HYDROGEN STORAGE VIA SODIUM BOROHYDRIDE

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MASTER OF TECHNOLOGY
IN
CHEMICAL ENGINEERING

Submitted by

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CERTIFICATE

This is certified that the thesis entitled **Hydrogen storage via Sodium Borohydride** which is being submitted by **Ms. Arshdeep Kaur** in partial fulfillment of the requirements for the award of the degree of **M.Tech. (Chemical Engineering)** in the Department of Chemical Engineering, Thapar University, Patiala, is a bonafide work carried out by her under my guidance and supervision and that no part of this thesis has been submitted for the award of any other degree.

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DECLARATION

I hereby declare that thesis entitled **"HYDROGEN STORAGE VIA SODIUM BOROHYDRIDE"** is an authentic record of my study carried out as requirements for the award of degree of **M.Tech. (Chemical Engineering)** at **Thapar University, Patiala**, under the guidance of **Dr. D. Gangacharyulu**, Professor, **Department of Chemical Engineering**, Thapar University, Patiala during **July 2011 to June 2012**. The matter embodied in this thesis has not been submitted in part or full to any other university or institute for the award of any degree.

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ABSTRACT

Global energy consumption is expected to rise hugely in the next decades, driven by rising standards of living and a growing population worldwide. Among the various alternative energy strategies, building an energy infrastructure that uses hydrogen as the primary carrier connecting a host of energy sources to diverse end-users may enable a secure and clean energy future.

Fuel cell hybrid electric vehicle (FCHEV) is strongly attractive as a zero emission vehicle. However, FCHEV has not been used widely by current state. One of the reasons is the construction cost of infrastructure such as hydrogen gas station is too expensive. As a solution, several high-pressure hydrogen gas tank less FCHEVs have been proposed. One of them is FCHEV fuelled by sodium borohydride ($NaBH_4$). This hydride has high energy density however the energy density of conventional system is low. Thus, a novel hydrogen gas supply system, which can improve the volumetric-and-gravimetric-density than a conventional one is also discussed in thesis.

Sodium borohydride ($NaBH_4$) has been considered most attractive hydrogen storage material for portable fuel cell applications, as it provide safe and practical means of producing hydrogen. The concentration of $NaBH_4$ should be as high as possible in order to improve energy density.

The report also emphasizes on Catalysis, Cobalt Chloride ($CoCl_2$), used to enhance the hydrolysis reaction. Therefore, taking into account that cost factor of catalyst and easy availability, $CoCl_2$ is considered as a most efficient catalyst and accordingly rate kinetics is discussed in the thesis.

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NOMENCLATURE

Symbol	Symbol description
^{o}C	Degree Celsius
kg	Kilogram
m	Meter
km	Kilometer
%	Percentage
kW	Kilo Watt
wt	Weight
MJ	Mega Joules
psi	Pounds per square inch
K	Kelvin
l	Litre
kWh	Kilo Watt hour
MPa	Mega Pascal
x	Hydration Factor
g	Grams

ABBREVIATIONS

Abbreviation	Abbreviation description
GHG	Green House Gases
CO	Carbon Monoxide
S	Sulphur
SBH	Sodium Borohydride
GC	Gas Chromatography
HGR	Hydrogen Generation Rate

CHAPTER – 1

INTRODUCTION

Interest in hydrogen as a fuel has grown dramatically, and many advances in hydrogen production and utilization technologies have been made. However, hydrogen-storage technologies must be significantly advanced if a hydrogen-based energy system, particularly in the transportation sector, is to be established [1].

As Global energy consumption is expected to rise hugely in the next decades, driven by rising standards of living and a growing population worldwide. The increased demand for more energy will require enormous growth in energy generation capacity, more secure and diversified energy sources, and a successful strategy to control greenhouse gas emissions. Among the various alternative energy strategies, building an energy infrastructure that uses hydrogen as the primary carrier connecting a host of energy sources to diverse end-users may enable a secure and clean energy future [2].

Moreover, the growing demand for the use of hydrogen energy has accelerated research for hydrogen generation and its storage for fuel cell applications. Hydrogen is being considered as a clean energy source mainly because of its advantages in overcoming problems with energy resources and in environmental issues. One of the important advantages of hydrogen fuel economy is that energy can be stored in the form of hydrogen and can be transported [3].

In general, the hydrogen economy refers to a vision of the future in which electric power will be generated not by direct combustion of fossil fuels or by nuclear fission, but by electrochemical oxidation of hydrogen in a fuel cell device. There are substantial opportunities to replace conventional power plants, whether on the grid system or in distributed power applications, with hydrogen-powered fuel cells. In addition, there is intense interest in finding replacements for fossil fuels in transportation applications. For transportation, hydrogen-fuelled internal combustion engines (ICEs) are also an option, and so this approach to hydrogen utilization is also considered part of the hydrogen economy vision anywhere as the need arises [4].

The main obstacle in the way of transition to a hydrogen economy is the absence of a practical means for hydrogen storage. For years, the goal of researchers has been to develop a high-density hydrogen-storage system that can release hydrogen at temperatures lower than 100 °C. A hydrogen economy will flourish when adequate storage technology exists, allowing people to tap and trade regional, renewable power sources. This cache of stored energy will offer viability to the full range of local and global renewable energy sources. For a hydrogen-storage system to be put into practical use, the energy density must reach a high level. For example, U.S. Department of Energy recommended that an energy density of 6.5% and 62 kg/m^3 must be achieved in order for a hydrogen storage system to be the appropriate weight and size to facilitate a fuel-cell vehicle driving a distance of 560 km. Storing hydrogen is somewhat difficult because of its low density and low critical temperature. Currently, there are a number of technologies available for hydrogen storage, such as high pressure cylinder, liquefaction, adsorption on high surface carbon materials, and metal hydrides [1].

1.1 Importance of hydrogen

Hydrogen is an energy carrier, not an energy source, meaning that it stores and delivers energy in a usable form. Hydrogen, the electrically neutral atom contains a single positively-charged proton and a single negatively-charged electron. Hydrogen is only UNIVERSAL FUEL that can power virtually all automobiles, aircrafts, spacecrafts, power plants or application, including a Coleman stove operating on a mountain top [5].

Widespread use of hydrogen as an energy source in this country could help address concerns about energy security, global climate change, and air quality. Fuel cells are an important enabling technology for the Hydrogen Future and have the potential to revolutionize the way we power our nation, offering cleaner, more-efficient alternatives to the combustion of gasoline and other fossil fuels [5].

The effective storage of hydrogen is one of the key elements of the hydrogen economy, and the chemical hydrides have been tested as hydrogen-storage materials. Among these chemical hydrides, sodium borohydride, $NaBH_4$, has been considered as the most attractive hydrogen storage material, as it provides a safe and practical mean of producing hydrogen and has high hydrogen content (10.7% wt). Although a cost-effective process for the recyclability of hydrolysis product, the conversion of metaborate to borohydride, is still lacking, the hydrolysis of sodium borohydride, is a convenient method of hydrogen generation for portable fuel cell applications. The only by product, sodium metaborate, is water soluble and environmentally benign. The reaction is very fast in the presence of a catalyst, and there is no need to supply external heat for the reaction to occur. In this context, generation of hydrogen via hydrolysis of alkaline solution of sodium borohydride is a promising method for hydrogen storage/production [5].

$$NaBH_4 + 2\ H_2O\ (\text{liquid}) \rightarrow NaBO_2 + 4\ H_2 \qquad (1)$$

1.2 Benefits of Hydrogen as an energy source:

1. Hydrogen & Fuel Cells Strengthen National Energy Security: Hydrogen and fuel cell technology have the potential to strengthen our national energy security by reducing our dependence on foreign oil. Hydrogen can be derived from a variety of domestically available primary sources, including fossil fuels, renewable, and nuclear power. This flexibility would make us less dependent upon oil from foreign countries. Hydrogen can be produced locally from numerous sources as it can be produced either centrally, and then distributed, or onsite where it will be used. Hydrogen gas can be produced from methane, gasoline, biomass, coal or water. Each of these sources brings with it different amounts of pollution, technical challenges, and energy requirements.

2. Hydrogen & Fuel Cells Reduce Greenhouse Gas Emissions: Greenhouse gases are thought to be responsible for changes in global climate. They trap excess heat from the sun's infrared radiation that would otherwise escape into space much like a greenhouse is used to trap heat. When we drive our cars, and light, heat, and cool our homes, we generate greenhouse gases. But if we used hydrogen in very high efficiency fuel cells for our transportation and to generate power, we could significantly reduce the GHG emissions - especially if the hydrogen is produced using renewable resources, nuclear power, or clean fossil technologies.

3. Hydrogen & Fuel Cells Reduce Air Pollution: The combustion of fossil fuels by electric power plants, vehicles, and other sources is responsible for most of the smog and harmful particulates in the air. Fuel cells powered by pure hydrogen emit no harmful pollutants. Fuel cells that use a reformer to convert fuels such as natural gas, methanol, or gasoline to hydrogen do emit small amounts of air pollutants such as carbon monoxide (CO), although it is much less than the amount produced by the combustion of fossil fuels. When hydrogen is combined with oxygen in a fuel cell, energy in the form of electricity is produced. This electricity can be used to power vehicles, as a heat source and for many other uses. The advantage of using hydrogen as an energy carrier is that when it combines with oxygen the

only by-products are water and heat. No greenhouse gasses or other particulates are produced by the use of hydrogen fuel cells.

4. Hydrogen & Fuel Cells Improve Energy Efficiency: Fuel cells are significantly more energy efficient than combustion-based power generation technologies. A conventional combustion-based power plant typically generates electricity at efficiencies of 33 to 35 percent, while fuel cell plants can generate electricity at efficiencies of up to 60 percent.

4.3 Applications and Uses

- Hydrogen-powered fuel cells are not only pollution-free, but also can have two to three times the efficiency of traditional combustion technologies.
- A conventional combustion-based power plant typically generates electricity at efficiencies of 33 to 35 percent, while fuel cell systems can generate electricity at efficiencies up to 60 percent (and even higher with cogeneration).
- The gasoline engine in a conventional car is less than 20% efficient in converting the chemical energy in gasoline into power that moves the vehicle, under normal driving conditions. Hydrogen fuel cell vehicles, which use electric motors, are much more energy efficient and use 40-60 percent of the fuel’s energy — corresponding to more than a 50% reduction in fuel consumption, compared to a conventional vehicle with a gasoline internal combustion engine.
- In addition, fuel cells operate quietly, have fewer moving parts, and are well suited to a variety of applications.
- Stationary fuel cells can be used for backup power, power for remote locations, distributed power generation, and cogeneration (in which excess heat released during electricity generation is used for other applications). Fuel cells can power almost any portable application that typically uses batteries, from hand-held devices to portable generators. Fuel cells can also power our transportation, including personal vehicles, trucks, buses, and marine vessels, as well as provide auxiliary power to traditional transportation technologies. Hydrogen can play a particularly important role in the future by replacing the imported petroleum we currently use in our cars and trucks.
- When fuel cells are used to generate electricity and heat (co-generation), they can reach efficiencies of up to 85 percent. Internal-combustion engines in today's automobiles convert less than 30 percent of the energy in gasoline into power that moves the vehicle. Vehicles using electric motors powered by hydrogen fuel cells are much

more energy efficient, utilizing 40-60 percent of the fuel's energy. Even Fuel Cell Vehicles (FCVs) that reform hydrogen from gasoline can about 40 percent of the energy in the fuel.

