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Application of Liquid Nitrogen Cold Trap for Purification of Hydrogen Gas Stream Generated from $NaBH_4$

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Abstract: The feasibility of using liquid nitrogen cold trap (LNCT) for the removal of water vapour and alkaline mist from the hydrogen gas stream which is generated from the catalytic and acidic decomposition of sodium borohydride is investigated. Practically, the target application is mobile fuel cells based on hydrogen production from storage in chemical hydrides. The LNCT would be used as a one step purification method with less cost and space requirements instead of applying the conventional purification techniques. Two catalysts were investigated for the production of hydrogen from the aqueous solution of $NaBH_4$ in a small scale packed bed reaction column. The hydrogen generated from the catalytic decomposition of $NaBH_4$ was accompanied by limited quantity of water vapour and alkaline mist. Nonetheless, higher quantities were generated when applying the acidic decomposition of $NaBH_4$ and consequently the utilization of LNCT for H_2 purification has proved useful and lead to a reduction in the content of these impurities; thereby the concentration of hydrogen in the outlet stream has increased.

Key words: Solid state hydrogen storage, hydrogen generation from sodium borohydride, liquid nitrogen cold trap.

1. Introduction

In the efforts to reduce CO_2 emissions, hydrogen has been remarked as the most favorable clean alternative to fossil fuels because it holds the greatest heating value per mass of the entire chemical fuels and can be generated from various energy resources [1-2]. Because hydrogen does not store well, it is more efficient to integrate the production process with the consumption (e.g. vehicle engine) which can offer enormous potential for vehicular and other portable applications with high efficiency and zero emissions [3]. However, weight and volume of on-board hydrogen storage system is limited by the standard regulations (target storage capacity of 5.5 wt% hydrogen by 2015 according to U.S. department of energy). Several methods such as compression, liquefaction, adsorption on activated carbon and carbon nanotubes or alloys have been tried so far to store the hydrogen in different ways [4]. Nonetheless, none of these solutions proved useful for the portable applications since they cannot provide a practical hydrogen storage conditions with sufficient volumetric and gravimetric efficiency and thermodynamic stability. Moreover, the related safety issues as well as highly operating costs are also important obstacles against their application. Other techniques for hydrogen storage were based on using the liquid fuels or solid state hydrogen storage. In practice, the liquid fuels (e.g. methanol, ethanol and gasoline) cannot be utilized for fuel cell applications because it requires reforming processes with high temperatures as well as other problems which are caused by the carbon monoxide which accompanies the hydrogen generation [5-6]. On the other hand, the solid state hydrogen storage alternatives (metal or chemical hydrides) were found to be more feasible for the application of fuel cells since they have great

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potentials to store hydrogen effectively and safely [7]. Generally speaking, both of solid state forms are safe handling methods; nevertheless, metal hydrides (e.g. sodium-aluminum hydrides) were demonstrated to offer low storage capacity compared with the chemical hydrides. Moreover, the metal hydrides required to be processed at high temperature working levels which are not favorable for the fuel cell applications [8]. On the other hand, chemical hydrides were known to have greater hydrogen absorption potential than the conventional metal hydrides; thus, hydrogen can be generated effectively and safely on board from the controlled hydrolysis reaction of chemical hydrides (e.g. $NaBH_4$, KBH_4, LiH or NaH).

In principal, the chemical hydrides are known to incorporate easy handling and safe transferring in liquid phase as well as considerable hydrogen content (e.g. $NaBH_4$ has 10.7% theoretical hydrogen content) compared with other options [9]. Practically, the hydrogen can be generated from $NaBH_4$ either by thermolysis or by hydrolysis reactions. However, as shown in Eq. (1), the hydrolysis reaction was reported to have specific features such as non-violent slow kinetics and the ability to stop the reaction through introducing small amounts of sodium hydroxide as a stabilizer [10]. This identity has been considered to be a very important target in the applications of on-demand fuel cells.

