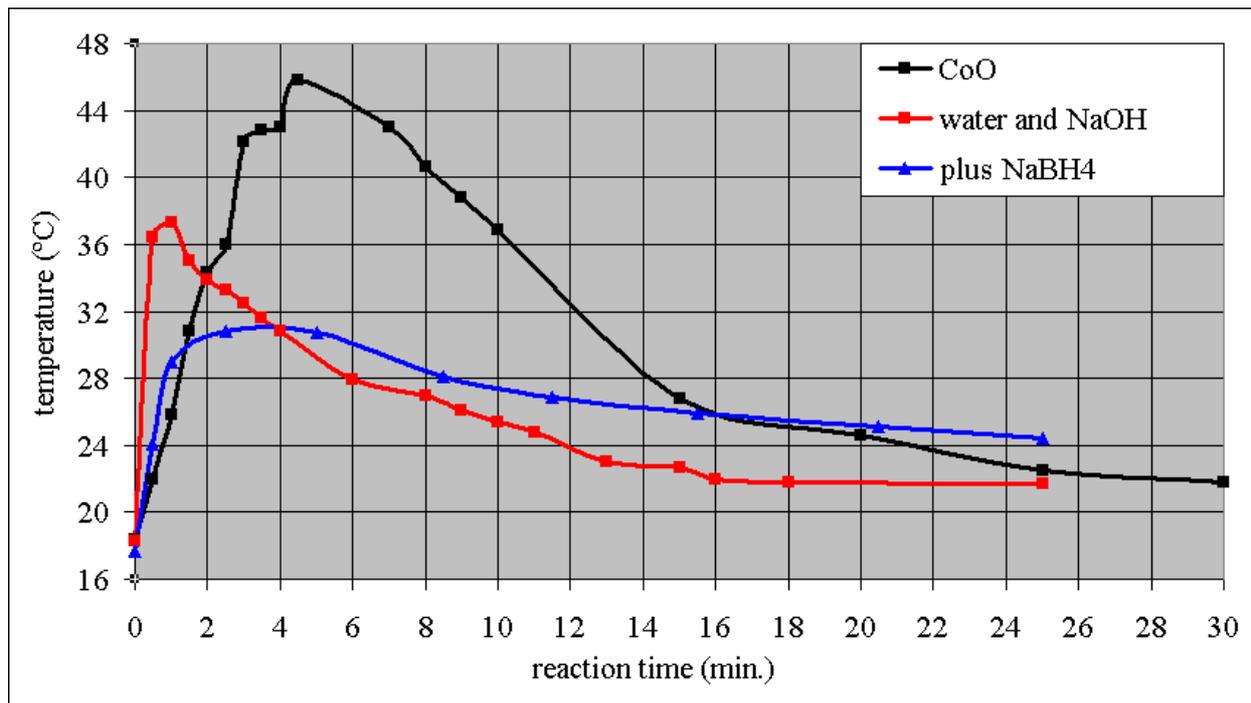


Figure 5 - Evolution of temperatures during preparation of solution and during catalytic reaction

Immediately after preparation of solution, one of the catalysts was put in a small glass flask where a chemical reaction was performed. Subsequently, two milliliters of this solution was applied in the catalyst. Immediately a catalytic generation of hydrogen occurred, counting the generated hydrogen. In the first 40 minutes (the period that most of hydrogen was generated), the volume of generated hydrogen at each minute was counted. After this period, it was verified the hydrogen production at each 5 minutes, finalizing it in the moment when the reaction ended.