- Applications for hydrogen-powered fuel cells range from microwatts to megawatts. Regardless of the energy conversion device, the demands on the hydrogen storage system are severe. An international group conducted market survey for fuel cells for commercial portable power (< 1 kW) which is in great demand. Devices that fall in this range include portable computers, cell phones, camcorders, and digital cameras. Fuel cells are also being considered for emergency backup power systems, and for providing field power in emergencies. Examples of such applications include power for communications towers (cell phones), and for satellite phones and mobile communications used in areas where the hard-wired communications infrastructure has been damaged by storms or earthquakes [4].

1.4 Conclusion:

Among the chemical hydrides of interest, sodium borohydride ($NaBH_4$) receives the most extensive attention owing to its combined advantages of high hydrogen capacity (with a theoretical value of 10.8 wt %), good storability and reaction controllability, low reaction-initiating temperature, and environmental friendly hydrolysis product borax, ($NaBO_2$). Sodium Borohydride has high intrinsic gravimetric and volumetric hydrogen storage density, which can yield practical hydrogen generation systems with proper engineering. Progress is being made to improve current Sodium Borohydride synthesis technology aimed at reducing manufacturing cost. Further, scope of work is to study kinetics of hydrolysis reaction of sodium borohydride by semi empirical hydrogen generation model with easily available and effective catalyst considering the cost factors of the catalyst.

CHAPTER-2

LITERATURE REVIEW

2.1 Introduction

Various studies on storage for hydrogen as fuel were carried out by many researchers in the past. This chapter reviews the previous published literatures, which lays foundation and basis for further work in this investigation. This helps to give a better understanding about the topic and also acts as a guideline for this thesis. The major focus of the following study is on the past hydrogen storage methods and among them storage media by chemical hydrides. This section deals with literature review on various hydrogen storage methods and hydrogen storage challenges.

2.2 Modes of storage of hydrogen in vehicles

Cleveland [6] stated storing enough hydrogen onboard a vehicle to achieve a driving range of greater than 300 miles is a significant challenge. On a weight basis, hydrogen has nearly three times the energy content of gasoline (120 MJ/kg for hydrogen versus 44 MJ/kg for gasoline). However, on a volume basis the situation is reversed (8 MJ/litre for liquid hydrogen versus 32 MJ/litre for gasoline). On-board hydrogen storage in the range of 5-13 kg H_2 is required to encompass the full platform of light-duty vehicles. Today's state-of-the-art for hydrogen storage includes 5000 psig and 10,000 psig compressed gas tanks and cryogenic liquid hydrogen tanks for on-board hydrogen storage.

2.2.1 Compressed hydrogen gas tank

The energy density of gaseous hydrogen can be improved by storing hydrogen at higher pressures. This 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. As shown in Figure 2.1, Carbon fibre-reinforced 5000 psig and 10,000 psig compressed hydrogen gas tanks are under development by manufactures like Quantum Technologies and others. Such tanks are already in use in prototype hydrogen-powered vehicles. The pressure regulator for the 10,000 psig tank is located in the interior of the tank. There is also an in-tank gas temperature sensor to monitor the tank temperature during the gas-filling process when heating of the tank occurs.

The driving range of fuel cell vehicles with compressed hydrogen tanks depends, of course, on vehicle type, design and the amount and pressure of stored hydrogen. By increasing the amount and pressure of hydrogen, a greater driving range can be achieved but at the expense of cost and valuable space within the vehicle.

Figure 2.1: Quantum Pressurized Storage Tank

According to Klancher et al. [8] issues with compressed hydrogen gas tanks revolve around volumetric capacity, high pressure, weight, conformability and cost. The cost of high-pressure compressed gas tanks is essentially dictated by the cost of the carbon fibre that must be used for light-weight structural reinforcement. Efforts are underway to identify lower-cost carbon fibre that can meet the required high pressure and safety specifications for hydrogen gas tanks. However, lower-cost carbon fibres must still be capable of meeting tank thickness constraints in order to help meet volumetric capacity targets. Thus lowering cost without compromising weight and volume is a key challenge.

Two approaches are being pursued to increase the gravimetric and volumetric storage capacities of compressed gas tanks from their current levels. The first approach involves cryo-compressed tanks. This is based on the fact that, at fixed pressure and volume, gas tank volumetric capacity increases as the tank temperature decreases. Thus, by cooling a tank from room temperature to liquid nitrogen temperature (77 K), its volumetric capacity will increase by a factor of four, although system volumetric capacity will be less than this due to the increased volume required for the cooling system.

The second approach involves the development of conformable tanks. Present liquid gasoline tanks in vehicles are highly conformable in order to take maximum advantage of available vehicle space. Concepts for conformable tank structures are based on the location of structural supporting walls. Internal cellular-type load bearing structures may also be a possibility for greater degrees of conformability.

2.2.2 Liquid Hydrogen Tanks

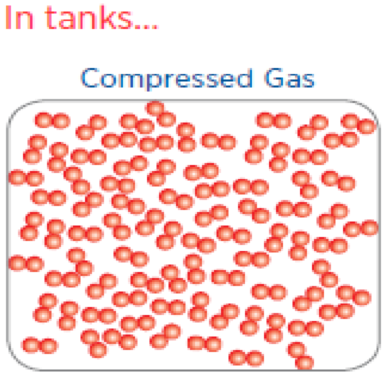


Figure 2.2(a): Compressed Gas

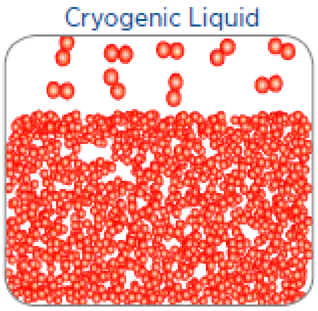


Figure 2.2(b): Cryogenic Liquid

The energy density of hydrogen can be improved by storing hydrogen in a liquid state. As shown in Figure 2.2(a), liquefied hydrogen is denser than gaseous hydrogen and thus it contains more energy in a given volume. Liquid hydrogen (LH_2) 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 10,000 psig gas tanks. Similar sized liquid hydrogen tanks can store more hydrogen than compressed gas tanks, but it takes energy to liquefy hydrogen. The energy requirement for hydrogen liquefaction is high; typically 30% of the heating value of hydrogen is required for liquefaction.

However, the issues with liquid hydrogen (LH_2) tanks are hydrogen boil-off, the energy required for hydrogen liquefaction, volume, weight, and tank cost and the tank insulation required to prevent hydrogen loss adds to the weight, volume, and costs of liquid hydrogen tanks. Hybrid tank concept combining both high-pressure gaseous and cryogenic storage is being studied that can store high-pressure hydrogen gas under cryogenic conditions (cooled to around 120 to 196°C). Figure 2.2(b) shows "cryo-compressed" state in tanks may allow relatively lighter weight, more compact storage. These hybrid (cryo-compressed tanks) insulated pressure vessels are lighter than hydrides and more compact than ambient-temperature, high pressure vessels. New approaches that can lower these energy requirements and thus the cost of liquefaction are needed.

2.2.3 Materials-based Hydrogen Storage

There are presently three generic mechanisms known for storing hydrogen in materials: absorption, adsorption, and chemical reaction. Hydrogen can be stored on the surfaces of solids as shown in Figure 2.3(a) by adsorption or within solids Figure 2.3(b) by absorption. Density of hydrogen increases from cases A to D as shown in Figures from 2.3 (a) to 2.4 (b).

Adsorption:

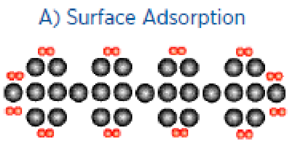


Figure 2.3(a): Surface Adsorption

Absorption:

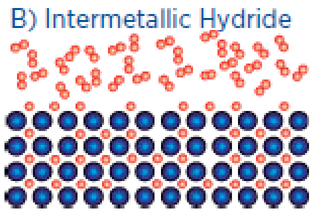


Figure 2.3(b): Intermetallic Hydride

In adsorption (A), hydrogen attaches to the surface of a material as in figure above either as hydrogen molecules (H_2) or hydrogen atoms (H). Adsorption may be subdivided into physisorption and chemisorption, based on the energetics of the adsorption mechanism. Physisorbed hydrogen is more weakly energetically bound to the material than is chemisorbed hydrogen. Sorptive processes typically require highly porous materials to maximize the surface area available for hydrogen sorption to occur, and to allow for easy uptake and release of hydrogen from the material.

In absorption (B), as in figure above hydrogen molecules dissociate into hydrogen atoms that are incorporated into the solid lattice framework – this method may make it possible to store larger quantities of hydrogen in smaller volumes at low pressure and at temperatures close to room temperature. In absorptive hydrogen storage, hydrogen is absorbed directly into the bulk of the material. In simple crystalline metal hydrides, this absorption occurs by the incorporation of atomic hydrogen into interstitial sites in the crystallographic lattice structure [7].

2.2.4 Chemical reaction

Finally, hydrogen can be strongly bound within molecular structures, as chemical compounds containing hydrogen atoms in cases C & D as shown in figures 2.4 (a) and 2.4 (b).

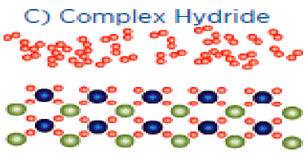


Figure 2.4(a): Complex Hydride

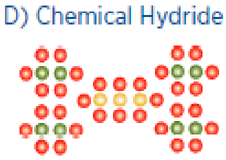


Figure 2.4(b): Chemical Hydride

The chemical reaction route for hydrogen storage involves chemical reactions for both hydrogen generation and hydrogen storage. For reactions that may be reversible, hydrogen generation and hydrogen storage take place by a simple reversal of the chemical reaction as a result of modest changes in the temperature and pressure. Sodium alanate-based complex metal hydrides are an example [8].

2.2.5 Chemical Hydrogen Storage

The term 'chemical hydrogen storage' is used to describe storage technologies in which hydrogen is generated through a chemical reaction. Common reactions involve chemical hydrides with water or alcohols. Typically, these reactions are not easily reversible on-board a vehicle. Hence, the spent fuel and by-products must be removed from the vehicle and regenerated off-board.

2.2.5.1 Hydrolysis Reactions

Hydrogen generation from insertion of a catalyst into sodium borohydride aqueous solution defines hydrolysis reaction. Hydrolysis reactions involve the oxidation reaction of chemical hydrides with water to produce hydrogen. The reaction of sodium borohydride has been the most studied to date, formula for converting sodium borohydride to hydrogen.

$$NaBH_4 + 2H_2O = NaBO_2 + 4H_2 \qquad (2)$$

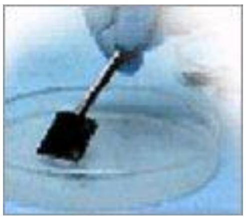


Figure 2.5: Hydrolisis Reactions

The reaction can be controlled in an aqueous medium via pH and the use of catalyst. While the material hydrogen capacity can be high and the hydrogen release kinetics is fast, the borohydride regeneration reaction must take place off-board. Regeneration energy requirements cost and life-cycle impacts are key issues that are being investigated.

2.2.6 Carbon-Based Materials

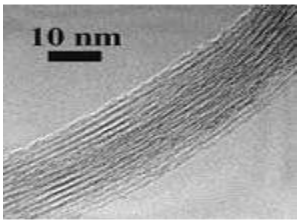


Figure 2.6: Carbon Based Materials

As stated by Zuttel [12] single-walled carbon nanotubes are being studied as hydrogen storage materials because of published hydrogen gravimetric capacities in the range of 3-10 wt% at room temperature. However, there has been controversy due to difficulty in reproducing these results. Hence, the current research and development focus for carbon nanotubes has been on establishing reproducibility. Recent results at the National Renewable Energy Laboratory (NREL) show that while no hydrogen storage was observed in pure single-walled carbon nanotubes, roughly 3wt% was measured in metal-doped nanotubes at room temperature. At room temperature gravimetric capacity measured in carbon nanotubes is below the 6.0 wt% and further improvements must be made. In addition, low-cost, high-volume manufacture processes must be developed for single-walled carbon nanotubes for them to be economically viable in vehicular applications.