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \qquad (1)$$
$$\Delta H = -212.1 \text{ kJ/mol (at 25 °C)}$$

Another unique advantages are: (a) the ability to accelerate the reaction in acidic medium or in presence of a catalyst which gives rise to control the hydrogen production on-demand and meanwhile keeping the $NaBH_4$ solution stable for a long term storage; (b) the reaction can be initiated at low temperature; (c) the side product of sodium metaborate ($NaBO_2$) which is environmentally friendly can be recycled to produce $NaBH_4$. All above mentioned features supported the adoption of $NaBH_4$ hydrolysis system as a promising safe and fast response source for demand of hydrogen generation system in the field of fuel cells developments [11].

It should be mentioned that in other applications such as using $NaBH_4$ as a reducing agent in the fields of analytical chemistry, the massive quantity of the hydrogen generated in the system has been found to be real obstacle because it leads to disturb the consistency of plasma in the spectro-chemistry devices (e.g. ICP-OES, DBD-OES). This problem is observed in a parallel study followed the work [12], when $NaBH_4$ was applied in the prescribed system to determine inorganic mercury and other heavy metals. The hydrogen generated in the system leads to disturb the plasma and consequently affected the recorded spectral signals. In order to adopt the borohydride system to generate hydrogen for a commercial use, it is essential to overcome several drawbacks addressed in the literature other than the cost of $NaBH_4$. System limitations were attributed to particular shortcomings such as catalyst durability, product crystallization and purification of the generated hydrogen before use in the fuel cell. In practice, the hydrogen should be purified effectively before entering the fuel cell. Otherwise, it may cause serious damages to the cell and its performance [8]. The most dominant accompanying residues which would be generated with the hydrogen are the water vapour, which might also carry unreacted $NaBH_4$, by-product $NaBO_2$ and NaOH within it. It has been mentioned that the operation of fuel cell based on $NaBH_4$ system could be disrupted by the presence of alkaline substances ($NaBH_4$, $NaBO_2$, NaOH) in the mist from the solution [8]; however, the water vapour itself is detrimental for operation of the polymer electrolyte membrane fuel cells which are designed to operate at low relative humidity [13]. This tendency would be more obvious in the system of highly generation rate, in which the traditional gas-liquid separator cannot be effective enough to remove all the water vapour and the accompanying mist from the hydrogen stream.

According to the literature, only few attentions have been given to the hydrogen purification so far. In most

previous studies, researchers just employed a gas-liquid separator to remove the water from the hydrogen without focusing on the purification efficiency. A unique study in this sense was conducted by Zhang et al. [14], in which multiple purification stages were applied. In their work, a compact brazed-plate heat exchanger based on a chilled water system was used to condense the water vapour in the hydrogen stream. The outlet stream was directed into a second gas-liquid separator, and finally the hydrogen was passed through a silica gel-based desiccant dryer to remove the remaining water vapour in the stream. Although good purification efficiency, the applied methodology was found to be irrelevant for fuel cell applications due to many reasons such as high energy cost and large space requirements. Therefore, it is worthwhile to contemplate another purification technique which aims to achieve high purification efficiency with low operating cost. One efficient purification strategy could be applied by utilizing a sophisticated refrigeration apparatus which could maintain cryogenic temperature for separation, increasing energy demand and decreasing gravimetric hydrogen storage density of the system, the latter one is already a major issue as identified by DOE [7].

In this paper, the performance of one-step purification system based on a U-tube liquid nitrogen cold trap (LNCT) as alternative for the conventional multiple stages technique was investigated. The cryogenic separation based on LNCT is expected to achieve the separation of water vapour and the undesired alkaline mist accompanying the hydrogen stream with high efficiency. To the best of our knowledge, the application of cryogenic separation for the targeted system has not been tried previously. This paper also discussed the experimental parameters required for the best system performance such as the chemicals concentrations, catalysts activities and their durability's ones. This paper is organized as follows: In Section 2, the experimental methodology, the equipments and the reagents used are discussed, whereas the results are discussed in Section 3 and the conclusions are summarized in Section 4.