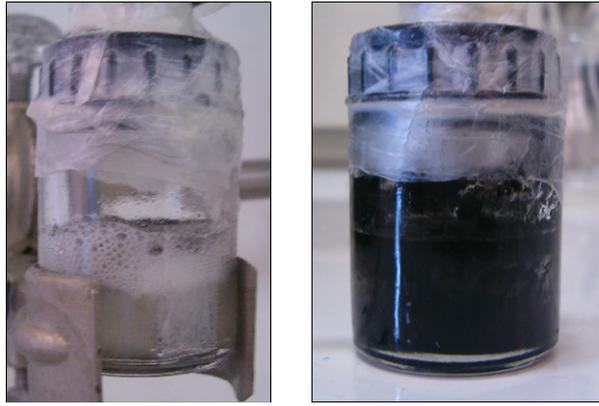
After ending the hydrogen production, an additional volume of 2 ml was applied and the hydrogen production was counted again. The application of 2 ml of this solution was performed five times with the objective to evaluate the catalyst performance.

Figure 6 shows the process of hydrogen generation. The Figs. 7 and 8 depict this process utilizing CoO. In the Fig. 6 dispersion of some catalytic material occurred with the contact with the solution was detected.



Figure 6 - Hydrogen production in progress

As follows Fig. 9 (which depicts the solubility of product of reaction NaBO_2), cited by Garrett [28], the amount of NaBO_2 is about 18%wt. at 18°C (temperature of which the catalytic reaction was initiated). After 30 minutes of the catalytic reaction, the temperature of solution was about 22°C (having an amount of NaBO_2 of about 22%wt.). In this case, some water of reaction is utilized to generate Sodium metaborate tetrahydrate ($\text{NaBO}_2 + 4 \cdot \text{H}_2\text{O}$).



Figures 7 and 8 - Hydrogen production utilizing CoO and result of the reaction utilizing this catalyst.

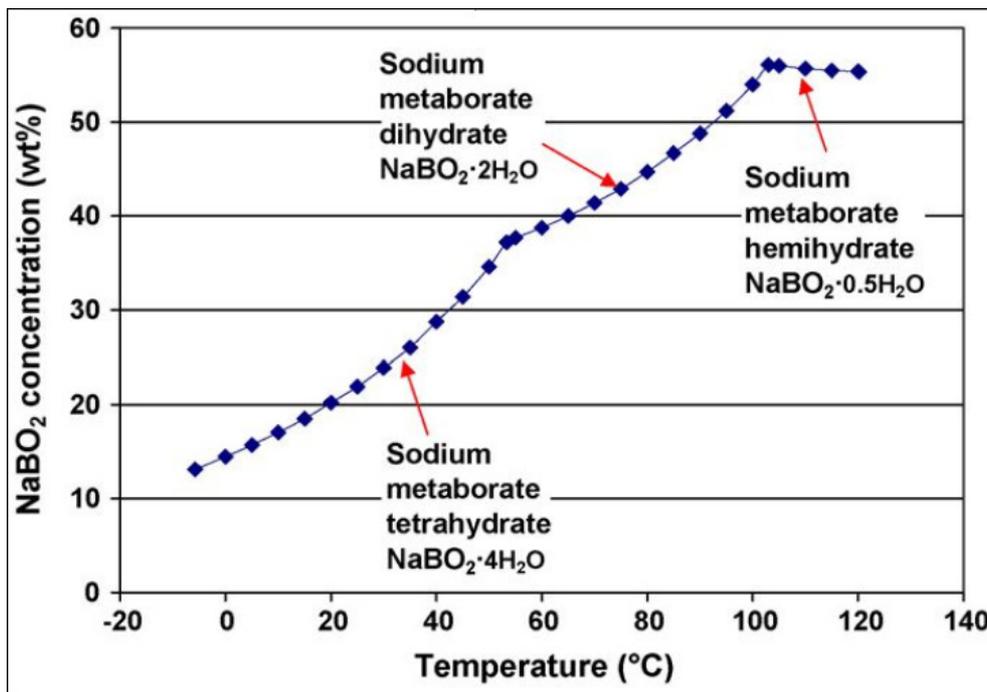


Fig. 9 - Diagram of solubility of NaBO₂ in water (Garrett [28]).