2.3 Storage Challenges:

Cleveland [6] also stated storage challenges for transportation, the overarching technical challenge for hydrogen storage is how to store the amount of hydrogen required for a conventional driving range (> 300 miles), within the vehicular constraints of weight, volume, efficiency, safety, and cost. Durability over the performance lifetime of these systems must also be verified and validated and acceptable refuelling times must be achieved. Requirements for off-board bulk storage are generally less restrictive than on-board requirements.

The key challenges include:

- **Weight and Volume**: The weight and volume of hydrogen storage systems are presently too high, resulting in inadequate vehicle range compared to conventional petroleum-fuelled vehicles. Materials and components are needed that allow compact, lightweight hydrogen storage systems while enabling greater than 300-mile range in all light-duty vehicle platforms.
- **Efficiency**: Energy efficiency is a challenge for all hydrogen storage approaches. The energy required to get hydrogen in and out is an issue for reversible solid-state materials.

Life-cycle energy efficiency is a challenge for chemical hydride storage in which the by-product is regenerated off-board. In addition, the energy associated with compression and liquefaction must be considered for compressed and liquid hydrogen technologies.

- **Durability**: Durability of hydrogen storage systems is inadequate. Materials and components are needed that allow hydrogen storage systems with a life time of 1500 cycles.
- **Refuelling Time**: Refuelling times are too long. There is a need to develop hydrogen storage systems with refuelling times of less than three minutes, over the lifetime of the system.
- **Cost**: The cost of on-board hydrogen storage systems is too high, particularly in comparison with conventional storage systems for petroleum fuels. Low-cost materials and components for hydrogen storage systems are needed, as well as low-cost; high-volume manufacturing methods are also needed.
- **Codes & Standards**: Applicable codes and standards for hydrogen storage systems and interface technologies, which will facilitate implementation/commercialization and assure safety and public acceptance, have not been established. Standardized hardware and operating procedures, and applicable codes and standards, are required.
- **Life-Cycle and Efficiency Analyses**: Lack of analyses of the full life-cycle cost and efficiency for hydrogen storage system are required.

2.4 Hydrogen storage via sodium borohydride

Klanchar et al. [7] briefed why hydrogen storage via chemical hydride is advantageous then other storage techniques. As Table 1 shows the primary reactions equation and associated hydrogen storage properties of some well-known chemical hydride materials, including lithium hydride (LiH), sodium hydride (NaH), calcium hydride (CaH_2), magnesium hydride (MgH_2), lithium Aluminium hydride (LiAlH), titanium hydride (TiH_2), lithium borohydride ($LiBH_4$) and sodium borohydride ($NaBH_4$).

The physical, chemical and safety properties of these reactants and products suggest that they could be used in a complete hydride-based storage system. Typically, hydrogen can be generated from chemical hydrides through a direct reaction with water. Thus, LiH, NaH, CaH_2, $LiAlH_4$, $LiBH_4$, and $NaBH_4$ were assumed to react with water. The water reactions also assumed low-to-moderate temperatures, which results in hydroxides being formed rather than oxides as predicted by standard chemical equilibrium analyses. However, elevating the reaction temperature will produce metal oxide products rather than hydroxides in some cases (e.g., Li_2O rather than LiOH), which in turn could decrease reprocessor energy need.

The hydrogen storage properties listed in Table 1 below include:

- Fraction H, which is the number of hydrogen atoms in the hydride divided by the molecular weight of the hydride.
- Hydrogen specific mass, defined as the mass (kg) of H_2 produced per mass of original hydride material or solid product, whichever is larger (kg H_2/kg material).
- Hydrogen density, determined from the mass of hydrogen produced per volume of hydride or solid product, whichever is larger (kg H_2/litre).

Peters [8] reported since the energy convertor will supply reactant water, almost all of the storage property listings (specific mass and density) exclude the volume of water. The only exception is the last reaction, which describes Millennium Cell's Hydrogen on Demand System™. This process uses an aqueous solution containing 35 wt% $NaBH_4$ and liberates hydrogen when it comes into contact with a catalyst.

Table 2.1: Hydrogen Specific Mass and Density

Hydride Reactions and Hydrogen Storage Properties Hydride and Reaction	**Fraction H**	**H_2 Specific Mass (kg H_2/ kg)**	**H_2 Density (kg H_2/ liter)**
$LiH + H_2O \rightarrow LiOH + H_2$	0.126	0.252	0.122
$NaH + H_2O \rightarrow NaOH + H_2$	0.042	0.083	0.106
$CaH_2 + 2\ H_2O \rightarrow Ca(OH)_2 + 2\ H_2$	0.048	0.095	0.121
$MgH_2 \rightarrow Mg + H_2$	0.076	0.076	0.110
$LiAlH_4 + H_2O \rightarrow LiOH + Al + 2.5\ H_2$	0.105	0.132	0.121
$TiH_2 \rightarrow Ti + H_2$	0.040	0.040	0.152
$LiBH_4 + H_2O \rightarrow LiOH + HBO_2 + 4\ H_2$	0.184	0.367	0.235
$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4\ H_2$	0.105	0.211	0.226
Millennium Cell 35% Solution $NaBH_4 + 4\ H_2O \rightarrow NaBO_2 + 4\ H_2 + 2\ H_2O$		0.077	0.077

McClaine and Wu [9 & 10] compared hydrogen storage properties and the hydrogen storage potential of the leading chemical hydride reactions as shown in Figure 2.7 and also includes data from more conventional storage systems such as 5000 psig gas, cryogenic liquid, and metal (reversible) hydrides, the lithium-containing hydrides of LiH, $LiAlH_4$, and $LiBH_4$ rate especially well and represent a class of materials that can exceed the 2015 DOE storage targets based on reaction chemistry. More importantly, these hydrides have sufficient hydrogen storage potential to allow for the inclusion of necessary supporting hardware.

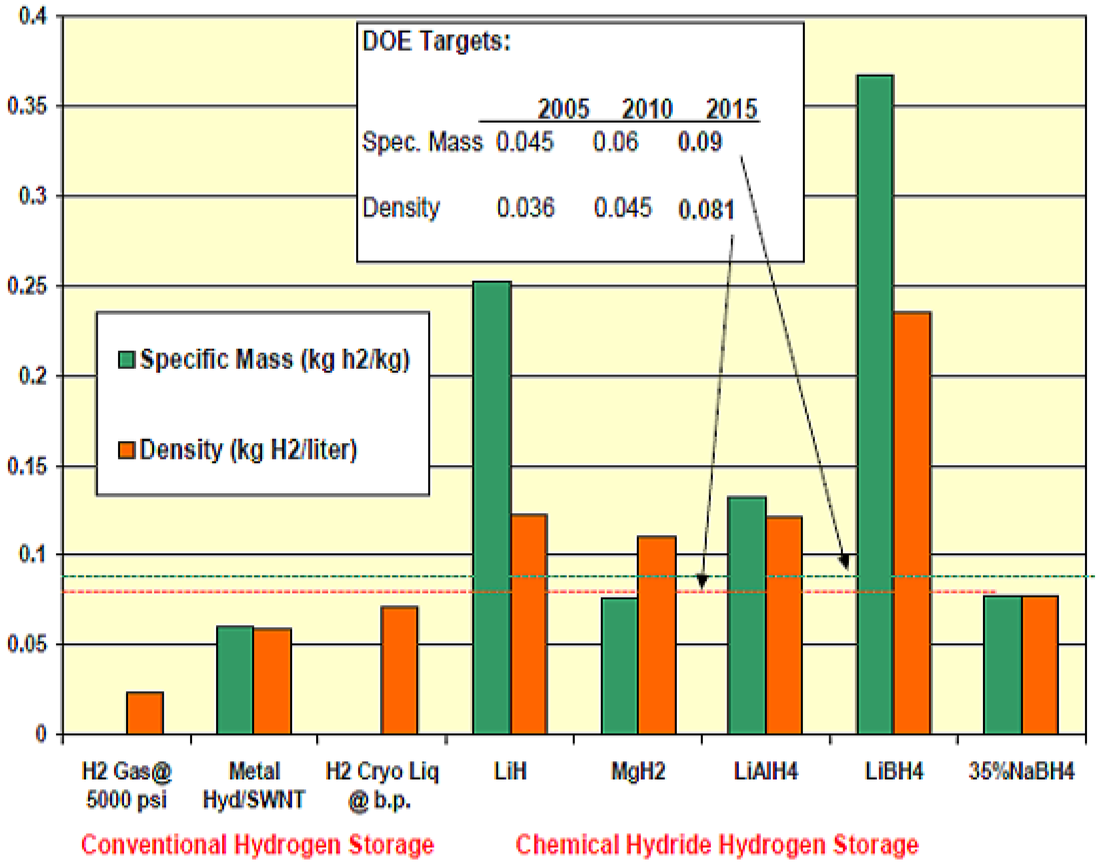
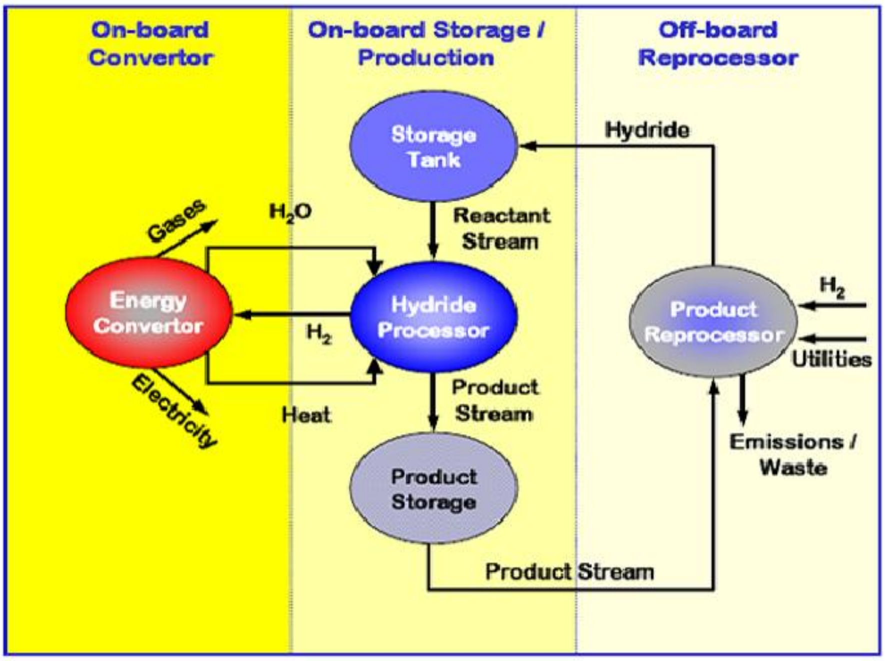


Figure 2.7: Comparison of Hydrogen Storage Properties.

A general electrical concept shown in figure 2.8 is described.

- The source chemical hydrides can be delivered to the on-board storage tank in their near-solid storage densities.
- That water and other products of the convertor will be available to the hydride processor to maximize its efficiency.
- That the products can be collected in a form that will permit easy transfer to the off-board reprocessor station at the time of refuelling.
- That the resulting products can be economically returned to source metal hydrides at the off-board station.