2. Experiment

The main target of the current work was aimed to test the feasibility of using a U-tube liquid nitrogen cold trap for purifying the hydrogen generated from the catalytic and acidic hydrolysis of $NaBH_4$ system. It is expected that a U-tube liquid nitrogen cold trap packed with a suitable adsorbent material would be effective to purify the hydrogen stream in one single step. Since the boiling point of hydrogen as low as -252.87 °C, it would pass through the U-tube which is immersed in liquid nitrogen (boiling point of -196 °C), whereas other impurities in the hydrogen stream would be condensed and trapped on the adsorbent material inside the tube. Therefore, a water and alkaline mist removal from the hydrogen stream with high efficiency would be achieved by only using the cold trap. This approach would not only eliminate the requirements for additional equipments and hence space, it would also increase the overall system efficiency by decreasing the total energy consumption and the cost. Therefore, it is proposed that utilization of liquid nitrogen cold trap would increase the potential of the system for fuel cell applications.

A simple hydrogen generation system from $NaBH_4$ solution hydrolysis on a catalyst in a packed bed column was to meet the targets of the project. It was planned to produce the hydrogen in controlled amounts. Therefore, apparatus choice and design were based on a small-scaled study as a first try. The experimental setup designed for the current study is illustrated in Fig. 1.

A glass tube (28 mm length and 10 mm ID) was used to reside the catalyst in order to act as a packed bed reactor. A peristaltic pump with a calibrated feed rate of 1.15 mL/min (Williamson Manufacturing Company, UK) was used to feed $NaBH_4$ solution from the fuel container. The generated hydrogen and the

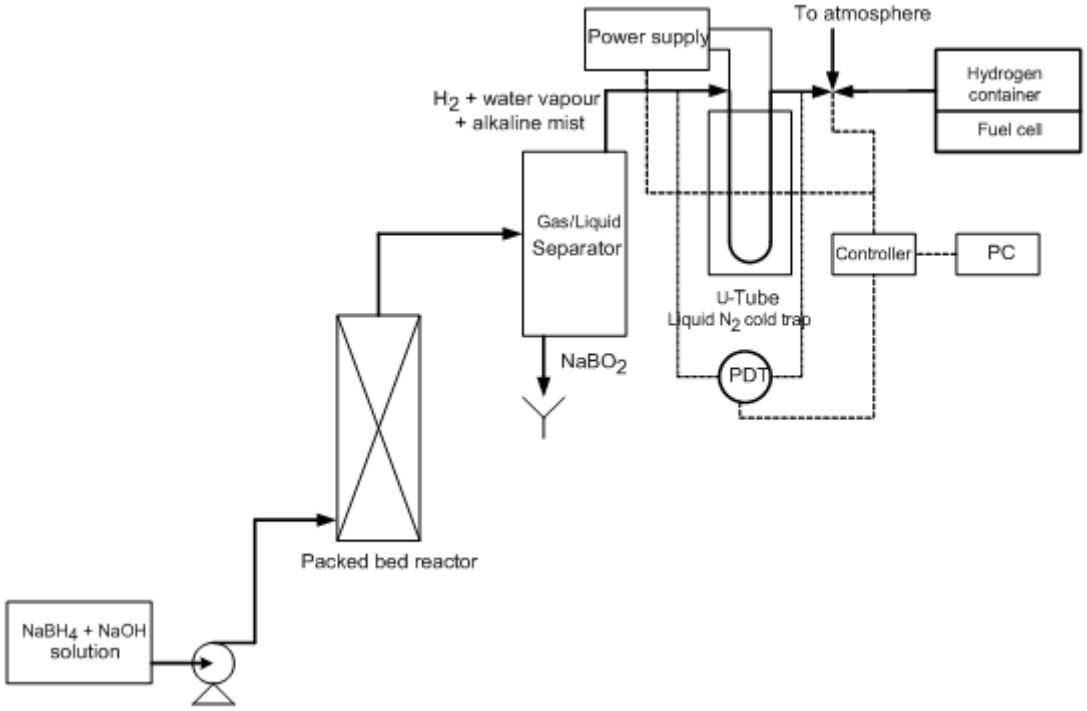

Fig. 1 A process flow diagram which illustrates the proposed system.

accompanying water vapor and other residues were then directed into a gas-liquid separator made of 50 mL glass bottle which was provided with a plastic lid and two glass tubes which were served as an inlet and outlet. The separated hydrogen and other vapour species were forwarded into a U-tube liquid nitrogen cold trap which was used to retain the water vapour as well as the alkaline mist with aid of adsorbing media (Chromosorb G/AW-DMCS 45-60 mesh, purchased from Sigma Aldrich). A borosilicate U-tube (60 cm length and 6 mm ID) passed through a lid made of PTFE was immersed in a Styrofoam container (3 L volume) which was used to reside the liquid nitrogen. The evaporated nitrogen was intended to release from LNCT through a tube opened to the atmosphere; nonetheless, the lid was also provided with a pressure safety valve set at 0.5 barg and a pressure gauge for safety reasons. The U-tube was wrapped with electric rope heater which was used to heat the tube when applying the purging stage.