It could be also suggested a study to determine conditions where disintegration of catalysts could occur. These conditions are the fractions of reactants and the reaction temperatures. Despite of probable increase of hydrogen production rate in the case of disintegration of catalysts, this generally must be discarded (or recycled), beyond to contain a high amount of products of this reaction such as NaBO₂. This phenomenon must be avoided because the accumulation of product of reaction in the pores contributes to diminish the surface area of catalyst that hence contributes to diminish the catalytic activity.

Generally the disintegrated catalysts are in powder, which becomes its separation in the solution more difficult, especially in continuous flow systems. The suspended catalyst in the solution has also the trend to aggregate, especially when at high concentrations (Patel et al. [29]).

3 RESULTS OF HYDROGEN PRODUCTION

The efficiencies and the times of reaction (after first and fifth applications of solution) are in the Table 3. The evolution of hydrogen production is depicted in the Fig. 10.

In the first application of solution, the greatest hydrogen production rate and the greatest hydrogen volume production in comparison to results obtained after fifth application of solution were detected.

Table 3: Generation efficiency and time of hydrogen production:

	Efficiency (%)	Time (min.)
In the 1 st application	99.2	60
From 1 st to 5 th application	95.1	190

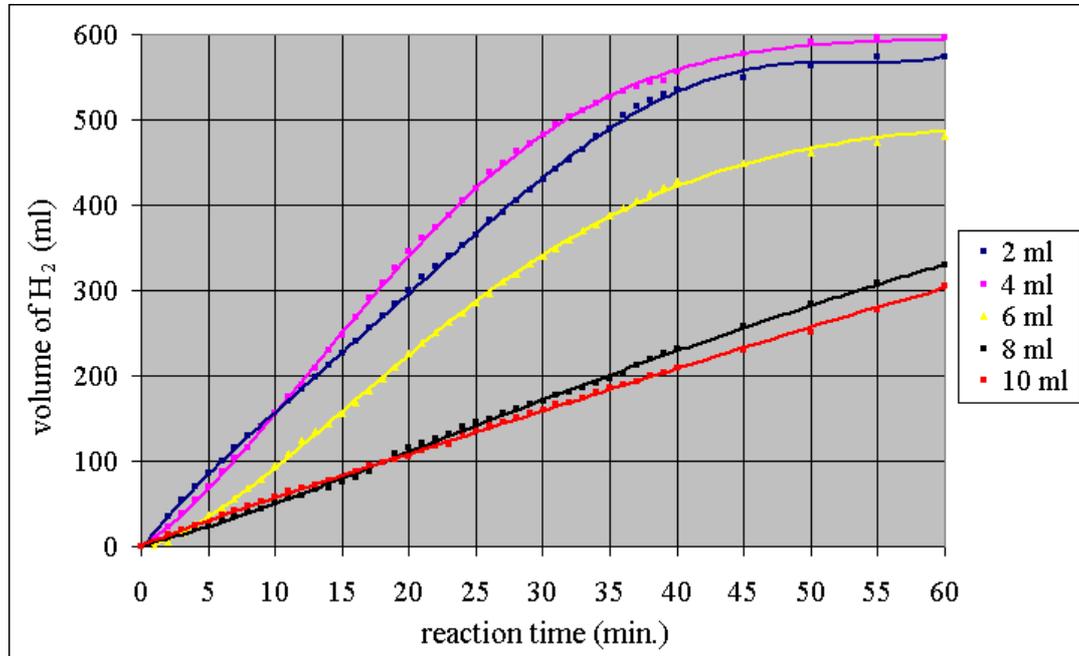


Figure 10 - Volumes of hydrogen production in the first up to fifth time when the solution was applied

In subsequent applications of solution, it was verified that hydrogen production ended after greater periods of time, having lower and more stable hydrogen production rates. The lower hydrogen production rates are due to decrease of contact area of catalysts, whose pores are filled by solid products of reaction. This phenomenon is generally observed in other experiments about hydrolysis of NaBH_4 , independently to the utilized catalyst utilized, temperature of reaction and fraction of reactants.