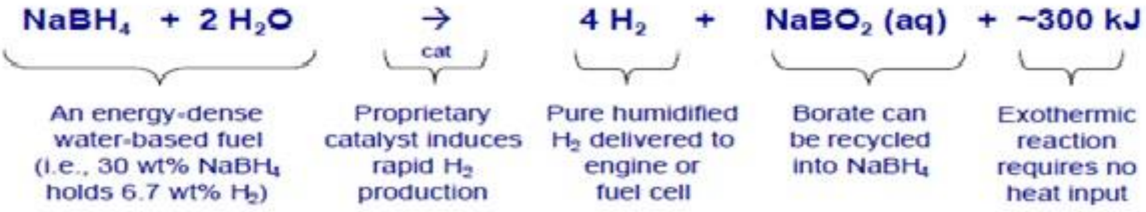


Energy System Concept Using Chemical Hydride Hydrogen Storage

Figure 2.8: Energy System Concept using Chemical Hydride Hydrogen Storage

2.5 Importance of sodium borohydride in hydrogen storage

Shang et al. [1] found that Sodium borohydride ($NaBH_4$) reacts with water to produce pure hydrogen and a by product, sodium borate. As shown in Figure 2.9 heat of hydrolysis of sodium borohydride among other hydrides is less which adds it to one of its advantages.



$$\underbrace{NaBH_4 + 2\,H_2O}_{\text{An energy-dense water-based fuel (i.e., 30 wt\% } NaBH_4 \text{ holds 6.7 wt\% } H_2)} \underbrace{\xrightarrow{cat}}_{\text{Proprietary catalyst induces rapid } H_2 \text{ production}} \underbrace{4\,H_2}_{\text{Pure humidified } H_2 \text{ delivered to engine or fuel cell}} + \underbrace{NaBO_2\,(aq)}_{\text{Borate can be recycled into } NaBH_4} + \underbrace{\sim 300\text{ kJ}}_{\text{Exothermic reaction requires no heat input}}$$

The advantages and benefits of hydrogen generation from this hydrolysis reaction are given below:

- Hydrogen is generated in a controllable, heat releasing reaction.
- Fuel is a room temperature, non flammable liquid under no pressure.
- No side reactions or no volatile by products.
- Generated H_2 is high purity (no traces of CO and S) and humidified (heat generates some water vapour).
- It is the least expensive metal hydride commercially available, and it is safe to use, handle, and store.

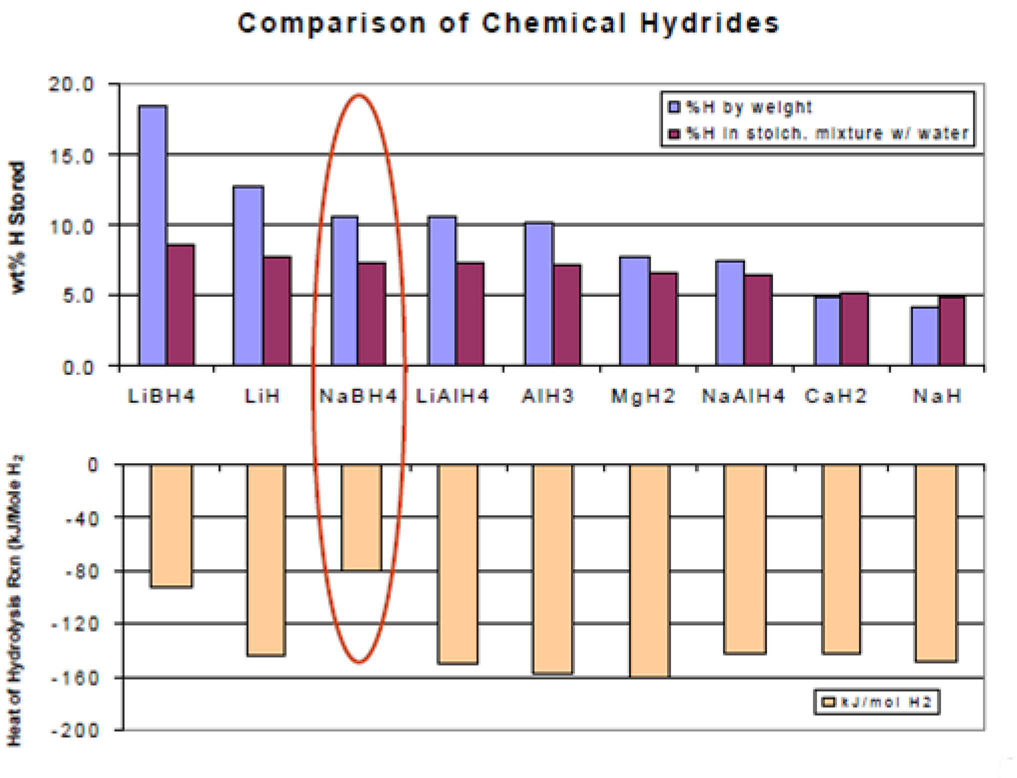


Figure 2.9: Comparisons of Chemical Hydrides

Other advantages are:

- It requires no or limited equipment investment for the system implementation of the reaction.
- The by-product of the reaction is in the form of an aqueous solution; therefore, it is easy to be removed from the system.
- Also, the hydrogen-storage densities of the system with an optimized design can meet the technical target of 6% hydrogen capacity (mass %) set by U.S. Department of Energy (DOE).
- Sodium borohydride has thus been proposed to be an effective hydrogen-storage medium for a wide variety of applications in both distributed power generation and transportation applications. Recently, extensive research has been performed using $NaBH_4$ aqueous solution for hydrogen supply, and the results have been reported by a number of publications.

2.6 Storage system technologies

According to Zuttel [12] and Agrawal [13] pure liquefied hydrogen, at about 20 K and atmospheric pressure, have a volumetric storage capacity of 2.35 kWh/L and a gravimetric capacity of 33.3 kWh/kg. By comparison, pure gasoline has a storage efficiency equivalent of 8.8 kWh/L and 11.8 kWh/kg, and other liquid hydrocarbons are also extremely efficient even compared to pure liquid hydrogen. Whereas liquid hydrocarbon fuels can be stored and delivered from lightweight tanks near ambient conditions, pure H_2 requires either high pressure tanks or highly insulated cryogenic storage. These system requirements lower the gravimetric and volumetric capacities significantly, as shown in Figure 2.10. Zuttel [12] found hydrogen poses a unique challenge for storage because it is the lightest and least dense gas at only 0.0898 kg/m^3 at standard temperature and pressure (STP).Compressed hydrogen gas is the most developed of the storage technologies and has already been used in early prototype fuel cell vehicles.

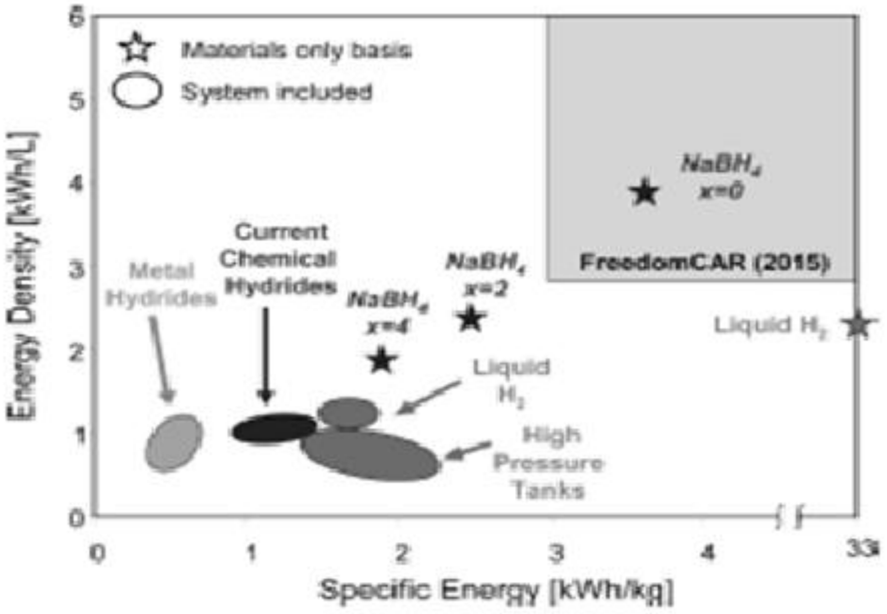


Figure 2.10: Volumetric and gravimetric properties.

Ritter & Ebner [15] discussed the method involves pressurizing H_2 to 5000-10000 psig (35-70 MPa) in specialized reinforced tanks. Despite increasing the density to 30 kg/m^3 for 10000 psi gas tanks, the volumetric capacity is the lowest of the technologies, making it inconvenient for portable or automotive applications. Cryogenic liquid hydrogen further increases the density to 70.8 kg/m^3 by condensing the hydrogen at 21.2 K [12]. However, the liquefaction process requires large amounts of energy, approximately 30% of the overall energy content of the H_2 to be liquefied.

A current chemical hydride system evaluated by DOE in Figure 2.10 is based on aqueous-phase, catalyzed hydrolysis of $NaBH_4$. The materials-only H_2 storage capacities shown for $NaBH_4$ (stars) are based on the reaction below (equation 3) and include the mass and volume of both hydride and water.

$$NaBH_4(s) + (2 + x)\ H_2O\ (g) \rightarrow 4\ H_2\ (g) + NaBO_2 \cdot xH_2O(s) \qquad (3)$$

Ying Wu [2] ideally described only two moles of water are required to release four moles of H_2, but in fact the product sodium metaborate can exist in several degrees of hydration, with the generic stoichiometry x. This reaction gives 10.9 kg H_2/kg reactants if $x = 0$. If x is 2 or even 4 the materials-only storage capacity is still promising for some applications. However, in practice to date the best systems require that the $NaBH_4$ be pre-dissolved in a large excess of water to keep the solids in solution. The excess water, as well as the mass of the system hardware, significantly reduces the storage efficiency.

2.7 Stoichiometry of Hydrolysis and the Role of Water

Chemical hydrides contain hydrogen in a reduced or electron rich state [17]. Hydrides can be categorized as simple binary compounds or complex hydrides. In the simple hydrides (MH_n, for example CaH_2) the negative hydrogen is bonded covalently or ionically to a metal. In covalent hydrides the hydrogen-metal bond is created by a common electron pair. The ionic hydrides contain metal cations and negatively charged hydrogen ions. Simple hydrides react with water according to

$$MH_n + n\,H_2O \rightarrow M\,(OH)_n + n\,H_2 \qquad (4)$$

where, M is a metal of valence n. In simple chemical hydrides, the reaction product at near ambient conditions is always the hydroxide, not the oxide. Thus simple hydrides inherently have some inefficiency in that they retain n of the H atoms available in equation (5) as hydroxide. If the stable reaction product were the oxide, the gravimetric efficiency of hydrogen production would increase. In complex hydrides the hydrogen is combined with two other components, usually metallic elements. The complex hydrides ($M\,(M'H_4)_n$) react according to

$$M\,(M'H_4)_n + (2n + x)\,H_2O \rightarrow M(M'O_2)_n \cdot xH_2O + 4n\,H_2 \qquad (5)$$

where, n is the valence of the metal M, M′ is an element from group III of the periodic table, such as boron or aluminium, and x is structural water of crystallization. Equation (6) is written with the assumption that the reaction has been carried out under conditions that produce a dry solid and dry gas; in this case the solid phase product is best described as a hydrated mixed metal oxide. In many practical designs, the reaction is carried out in excess water, in which case the ($M'H_4$) anion and the metal oxide product are in the hydrated form in solution.

$$(M'H_4) + 4H_2O \rightarrow M'(OH)_4 + 4H_2 \qquad (6)$$

In the context of hydrogen storage efficiency, Marrero et al. [46] has also interpreted x as the excess hydration factor. Because the most efficient hydrolysis stoichiometry would lead to the anhydrous oxide x=0, any water in excess reduces the gravimetric efficiency proportionally.