The whole system was aimed to be operated and controlled through (Arduino-mega) microcontroller run by PC software. The concept is to control the rope heater and the three way valve, in order to associate a free path for passing the hydrogen out of the cold trap as shown in Fig. 1. Accordingly, the electric rope was supplied with pulses of 230 V AC in sequence form according to the requirements. As soon as the cold trap is being clogged with the condensed/solidified residues (this is indicated through a differential pressure transducer), the electric field passes through the rope heater. At the same moment, the three way valve should close the path to the hydrogen container and release the stream which comes from the cold trap to the atmosphere. In order to integrate the system, the fuel cell could be supplied from the hydrogen container attached to it; this is to ensure availability of enough hydrogen through the regeneration step.

All used chemicals were a sort of analytical reagent grades. Sodium borohydride powder (> 98%) and sodium hydroxide pellets (> 97%) which were purchased from (Sigma Aldrich) were used to prepare the solutions according to examined concentrations by using distilled water. Two types of catalysts were

examined in the experiments; non-homogeneous shape cobalt pieces with a size distribution (0.85-4.76 mm) which were purchased from Sigma Aldrich was sieved and the smallest size pieces were used. Another catalyst, cobalt boride powder which was purchased from Sigma Aldrich as a mixture of Co_2B and Co_3B with a particle size less than 200 μm was also employed in the experiments. A glass wool was used at the top and bottom ends of the packed layer to keep the catalyst inside the bed.

The analysis of the outlet gas stream from the gas-liquid separator was conducted through a gas chromatography (GC) device (Varian 3009) which was provided with a thermal conductivity detector (TCD). The analysis through TCD has proved useful for the detection of water vapour and hydrogen with a wide range of concentrations. Other analysis was conducted through another gas chromatography device (Varian CP-3800) in order to investigate the presence of other residues other than the water vapour and hydrogen. All the tested samples were collected by using gas sampling tubes and injected to the GC through a proper syringe.

3. Results and Discussion

The efficiency of the proposed system was assessed according to couple of parameters; the hydrogen generation rate as well as LNCT performance. The hydrogen generation rate was evaluated by testing two catalysts and applying different concentrations of $NaBH_4$ in the feed solution. A water displacement method was used to determine hydrogen generation rate. The first experimental set was conducted to interpret the optimal concentrations of chemicals which required for stable operation. Five concentrations of each $NaBH_4$ and NaOH were examined according to interpret the effects on system performance. The results are shown in Figs. 2 and 3, which indicate the values of 10 wt% $NaBH_4$ stabilized with 1 wt% NaOH were found to be appropriate for the

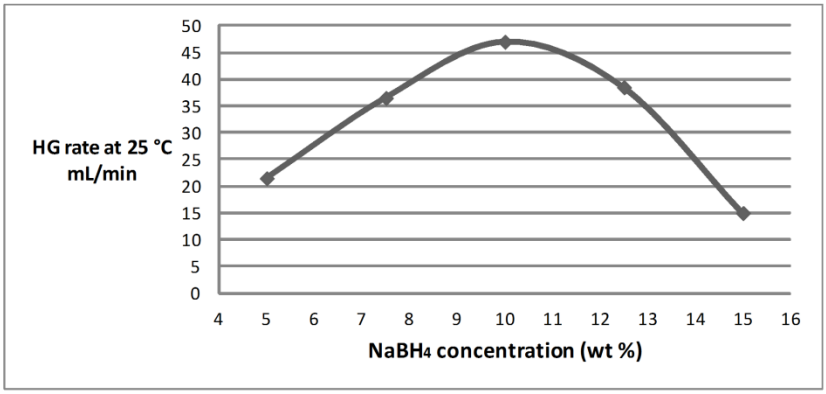

Fig. 2 The effect of $NaBH_4$ concentrations on HG rate at 1 wt% NaOH and applying cobalt pieces as a catalyst.