The work developed by Zhang et al. [16] also shows the degradation of utilized catalysts in function of time. However, in this work, the solution is utilized at continuous flow. The reaction of hydrolysis to hydrogen generation was performed at room temperature (18 to 20°C).

As seen in the Fig. 10, utilizing catalysts containing CoO , the produced hydrogen volume after first application of solution was lower than production after second application.

The permeability capacity of solution at each catalyst also contributes to the variation of hydrogen production rate. In this case, the capacity of permeability of solution attained its highest level after second application of solution.

This phenomenon is similar to observed phenomenon in the depicted work by Kim et al. [23], which utilized a catalyst containing nickel ("Filamentary Nickel with SBR"). Additionally, only in this work the description of hydrogen production applying various times the studied solution was encountered, as seen on this work.

In this work the measurements of generated hydrogen volume by the time, amount of catalyst, and amount of NaBH_4 were obtained. Only in the work developed by Peña-Alonso et al. [20] similar measurements were obtained. In this case volumes of produced hydrogen by the time, amount of catalyst, and molar concentration of NaBH_4 were obtained.

The comparisons among hydrogen specific volumes produced in this and specific productions cited in other works (seen in the references) are depicted in the Figs. 11 a 13. In the Fig. 11, the hydrogen production by the time of production and amount of utilized catalyst is considered. This measurement could be utilized to determine the best conditions of catalysis, to get the greatest

hydrogen production rates. More details of results could be sought in the Fig. 12. There, are depicted experiments where the lowest rates were registered. Its values are approximated. However the encountered results in these figures do not show the influence of reactant NaBH_4 in the catalysis, which would permit evaluating the performance of experiments more accurately. The great differences among the different registered experiments in the Figs. 11 and 13 diminished due to the insertion of amount of NaBH_4 , because an additional hydrogen volume could be simply produced with the additional insertion of this reactant.