The effective value of x for different amounts of water, and the corresponding hydrogen storage capacity on a materials-only basis is shown in Table 3. Ideal hydrolysis requires no excess water. Complete dissolution of $NaBH_4$ at 25 °C requires extra water corresponding to x= 1.81. If sufficient water is added to keep the $NaBO_2$ in solution, the effective value of x is 11.04. Furthermore, the addition of NaOH or other base to stabilize the solutions also affects the hydrogen storage density. On the basis of [20] the optimum $NaBH_4$ concentration as a function of alkali content and temperature and the optimum concentration is 8.5 wt % $NaBH_4$ and 5wt % NaOH resulting in a 1.81 wt % H_2. Clearly, addition of water to achieve solubility of the reactants and/or products decreases the storage efficiency significantly. In table 2 products with Varying Degrees of Hydration are given.

Table 2.2: Hydrogen Storage Capacity (H_2 wt %) for Hydrolysis.

Hydride	Hydration state of oxide product			
	x = 0	x =0.5	x=2	x=4
$NaBH_4$	10.92%	9.73%	7.34%	5.53%
$LiAlB_4$	10.90%	9.72%	7.33%	5.52%
$LiBH_4$	13.95%	12.07%	8.59%	6.21%

Table 2.3: Comparison of Gravimetric Efficiencies of Various Reactant Preparations.

Reactant deposition	Molar ratio ($NaBH_4$:H_2 O)	X (hydration factor)	H_2 storage capacity
Ideal hydrolysis (x=0)	1:2	0	10.92%
Saturated $NaBH_4$	1:3	1.81	7.57%
$NaBO_2$ solubility limit	1:13	11.04	2.96%
8.5wt%+5wt%NaOH	1:21	19.37	1.81%

As given by James [17], Table 3 shows how the solubility of the chemical hydride (55 g $NaBH_4$/100 g H_2O at 25 °C) is relatively low, and as given by Suzuki et al. [18] the solubility of the oxides is even lower (28 g $NaBO_2$/100g H_2O at 25°C), such systems inherently have a reduced gravimetric efficiency compared to the ideal.

2.8 Solubility for $NaBH_4$ in NaOH Aqueous Solutions

According to Shang et al. [5] the solubility for $NaBH_4$ in NaOH aqueous solutions are not available directly in the literature. However, the phase diagram of the $NaBH_4$-NaOH-H_2O system is available. As shown in Figure 2.11. For different temperatures, the solubility line consists of smooth parts and inflection points. In the smooth part, one crystalline form coexists with solution. A different smooth part has a different crystalline form. At the inflection point between two of the smooth parts, the two different crystalline forms coexist with the solution. The inflection point between the two smooth parts is called the invariant point, because the composition and temperature are fixed.

For example, at invariant point 1 in Figure 2.11, crystalline states $NaBH_42H_2O$ and $NaBH_4$ coexist with $NaBH_4$ in NaOH aqueous solutions. The temperature of the invariant point is 0 °C. The composition is 22.5% NaOH, 22.3% $NaBH_4$, and 55.2% water. There are seven invariant points in total, as shown by points 1-7 in the Figure 2.11. The line for 0 °C, line a, is divided into three parts by invariant points 1 and 2. Before point 1, the solution is saturated with the crystalline state $NaBH_4.2H_2O$. At point 1, crystalline states $NaBH_4.2H_2O$ and $NaBH_4$ exist simultaneously. With the increase in NaOH concentration, the crystalline state becomes $NaBH_4$. NaOH arrives at its saturated state at point 2 and precipitates together with $NaBH_4$ in the state of hydrated crystal $NaOH.H_2O$. After point 2, $NaBH_4$ is no longer saturated, and the solution saturated with NaOH has $NaOH.H_2O$ as the equilibrium solid state until no $NaBH_4$ exists in the system.

At 18 and 30 °C, the situations are similar to that at 0 °C except for the invariant point compositions. At 50 °C, there is only one invariant point, point 7. Before point 7, the solution coexists with the crystalline state $NaBH_4$. After point 7, the solution coexists with the crystalline state $NaOH.H_2O$. At point 7, the solution coexists with the two crystalline states NaOH, H_2O and $NaBH_4$.

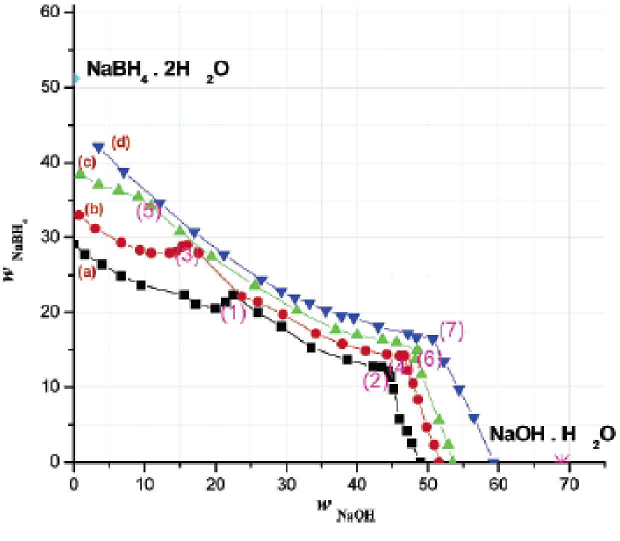


Figure 2.11: Phase diagram $NaBH_4$ - NaOH - H_2 O system at a) 0, b) 18, c) 30, and d) 50 ^{o}C.

2.9 More reactive cobalt chloride as a catalyst in the hydrolysis of sodium borohydride

Demirci et al. [22] observed that Cobalt chloride ($CoCl_2$) is highly reactive for catalyzing hydrogen release from $NaBH_4$.The present study reports results about the reactivity of the system $NaBH_4$-$CoCl_2$. Hydrogen generation through sodium borohydride ($NaBH_4$) hydrolysis has attracted much attention. This reaction has to be catalyzed by metal-based materials. Catalytic potential of cobalt (II) and (III) salts have been studied and $CoCl_2$ showed the best performance as catalyst for hydrolysis reaction. The hydrogen generation rate of $CoCl_2$ is one of the highest ones reported so far.

Catalytic acceleration of the hydrolysis reaction by addition of metal chlorides was studied and it was observed that manganese (II), iron (II), cobalt (II), nickel (II) and copper (II) chlorides reacted rapidly with borohydride solutions (20 g of H_2O per gram of $NaBH_4$) and the reaction led to the formation of metal borides. Cobalt (II) chloride was the most reactive, 97% of hydrogen being released in 10 min. Akdim et al. [30] reported that the presence of $CoCl_2$ boosts $NaBH_4$ decomposition to an extent that such contact raises a serious safety concern, the reaction was not violent, just quick, and the HGR obtained is one of the highest. $CoCl_2$ reactivity to the other cobalt (II) salts was also studied. Soluble salts were chosen: Co $(CH_3COO)_2$, $Co(NO_3)_2$, CoF_2, and $CoSO_4$. The performances of their aqueous solution are given in Figure 2.12. The most reactive (in terms of HGR) was $CoCl_2$, was followed by Co (CH3COO)$_2$> $CoSO_4$ > CoF_2 > $Co(NO_3)_2$. The HGR of $CoCl_2$ was more than four times higher than those of the other cobalt (II) salts.

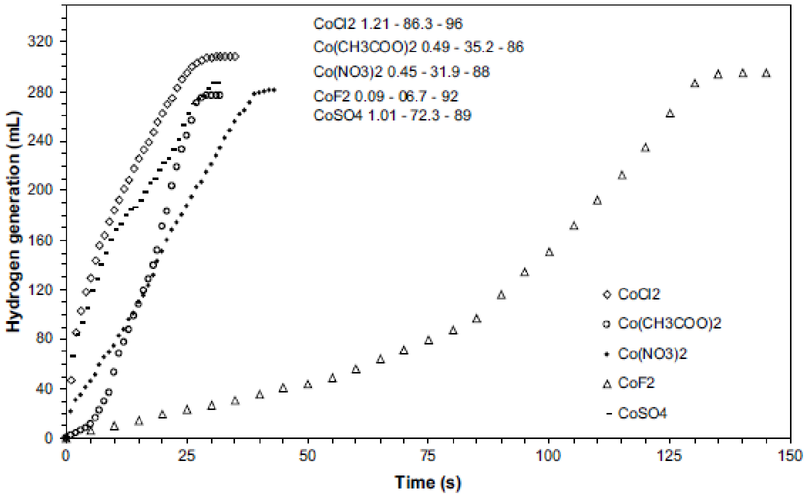


Figure 2.12: Hydrogen Generation Rate for Cobalt (II) salts in comparison with other solutions.

According to Levy et al. [23] it is usually admitted that the active species catalyzing $NaBH_4$ hydrolysis are cobalt borides denoted here as Co_xB_y, but not Co^{2+} in solution.

$$CoCl_2 + 2NaBH_4 + 3H_2O \rightarrow \frac{25}{4}H_2 + \frac{1}{2}Co_2B + 2NaCl + \frac{3}{2}HBO_2 \qquad (7)$$

The following reactions were also reported [24 & 25]

$$2Co^{2+} + 2BH^{4+} + 2H_2O \rightarrow \frac{25}{4}H_2 + \frac{1}{2}Co_2B + 2NaCl + \frac{3}{2}HBO_2 \qquad (8)$$

$$6Co^{2+} + 2BH^{4-} + 2H_2O \rightarrow Co_2B + HBO_2 + 2H^+ + \frac{9}{2}H_2 \qquad (9)$$

$CoCl_2$ generates Co^{2+} and Cl^-, and because chlorine is among the most electronegative elements, Co^{2+} is certainly more electrophilic from the other salts. Electrophilic character is essential in metal catalysis because strong positive charge attracts strongly polar molecules and anions. Increasing the metal electrophilicity leads to an increase of its reactivity towards BH_4^-. This may explain a better reactivity for $CoCl_2$.

2.10 Graphs showing volumetric and gravimetric hydrogen storage capacities.

The volumetric and gravimetric hydrogen storage capacities are given in Figure 2.13 and Figure 2.14, respectively.

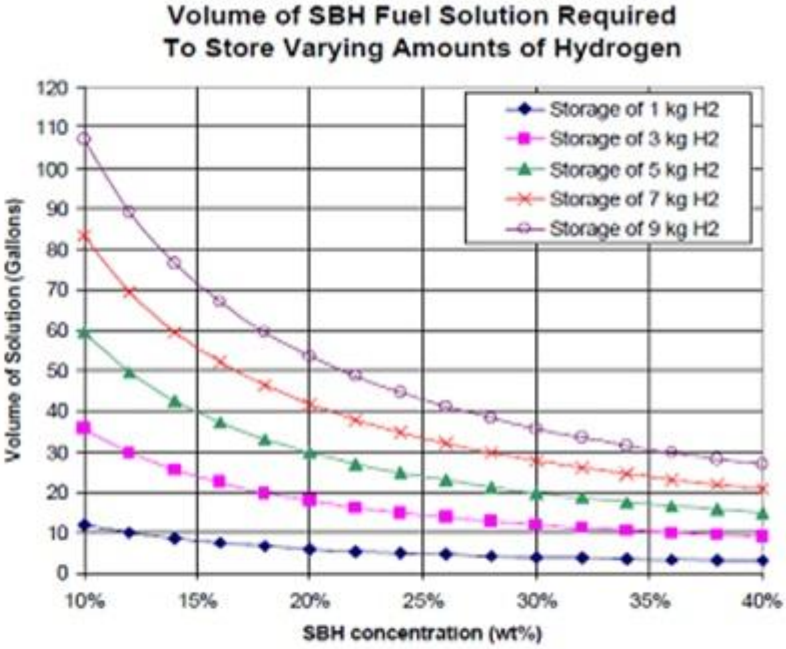


Figure 2.13: Volumetric storage efficiency.