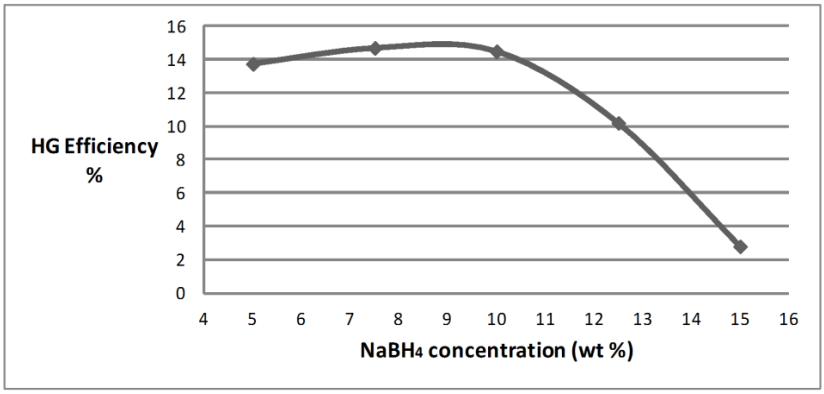

Fig. 3 The effect of $NaBH_4$ concentrations on HG efficiency at 1 wt% NaOH and applying cobalt pieces as a catalyst.

best system performance when applying the cobalt pieces as a catalyst. On the other hand, increasing NaOH concentration has also ameliorated the hydrogen generation rate and efficiency as illustrated in Figs. 4 and 5. The estimated values were found to be compatible with the findings of Liang et al. [1] and Hung et al. [15] who recommended the same values for the optimum hydrogen generation rate. Nonetheless, it is also reported that stabilizing the fuel solution with higher concentrations of NaOH is not preferable and may lead to a significant reduction in the hydrogen generation rate. Most probably, the reason could be attributed to the alkaline medium which is not preferable for the used catalysts and may reduce their activities. Another reason would be the formation of settlements on the catalyst surface which produced from the by-product crystallization and might lead to block the catalyst voids on the surface.

The hydride generation (HG) efficiency was calculated using the hydrogen generation rate and reaction stoichiometry, according to Eq. (2):

$$Efficiency\ (\%) = (real\ HG\ rate/theoretical\ HG\ rate) \times 100 \quad (2)$$

where: *real HG rate* is experimentally estimated (mL/min), whereas *theoretical HG rate* is estimated according to Eq. (1), in which 4 moles are produced from the hydrolysis of one mole of $NaBH_4$. The estimated amount of the hydrogen was converted to a volume flow rate by considering the ideal gas law which is applicable for the described reaction.

On the other hand, the effect of fuel solution inlet temperature on HG efficiency was also investigated by applying four inlet temperatures. The results show that increasing the temperatures of the inlet solution from 25 ^{o}C to 50 ^{o}C lead to a slight increase in HG efficiency. However, no further increase was observed

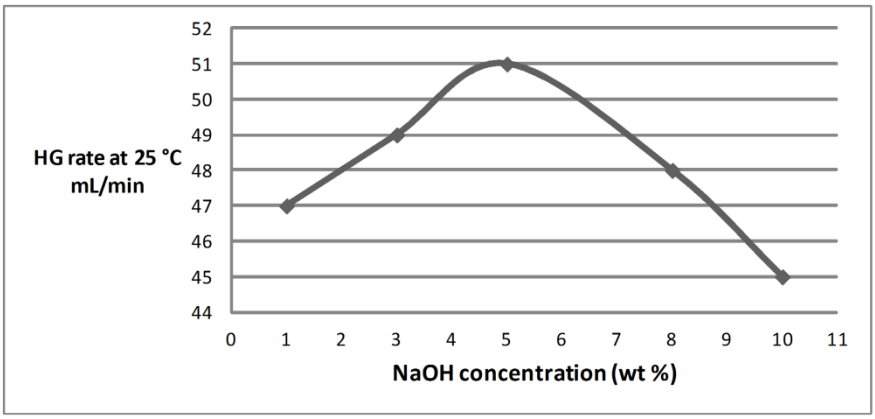

Fig. 4 The effect of NaOH concentration on HG rate at 10 wt% $NaBH_4$ and applying cobalt pieces as a catalyst.