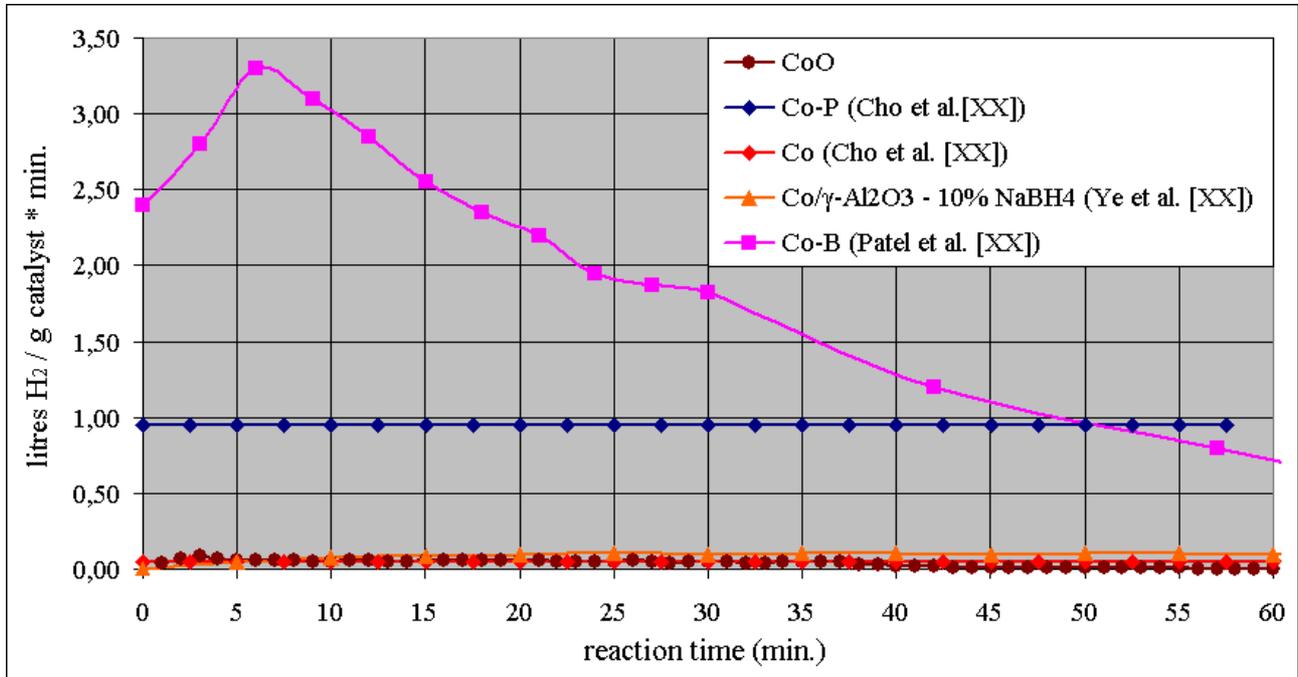


Figure 11 - Specific volumes of hydrogen production utilizing catalysts containing Co by the time.

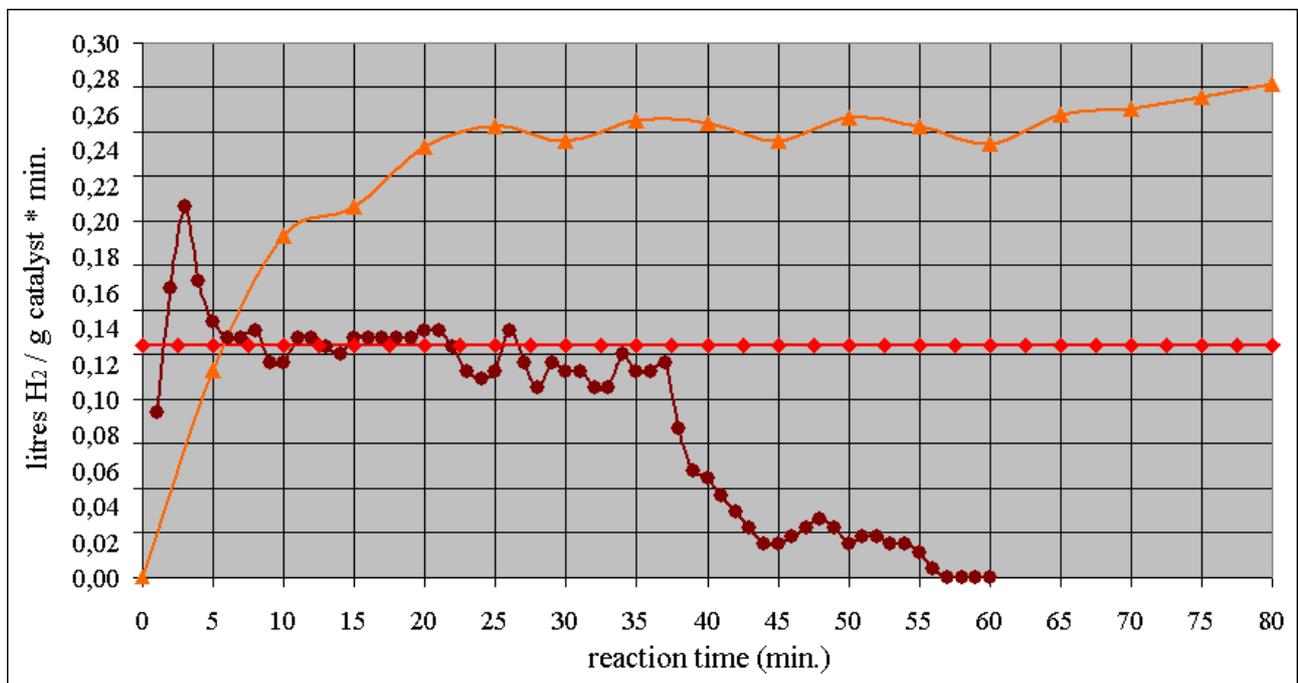


Figure 12 - Specific volumes of hydrogen production utilizing catalysts containing Co by the time. A more detailed version of the previous figure.