Volumetric storage efficiency of 30 wt % fuel = 63g H_2/L, Liquid H_2= 71g H_2/L, 5000 psig compressed = 23g H_2/L, 10000 psig compressed = 39g H_2/L [2].

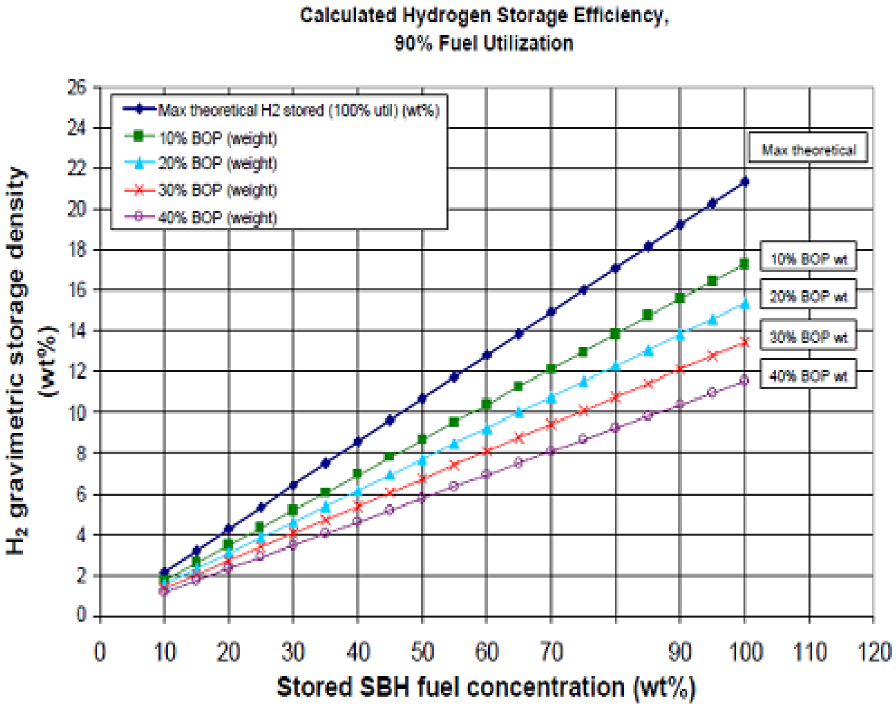


Figure 2.14: Gravimetric storage efficiency.

Figure 2.14 shows Gravimetric storage efficiency SBH has intrinsically high storage density for H_2 which can yield practical Hydrogen System with proper energy [2].

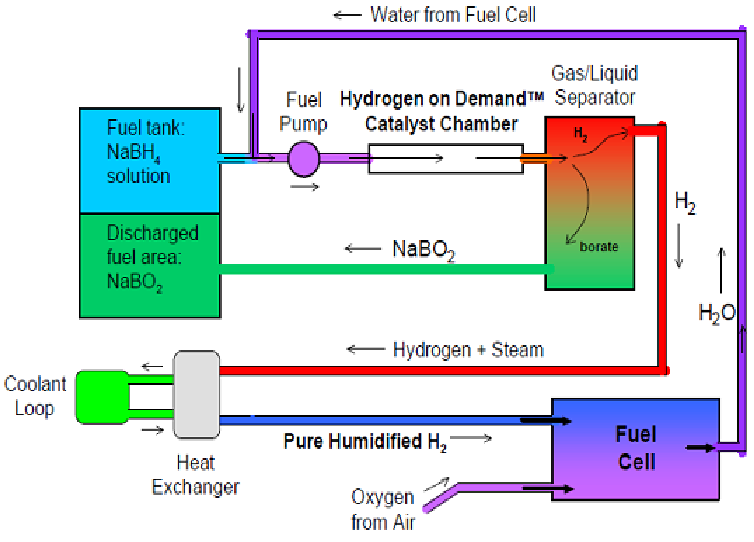


Figure 2.15: Practical hydrogen on demand Schematic [2].

2.11 Limitations of $NaBH_4$ Storage Technology

1. **$NaBH_4$ aqueous solutions:** $NaBH_4$ aqueous solution is a convenient storage way but it has limitations. The main one is NaBH4 solubility. It is 55 g ($NaBH_4$) per 100 g (H_2O) means a gravimetric hydrogen storage capacity of 7.5 wt%. This value neglects the reaction by-product $NaBO_2$ solubility. If now $NaBO_2$ solubility is taken into account, that is, 28 g ($NaBO_2$) per 100 g (H_2O), the $NaBH_4$ concentration at 25 ^{o} C should be below 16 g ($NaBH_4$) per 100 g (H_2O) to keep the liquid state of $NaBO_2$, which precipitation could cause losses in the catalytic performances.

2. **$NaBO_2$ Recycling:** $NaBH_4$ is not a reversible hydrogen storage system and thus the hydrolysis by-products must be recovered and regenerated, back to $NaBH_4$. According to finding a procedure for recycling $NaBO_2$ back to $NaBH_4$ is attractive. Finding such procedure is crucial from an application point of view.

3. **Cost:** High price of $NaBH_4$ is actually a significant barrier. The true commercial success of $NaBH_4$ will not be achievable without substantially reducing the $NaBH_4$ cost.

4. **Particular Challenge for Transportation Applications:** Convert a multi-component, high energy, high purity specialty chemical into an everyday commodity fuel.

5. Difficult to compete with the current cost of gasoline, but could compare favourably with other hydrogen storage technologies.

2.12 GAPS IDENTIFIED

Comparing the cost of catalysts that are used to enhance the rate of reaction that is for example price of 1gm of Ruthenium red is Rs 2080, 1 gm of Platinum oxide is 7020, 1gm of Platinum chloride is Rs 5720 where as 100 gm of Cobalt chloride (Hexahydrate) is Rs 1000. Therefore, Catalysts used in literature like platinum and nickel are costly and radioactive like ruthenium. Therefore, Cobalt chloride is chosen as catalyst for further thesis work due to its, cost effectiveness, easy availability and on basis of the above conclusion kinetics study is carried as shown in next chapters.

CHAPTER – 3
EXPERIMENTAL STUDY

3.1 Introduction

Sodium borohydride ($NaBH_4$) reacts with water to produce pure hydrogen and a byproduct sodium borate. The advantages of hydrogen generation from this hydrolysis reaction are, it is the least expensive metal hydride commercially available, and it is safe to use, handle, and store. It requires limited equipment investment for the system implementation of the reaction. The byproduct of the reaction is in the form of an aqueous solution therefore, it is easy to be removed from the system. Also, the hydrogen-storage densities of the system with an optimized design can meet the technical target of 6% hydrogen capacity (mass %) set by U.S. Department of Energy (DOE).

Sodium borohydride has thus been proposed to be an effective hydrogen-storage medium for a wide variety of applications in both distributed power generation and transportation applications. Recently, extensive research has been performed using $NaBH_4$ aqueous solution for hydrogen supply. Sodium borohydride solutions are unstable since the self-hydrolysis reactions can occur at low pH conditions. Such instabilities can be significantly avoided if the pH of the solution is maintained above a level of 9. One of the most convenient methods for achieving such a pH level is to use sodium hydroxide (NaOH) as the solution stabilizer. When such a stabilized solution is used for hydrogen generation, a selected metal catalyst is needed to accelerate the reaction.

To use $NaBH_4$ to generate hydrogen for power systems such as fuel cells, it is essential to control the rate of hydrogen evolution from its aqueous solutions. The reaction rate is affected by the temperature of hydrolysis reaction and concentration of NaOH and $NaBH_4$ [1].

3.2 Experimental Work:

3.2.1 Chemicals Used: The chemical materials used are supplied by Loba Chemie Ltd, 107, Wodehouse Road, Mumbai 400005, India and are all of reagent grade.

1. Sodium borohydride ($NaBH_4$) powder with molecular weight of 37.8 g/mol and purity of 97%.
2. Cobalt chloride ($CoCl_2$) salt powder in hexa-hydrate form, having molecular weight 237.93 g/mol with a purity of 98%.
3. NaOH pellets used were purchased from CDH Laboratory with a purity of 97% as it is used with water to stabilize the $NaBH_4$.

3.2.2 Schematic Diagram:

The laboratory experimental facility has been created by using different glassware and the schematic diagram is shown in Figure 3.1.

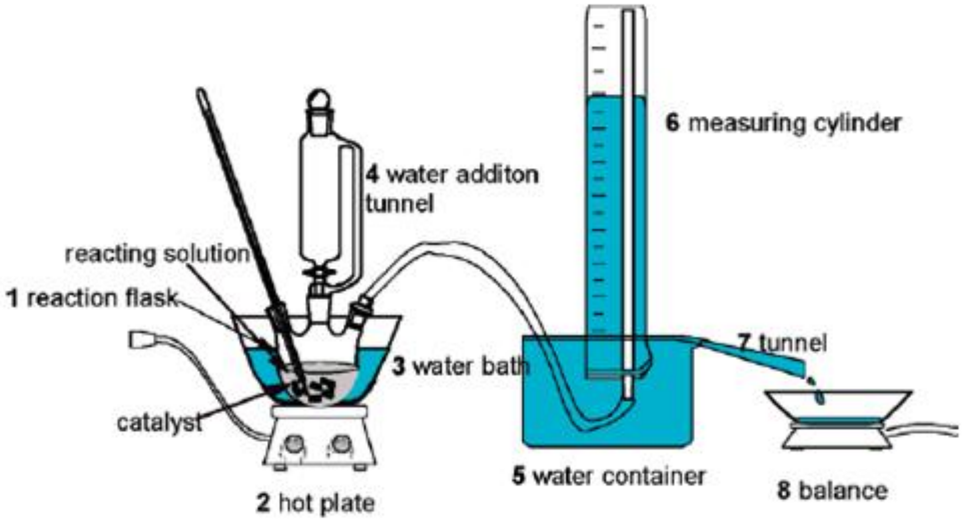


Figure 3.1: Schematic diagram of experimental setup.

Plate 3.1: Experimental setup

3.2.3 Experimental Setup:

The experimental rig consists mainly of:

1. **Three-port reactor**: The left-hand port was equipped with a thermometer to continuously monitor the temperature of the reactor. The right-hand port was used to guide the generated hydrogen gas into the water replacement system.
2. **Hot plate:** The water in the water bath was electrically heated using the hot plate to a predefined temperature.

3. **Water bath:** It is used to adjust reaction temperature.
4. **Water Addition Funnel:** It contains 10ml of solution of water and NaOH.
5. **Water container:** Water container was used to submerge the cylinder in water replacement system.
6. **Measuring Cylinder:** It is used to measure the volume of the hydrogen generated.