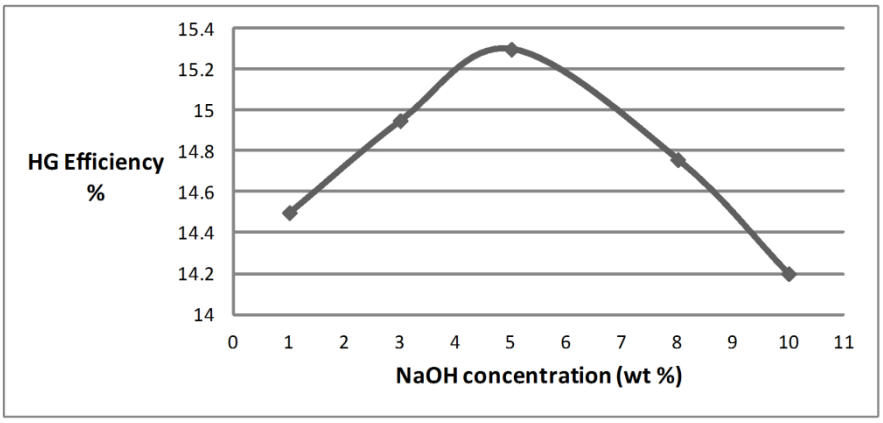

Fig. 5 The effect of NaOH concentration on HG efficiency at 10 wt% $NaBH_4$ and applying cobalt pieces as a catalyst.

when the temperature increased from 50 ^oC to 70 ^oC as illustrated in Fig.6. The increase in the HG efficiency could be attributed to a relatively lower initiation time that is required to commence the reaction of the heated fuel solution which is compared with the feed solution at normal temperature. The increase of the temperature has consequently result in a greater generation rate; nonetheless, heating the fuel solution to higher temperatures has probably caused a negative effect on the catalyst due to by-product crystallization which consequently results in blocking the voids of the catalyst and reduces the activity.

The performance of two catalysts which were employed in this study was compared with feed solution containing 10 wt% $NaBH_4$ stabilized by 1 wt% NaOH. Using lower concentration of NaOH other than the optimum (5 wt%) was aimed to overcome the formation of any possible settlement from by-product crystallization. Table 1 illustrates a comparison between the performances of two examined catalysts, which shows a reduction in the activity proportional to a reduction in the hydrogen generation rate after few experimental runs. The results clearly indicate that the cobalt boride was found to be more active in the first experiment; nevertheless, its exhaustion was observed to occur in a relatively lower operation time compared with the cobalt pieces. Moreover, the cobalt pieces were found to be more easily handling for recovery purposes. The reason for a significant reduction in cobalt boride activity could be attributed to a blockage of the particles voids on the surface by the formed by-product. The other parameter which might also contribute to the fast exhaustion of cobalt boride is the catalyst support which was applied in the current work.

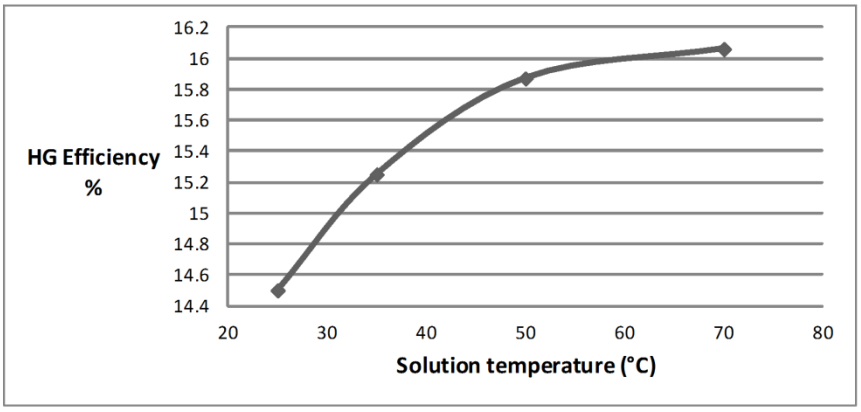

Fig. 6 the effect of increasing the temperature of the inlet solution on HG efficiency at 10 wt% $NaBH_4$ and 1 wt% NaOH and using cobalt pieces as a catalyst.