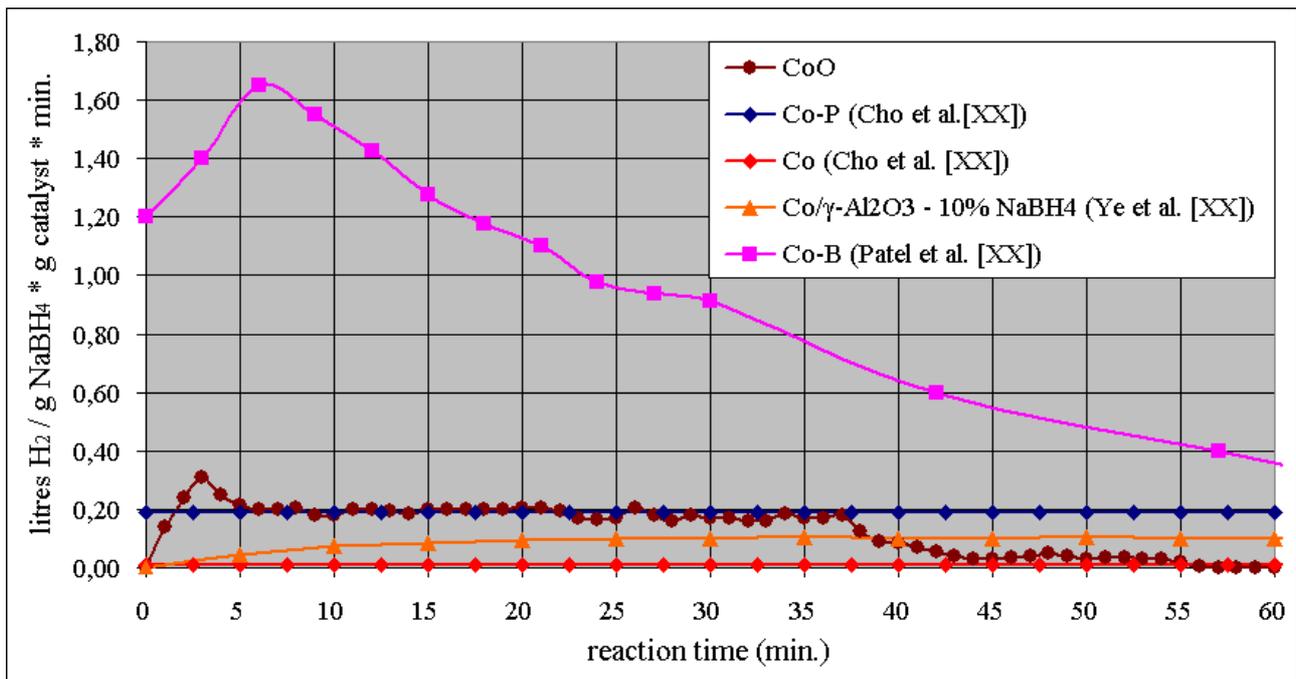


Figure 13 - Specific volumes of hydrogen production utilizing catalysts containing Co by the time.

Obviously a lower hydrogen volume is produced if lower amount of catalysts and (or) lower amount of active material are applied such as CoO. However, depending on reaction conditions, greatest specific volumes of hydrogen could be encountered, resulting in lower costs of generation because, in some catalysts high-cost materials could be encountered, especially noble metals such as platinum. Major specific volumes of hydrogen could also generate with the insertion of solutions containing lower concentrations of NaBH₄ due to cited items previously, guaranteeing lower costs of production.