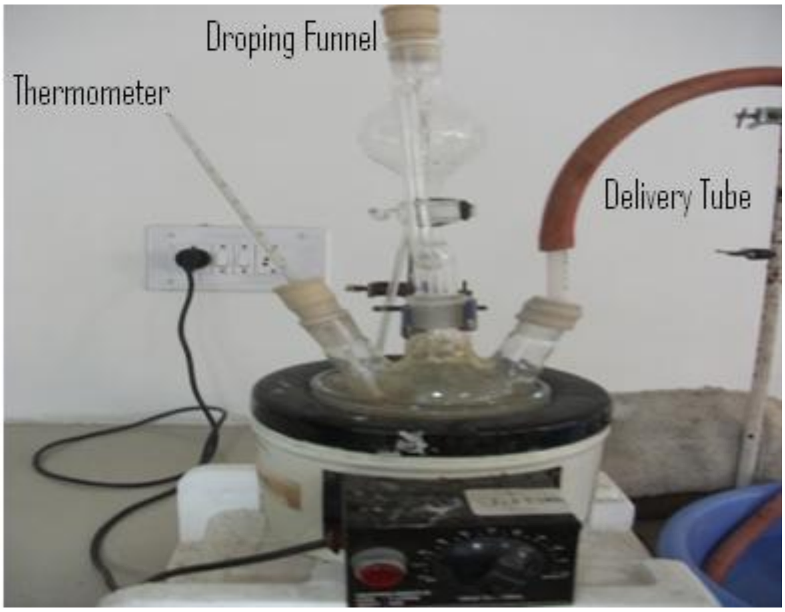


Plate 3.2: Three neck round bottom flask

The flask consists of three ports which are connected with (1) Thermometer, (2) Dropping Funnel, and (3) Delivery Tube connected to hydrogen measuring system.

Plate 3.3: Hydrogen Gas collecting cylinder, hydrogen is collected by downward displacement of water.

3.2.4 Experimental Procedure

1. Before starting the experiment, the reactor was cleaned and then dried.
2. A predetermined amount of $NaBH_4$ and $CoCl_2$ as catalyst was then put into the reactor.
3. Then 10 ml of NaOH and water solution is added with dropping funnel to the reactor.
4. Hydrogen gas is collected in measuring cylinder by downward displacement of water as Hydrogen is insoluble in water.
5. The Hydrogen produced is monitored in measuring cylinder with time.

Chapter 4

Hydrogen Gas and Residual Analysis

4.1 Properties of hydrogen

1. Hydrogen is colourless, odourless, tasteless, non toxic, highly combustible diatomic gas with molecular formula H_2.
2. Hydrogen gas burns with characteristic pop.
3. Hydrogen is insoluble in water, because hydrogen gas consists of non polar covalent molecules but water is polar covalent molecule. This signifies that non polar covalent molecule like hydrogen will dissolve in non covalent liquids, for example like dissolves like or a polar covalent molecule like hydrogen chloride will dissolve in water to produce hydrochloric acid.

4.2 Qualitative Analysis for Hydrogen Gas: The Pop Test

Hydrogen gas is recognized by ‘pop’ when it burns. The pop is the sound of a small explosion.

Procedure:

1. Light a wooden splint and then hold it to area that contain hydrogen, a squeaky pop is observed if hydrogen is present.

Plate 4.1: Pop Test

4.3 Qualitative Analysis for Hydrogen Gas: Gas Chromatography

Gas Chromatography (GC) is used to separate volatile components of a mixture. A small amount of the sample to be analyzed is drawn up into a syringe. The syringe needle is placed into a hot injector port of the gas chromatograph, and the sample is injected. The injector is set to a temperature higher than the components boiling points. So, components of the mixture evaporate into the gas phase inside the injector.

A carrier gas, such as nitrogen, flows through the injector and pushes the gaseous components of the sample into the GC column. It is within the column that separation of the components takes place. After components of the mixture move through the GC column, they reach a detector. The detector sends a signal to the chart recorder which results in a peak on the chart paper.

A quantitative analysis test was conducted for hydrogen gas by Gas Chromatography, as shown in Plate 4.2, from Sophisticated Analytical Instrument Laboratory, Thapar University Patiala. AIMIL-NUCON Gas Chromatograph CPRI- Bangalore is used for testing. The relevant ISI standard is IS: 10593-1983 and for hydrogen gas testing molecular sieve column is used with Thermal Conductivity Detector (TCD). Nitrogen is the carrier gas used in this specific Gas Chromatograph.

Plate 4.2: Gas Chromatograph

The Test shows the Purity of 85% with rest being nitrogen from air as per recovery basis from the sample. The report is given in Annexure-II.

4.4 Characterization of residual substance

- **Scanning Electron Microscope (SEM):** The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample.

  Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons, diffracted backscattered electrons that are used to determine crystal structures.

  SEM was performed for the residual substance from from Sophisticated Analytical Instrument Laboratory, Thapar University Patiala. The test shows that White colour clusters are present in excess which represents metals of high atomic number and dark colour clusters are less which represents metals of low atomic number.The morphology of this residue is not uniform, moreover they get aggregated and form clusters. The report is given in Annexure-II.

- **Energy Dispersive Electron Microscopy (EDAX):** Energy Dispersive Electron Microscopy is an analytical technique used for the elemental or chemical characterization of a sample. It relies on the investigation of an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons, or a beam of X-rays, is focused into the sample being studied.

  EDAX was performed in Sophisticated Analytical Instrument Laboratory, Thapar University Patiala, which shows the presence of Sodium (Na), Cobalt (Co), Chlorine (Cl), Oxygen (O). Atomic percentage of Sodium (Na) is 12.09 %, Cobalt is 32.20%, Chlorine is 0.66% and Oxygen is 55.05%.The report is given in Annexure-II.

CHAPTER 5
RESULTS AND DISCUSSIONS

Repeated experiments were performed during this work and readings were taken as per the procedure mentioned in previous chapter. In this chapter all the results and calculations are discussed.

5.1 Factors effecting rate of hydrolysis reaction

1. **The Reaction Temperature:** Usually, an increase in temperature is accompanied by an increase in the reaction rate. Temperature is a measure of the kinetic energy of a system, so higher temperature implies higher average kinetic energy of molecules and more collisions per unit time. As a rough approximation, for many reactions happening at room temperature, the rate of reaction doubles for every 10°C rise in temperature. This can be explained by collision theory that is, particles can only react when they collide, if a substance is heated particles move faster and collide frequently. They will speed up the rate of reaction. Collisions only result in a reaction if the particles collide with enough energy to get the reaction started. This minimum energy required is called the activation energy for the reaction.

   According to the Figure 5.1 and Table 5.1 given below, the hydrolysis reaction at concentration of $NaBH_4$ equal to 0.55g and $CoCl_2$ concentration 0.06g, rate of hydrogen generation increases with increase in temperature. On the basis of the above information the change of rate constant with temperature can be expressed by Arrhenius equation [8],

$$k = Ae^{-\frac{E}{RT}} \qquad (8)$$

   E is the apparent activation energy, A is the pre exponential factor R is the universal gas constant, and T is the reaction temperature, K. The values of E and A were estimated by substituting the k values at 45 and 63 °C into equation (8), where E = 37.931 kJ/mol and $A = 12.54 \times 10^8\ sec^{-1}$. Calculations carried out as shown in Annexure-1.

Table 5.1: Hydrogen generation rate (HGR) increases with increase in temperature:

Time (min)	HGR(ml/min) at 30°C	HGR (ml/min) at 35°C	HGR(ml/min) at 40°C	HGR(ml/min) at 45°C	HGR(ml/min) at 50°C
1	100	200	220	250	300
2	200	290	350	420	530
3	300	380	460	580	790
4	400	480	560	750	1030
5	500	580	660	900	1100
6	600	680	770	1000	
7	700	780	870		
8	800	880	1000		
9	900	1000			
10	1000				

Concentration of $NaBH_4$ and $CoCl_2$ is constant that is 0.55 g and 0.06 g respectively at NaOH 0%.

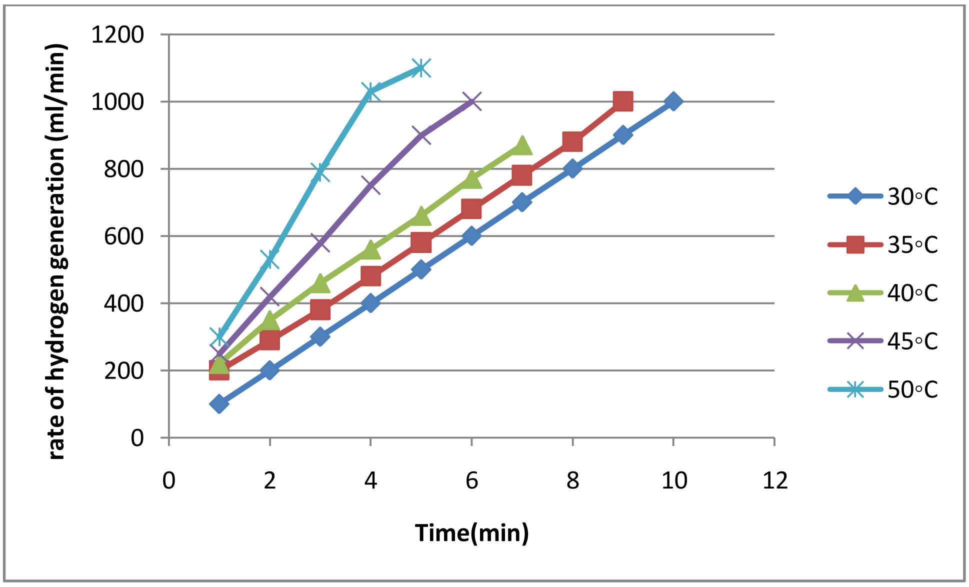


Figure 5.1 Hydrogen generation rate increases with increase in temperature.

2. The Sodium Hydroxide (NaOH) Concentration:

To increase the shelf life of $NaBH_4$ solutions and to suppress the self hydrolysis, sodium hydroxide is added. $NaBH_4$ solutions are typically maintained as a strongly alkaline solution by adding Sodium Hydroxide (NaOH). It can be added in various amounts but generally in the range of 5-15 wt%. It must be noted that the excess amount of NaOH decreases the hydrogen yield. Mostly NaOH in the amount of 3-5% of reactant is thought to be sufficient to control hydrogen release.

The reaction is known to be pH sensitive, reacting to completion under acidic conditions and stabilizing at low H_2 yields under strongly basic conditions. Because of this, acids have been used as catalysts and bases are utilized as stabilizers to prevent premature reaction. To promote reaction in basic solutions, metal catalysts are often employed and result in fast kinetics and high hydrogen yields that vary with catalyst preparation. It is observed from Table 5.2 given below that hydrogen generation rate decreases with increase NaOH concentration and temperature at constant $NaBH_4$ concentration and $CoCl_2$ concentration.

Table 5.2 showing hydrogen generation rate decreases with increase in NaOH conditions.

$NaBH_4$ (g)	$CoCl_2$ (g)	Molality(mol/kg)	Temperature (◦C)	NaOH %	initial hydrogen generation rate (ml/min)
0.45	0.05	1.19	35	0	260
0.45	0.05	1.19	35	1	300
0.45	0.05	1.19	35	3	280
0.45	0.05	1.19	45	0	300
0.45	0.05	1.19	45	1	500
0.45	0.05	1.19	45	3	420
0.45	0.05	1.19	55	0	320
0.45	0.05	1.19	55	1	500
0.45	0.05	1.19	55	3	500
0.45	0.05	1.19	63	0	340
0.45	0.05	1.19	63	1	1300
0.45	0.05	1.19	63	3	560

3. **The $NaBH_4$ Concentration:** The concentration of a reactant influence the rate of reaction is explained by the collision theory. As concentration increases collision between the molecules increases. Thus, by increasing the concentration, the number of collision increases making the probability for a successful collision to occur, at higher rate. Thus according to the Table 5.3 given below the hydrogen generation rate increases with increase $NaBH_4$ concentration with same NaOH percentage.