Table 1 Summary of the Catalysts Performance.

Performance of catalysts	Cobalt pieces	Cobalt boride
Form of catalyst	Non homogeneous shape	Powder ≈ 200 μm size
Amount of catalyst used in the packed bed	68.62 g	17 g
Catalyst density in the reactor	3.12 g/mL	3.4 g/mL
HG rate in the first experiment	47.36 mL/min	301.01 mL/min
HG rate after catalyst exhaustion	19.35 mL/min	19.30 mL/min
HG rate per gram of catalyst in the first experiment	0.69 mL/min/g cat.	17.71 mL/min/g cat.
HG rate per gram of catalyst after exhaustion	0.282 mL/min/g cat.	1.135 mL/min/g cat.
Test period before catalyst becoming exhausted	220 min	14 min
HG efficiency in the first experiment	15.06%	98.48%
HG efficiency after catalyst exhaustion	6.32%	6.32%
Amount of fuel solution consumed during the test period	250 mL	16 mL
Catalyst recovery, wash and re-use	Very easy	Difficult

Practically, the catalyst support was also considered an effective operational parameter, where a proper support for the catalyst in a powder form is essential to prevent the significant catalyst degradation and to improve the catalyst durability.

Accordingly, the catalyst with low particle sizes is not recommended for extra work even with very high performance. The cobalt boride would prove useful and become more reliable when using bigger particle sizes instead of the powder form.

Although lower activity and because of the stable performance, the cobalt pieces were used in the experiments conducted for evaluating the purification efficiency which obtained from utilizing the liquid nitrogen cold trap. The fuel solution was prepared by using 10 wt% $NaBH_4$ stabilized in 1 wt% NaOH. Upon injecting the fuel solution through the reactor, several samples were collected from two sampling points, the first point was located directly at the outlet stream of GLS whereas the second sampling point was located at the outlet stream from the cold trap. Three samples were collected from each point and the average of readings has been considered. The results are illustrated in Table 2 which shows a slight increase in the concentration of hydrogen in the outlet stream from the cold trap, which occurred due to a reduction in the impurities. As shown in Table 2, the analysis results have included the pure hydrogen percentage as well as the water percentage which is considered to be proportional to the pure water as well as the alkaline mist.

Table 2 Comparison between the contents of the samples collected before and after LNCT (by applying the catalytic decomposition of $NaBH_4$).

Contents of samples	Before LNCT	After LNCT
Hydrogen	99 .42%	99.71 %
Water vapour	0.58 %	0.29 %

The chromotogram is recorded for the purified stream after passing the LNCT, as shown in Fig. 7. Generally speaking, the results have clearly indicated that a very low amount of water vapour (including the alkaline mist) was generated with the hydrogen which is practically considered beneficial for the whole system performance. The limited quantity of the generated water vapour has led to operate the cold trap for the whole experiment period (≈ 5 min.) without a need for heating up the U-tube via the controller. Despite the fact is that a limited quantity of water vapour is generated, the cold trap acts to purify the hydrogen into such extent from water and other residues content, and this is clearly shown by the increased hydrogen percentage in the outlet stream from LNCT as well as a reduction in the water vapour percentage. Because of limited residues accompanied the hydrogen generation, the performance of the cold trap could not be evaluated accurately. Nonetheless, the effect of LNCT would be more obvious when higher