In contrary to the registered rates in the Figs. 8 and 9, in the Fig. 10 it was cited that the depicted experiment in this work registered the greatest hydrogen production rates, with exception of the obtained results in a depicted experiment by Patel et al. [29]. In near future experiments utilizing lower catalysts and lower amount of NaBH₄, could be performed, guaranteeing higher specific volumes of hydrogen and hence, lower costs of hydrogen production.

The findings about the catalysts, the compositions of utilized solutions, the greatest hydrogen production rates, and their efficiencies production are depicted in the Table 4.

After 60 minutes of reaction, in the depicted experiment in this work, an counted theoretical efficiency was about 99%, the greatest encountered efficiency among the experiments that utilized catalysts containing Co.

In the experiment depicted by Patel et al. [29], as seen on the Figs. 8 a 10 a major hydrogen production rate was registered. However, the composition of reactant solution was different compared to utilized compositions in registered experiments registered in this and in other works. Among the works where solutions containing 5 to 10%wt. NaBH₄, were utilized, the greatest hydrogen production rate was attained in the depicted experiment in this work.

4 CONCLUSIONS

The hydrolysis of NaBH₄ for hydrogen generation is an effective mean of high-purity hydrogen generation. This process does not require external heat sources to develop the reactions, minimizing the costs and becoming the process easier and more practical.

Differences among volumes of generated hydrogen and among hydrogen production rates were observed between the studied catalyst and cited catalysts in other works.

In the Fig. 3 the behaviour of temperatures utilizing the studied catalyst were depicted. The greatest temperatures were registered when the greatest hydrogen production rates were registered, that is, in the first minutes of reaction.

Table 4: Efficiency and time of hydrogen production:

	Catalyst:	Support:	Amount of NaOH (%wt.):	Amount of NaBH ₄ (%wt.):	Temperature (°C):
1	CoO	-	10	10	25
2	Co-P	-	1	10	30
3	Co	-	1	10	30
4	Co	γ-Al ₂ O ₃	5	10	30
5	Co	γ-Al ₂ O ₃	5	5	30
6	Co	γ-Al ₂ O ₃	10	5	30
7	Co-B	-	5	1	25
8	Pt (10%)	carbon	10	10	25
9	Pt-Ru (10%)	carbon	10	10	25

	Highest production rate (l _{H2} / g _{cat} * g _{NaBH4} * min.):	Efficiency of hydrogen production (%):	Time of production (min.):	Reference:
1	0.31	99	60	In this work
2	0.19	3.8	60	Cho et al. [30]
3	0.01	0.4	120	Cho et al. [30]
4	0.11	15*	80	Ye at al. [31]
5	0.21	31	80	Ye at al. [31]
6	0.29	37*	80	Ye at al. [31]
7	1.15	95	250	Patel et al. [29]
8	0.95	92	130	Souza et al. [32]
9	1.05	87.5	230	Souza et al. [32]

* Approximated values

A suggestion to a future study is a development of other techniques of catalysts production to obtain more-resistant materials and diminishes dispersion of some catalytic material, beyond to diminish the possibility of disintegration. According to the work developed by Xia et al. [24], which utilized catalysts containing Ru, the major amount of NaBH₄ in the solution could contribute to disintegrate totally a catalyst, which in this case occurred as soon as the solution contained 20%wt. NaBH₄.

The possibility of utilizes a smaller amount of CoO with the objective to develop hydrolysis of NaBH₄ at major hydrogen production rates could be also investigated. However a major amount of a determined catalyst would be necessary if major volumes of hydrogen production were necessary.

The investigation about influence of this catalyst with a continuous flow of solution application to evaluate the behaviour of hydrogen production is also suggested, an item widely cited in various works.

In this work it was verified that catalysts containing CoO are responsible for major hydrogen production rates, and major theoretical efficiency of hydrogen production, showing its technical viability. However, more investigations must being performed to evaluate the motives that contribute to diminish the efficiency of hydrogen production as soon as additional volumes of reactant solution are applied in the catalyst.

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SBR = Styrene - butadiene rubber