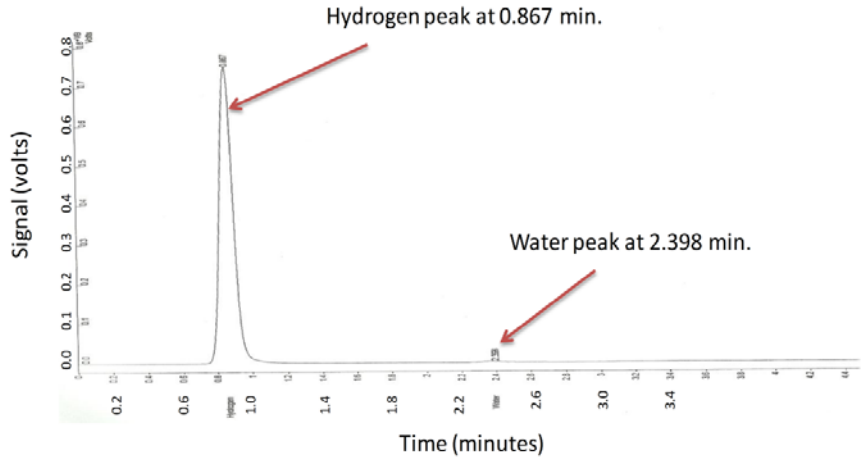

Fig. 7 The GC chromatogram for a sample collected after passing LNCT upon the catalytic decomposition of $NaBH_4$.

quantities of water vapour is generated based on large scale borohydride system, which is principally required to operate fuel cell for practical applications.

In order to assess the efficiency of cold trap with a stream containing higher quantity of water vapour and alkaline mist, an acidic decomposition of $NaBH_4$ was conducted by the reaction system which was described in our previous work [12], as illustrated in Fig. 8.

The HCl solution (1.5 M) and $NaBH_4$ solution (2% m/v stabilized by 0.5% m/v NaOH) were injected through two peristaltic pumps, PP1 and PP2 working at 2.8 mL/min feed rate. The mixed solutions through a tee junction were directed into a helical reaction coil (1 m length, 2.5 mm ID silicon tube) and then into a gas/liquid separator (GLS). The hydrogen gas stream which is accompanied by traces of water vapour and alkaline mist has been carried with aid of carrier gas (helium) into LNCT through a (20 cm length, 2.5 mm ID silicon tube). Low concentration of chemicals has been applied as mentioned above, this is to estimate the real efficiency of LNCT when lower hydrogen rate is generated in the system. The analysis results have shown a reduction in the water content by more than 5%, as illustrated in Table 3.

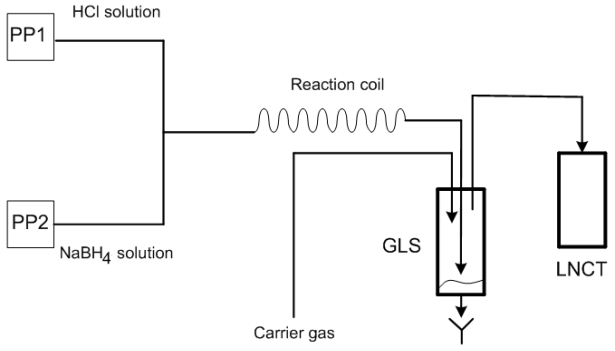

Fig. 8 a schematic diagram illustrating the reaction system used for the acidic decomposition of $NaBH_4$.

Table 3 Comparison between the contents of the samples collected before and after LNCT (by applying the acidic decomposition of $NaBH_4$).

Contents of samples	Before LNCT	After LNCT
Hydrogen	93 .12 %	98.76 %
Water vapour	6.88 %	1.24 %

4. Conclusions

Despite the fact is that low quantities of water vapour and alkaline mist generated in the examined small scale catalytic borohydride system, the application of the proposed liquid nitrogen cold trap has proved useful for purifying the hydrogen stream from a relatively higher quantity of impurities which generated from the acidic decomposition of $NaBH_4$ into such extent. This result would become more obvious when applying the large scale borohydride systems with higher flow rates of feed solution. The proposed system would be utilized as a one-step purification instead of expensive and bulky multiple stage purification system for the practical applications. Other experimental investigations were conducted to assess the performance of two catalysts (cobalt pieces and cobalt boride). The results have shown a stable performance and long time before exhaustion when cobalt pieces are applied which are compared with the cobalt boride. Nevertheless, using cobalt boride in other forms instead of the powder form would reduce the possibility of the catalyst exhaustion and lead to higher catalyst durability as well as higher hydrogen generation efficiency. It is also concluded that 10 wt% $NaBH_4$, 1 wt% NaOH and 50 ^oC (as a feed solution temperature) are appropriate for better catalytic system performance. The feasibility of LNCT would be more obvious when large scale borohydride system is applied, which is planned for future work.

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