Table 5.3 Showing hydrogen generation rate increases with $NaBH_4$ concentration:

Molality of $NaBH_4$ (mol/kg)	$CoCl_2$ (g)	Temperature (°C)	NaOH (%)	Hydrogen generation rate (ml/min)
1.19	0.05	25	0	160
1.45	0.06	25	0	200
1.71	0.07	25	0	260
1.98	0.08	25	0	320
1.19	0.05	45	0	300
1.45	0.06	45	0	480
1.71	0.07	45	0	520
1.98	0.08	45	0	600
1.19	0.05	55	0	320
1.45	0.06	55	0	420
1.71	0.07	55	0	480
1.98	0.08	55	0	560
1.19	0.05	63	0	340
1.45	0.06	63	0	480
1.71	0.07	63	0	560
1.98	0.08	63	0	620

5.2 Calculations and Observations:

When the kind and amount of catalyst is fixed, the reaction rate of $NaBH_4$ hydrolysis is affected by the reaction temperature, the NaOH concentration, the $NaBH_4$ concentration. For the convenience of calculation, it is assumed that the maximum hydrogen generation rate was the initial value of hydrogen generation rate.

From Table 5.3 it can be observed that hydrogen generation rate increased with the increase of $NaBH_4$ concentration at a fixed temperature and NaOH concentration. The rate can thus be expressed using equation (9), [24].

$$r_{H_2} \approx m^{\alpha}{}_{NaBH_4} \tag{9}$$

Where r_{H2} is the rate of hydrogen generation in milliliters per minute, m_{NaBH4} is the molality of $NaBH_4$, and α is the apparent reaction order. From Table 5.2, it can be observed that hydrogen generation rate decreased linearly with the increase of NaOH concentration at a fixed $NaBH_4$ concentration and temperature. A rate expression in which the NaOH concentration appears in the denominator could explain this dependency, as shown in equation (10), [24].

$$r_{H_2} = \frac{1}{(1 + k_1\ w_{NaOH})} \tag{10}$$

where w_{NaOH} is the concentration of NaOH in weight percent and k_1 is a proportional constant. In a combination of equations 1 and 2, the rate law of hydrogen generation from a basic $NaBH_4$ solution can be expressed using equation (11), where k is another proportional constant.

$$r_{H_2} = \frac{k m^{\alpha}_{NaBH_4}}{1 + k_1 w_{NaOH}} \qquad (11)$$

The equation may be rationalized as follows: when no NaOH is added, the hydrogen-generation rate is proportional to the molality of $NaBH_4$ in the solution. The constant k is the hydrolysis rate constant, measuring the hydrogen-generation rate from the solutions with a unity molality of $NaBH_4$. This is understandable since the reaction sites increase with the increase of the concentration of $NaBH_4$. When NaOH is added to the solution but its concentration is fixed, the denominator is a constant. Therefore, $k/(1 + k_1 w_{NaOH})$ now becomes less than k, indicating that the reaction rate constant becomes smaller, and thus hydrogen is generated in a slower rate. Hydrogen generation from the hydrolysis involves hydrogen ion. The addition of NaOH makes the concentration of hydrogen ion smaller resulting in a lower hydrogen-generation rate.

In equation (11), $k/(1 + k_1 w_{NaOH})$ is a constant at a fixed temperature and NaOH concentration. The parameters $k/(1 + k_1 w_{NaOH})$ and α in equation 3 can then be determined by regressing the maximum hydrogen-generation rate and the initial $NaBH_4$ concentration using a power function, and the curves obtained are shown in Figure 5.2(a), (b), (c) and parameters determined are listed in Table 5.4 below.

Table 5.4: Parameters determined at various temperature and NaOH concentrations, Calculations were carried out as shown in Annexure-1.

Temperature (◦C)	NaOH concentration (%)	$k/(1 + k_1 W_{NaOH})$	α (Reaction Order)
25	0	133.62	1.2
35	0	226.16	0.94
45	0	271.10	1.2
55	0	283.68	0.96
63	0	377.09	1
25	1	214.32	1
35	1	345.50	0.95
45	1	438.12	0.98
55	1	676.88	1
25	1	871.15	1
35	3	241.65	1.2
45	3	375.21	1.2
55	3	566.79	1.2
63	3	464.05	1

It can be seen from Table 5.4 above that the order of the reaction with respects to $NaBH_4$ concentration α equals 1 with the possibility of experimental error of (± 0.2). Regression of initial hydrogen generation rate with the molality of $NaBH_4$ is shown in Figure 5.2 (a), 5.2(b), and 5.2(c).

Regression of initial hydrogen generation rate with the molality of $NaBH_4$ is shown as under.

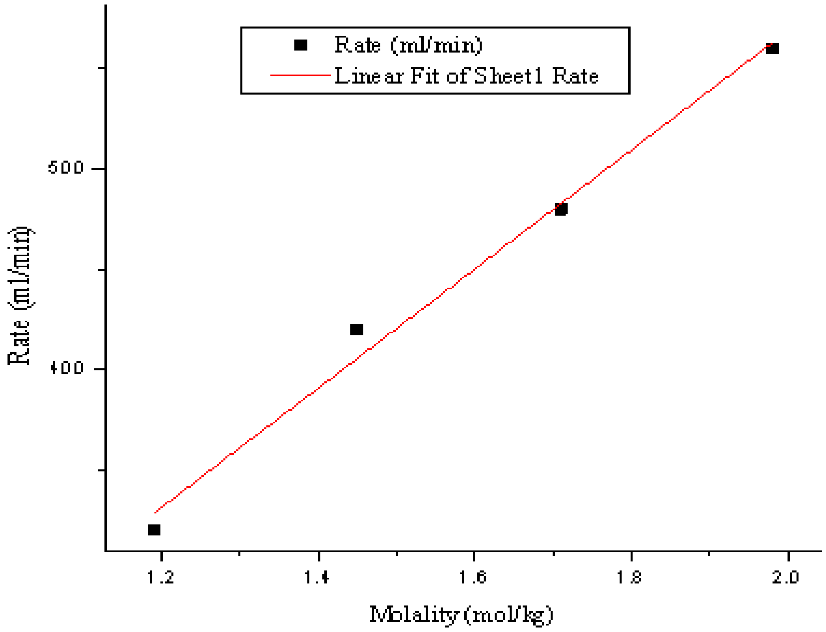


Figure 5.2(a): Regression of initial hydrogen generation rate with the molality of $NaBH_4$ for 0% NaOH at 55 °C.

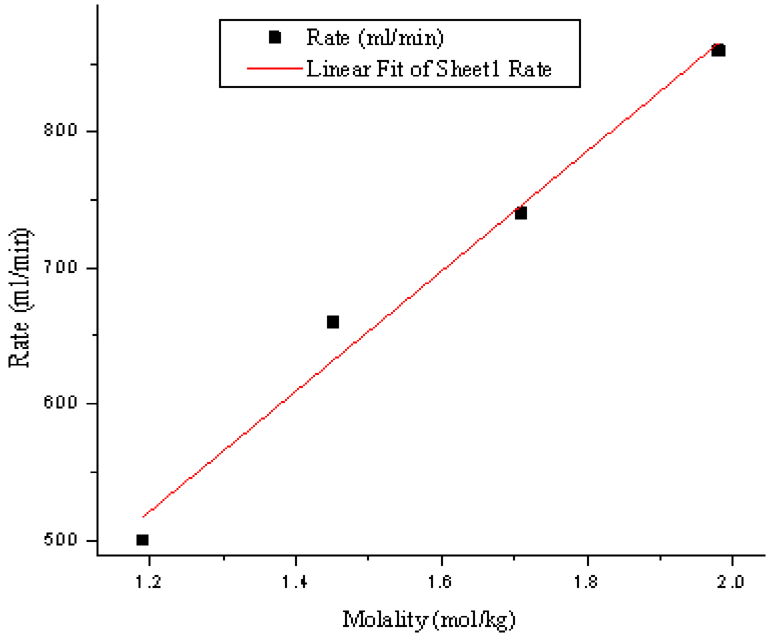


Figure 5.2(b): Regression of initial hydrogen generation rate with the molality of $NaBH_4$ for 1% NaOH at 45 °C.

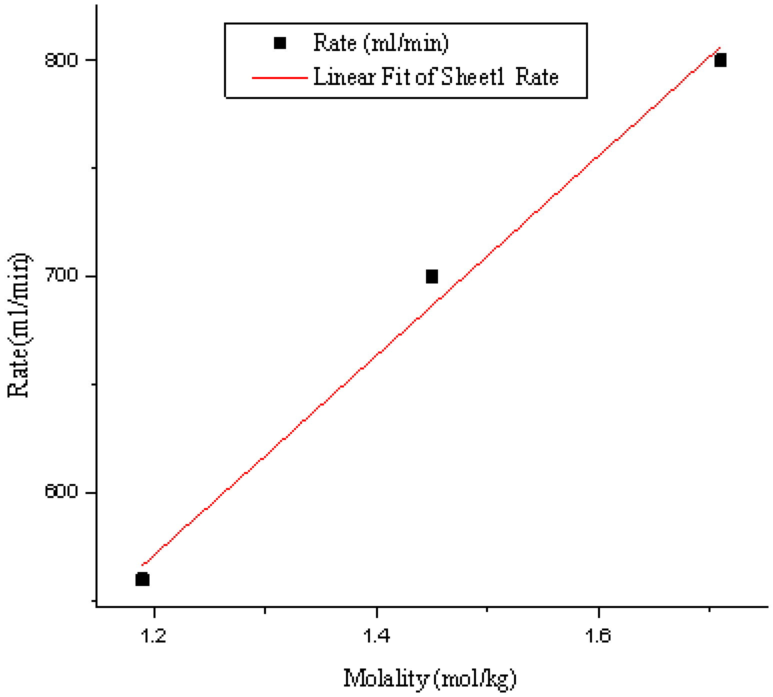


Figure 5.2(c): Regression of initial hydrogen generation rate with the molality of $NaBH_4$ for 3% NaOH at 63 ^{o}C

To determine parameters k and k_1, equation (11) was transformed into equation (12) given below.

$$\frac{1}{r_{H_2}} = \frac{1}{k} m_{NaBH_4} + \frac{k_1}{k} \frac{w_{NaOH}}{m_{NaBH_4}} \qquad (12)$$

As shown in Table 5.5 a plot of $1/r_{H2}$ versus w_{NaOH}/m_{NaBH4} gives a straight-line graph, whereby the intercept on the y axis is 1/k and the slope is k_1/k, from which both k and k_1 may be determined.

The relationship between (w_{NaOH}/m_{NaBH4}) against the reverse hydrogen-generation rate at 63 °C when the $NaBH_4$ concentration is 1.71mol/kg is shown in Figure 5.3 below.

It is observed that 'k' increased significantly from 555.5 to 1666.4 min^{-1} when the temperature increased from 45 to 63 °C.

Table 5.5: Parameters determined at various Temperatures and $NaBH_4$ concentration, Calculations carried out as shown in Annexure-1.

Molality (mol/kg)	Temperature (^{o}C)	K, min^{-1}	k_1, min^{-1}
1.19	35	192.30	0.02
1.19	45	555.55	0.13
1.19	63	1666.66	0.7
1.45	45	555.55	0.14
1.45	63	2000	0.8
1.17	35	740.74	0.4
1.17	45	769.23	0.6
1.17	63	2500	0.9

As given in Table 5.5 the values of k and k_1 are determined from slope and intercept of the graph, Therefore, the value of 'k' is calculated as 2000 min^{-1} and 'k_1' to be 0.8 min^{-1} at 1.45 mol/kg $NaBH_4$ and $63^{o}C$.

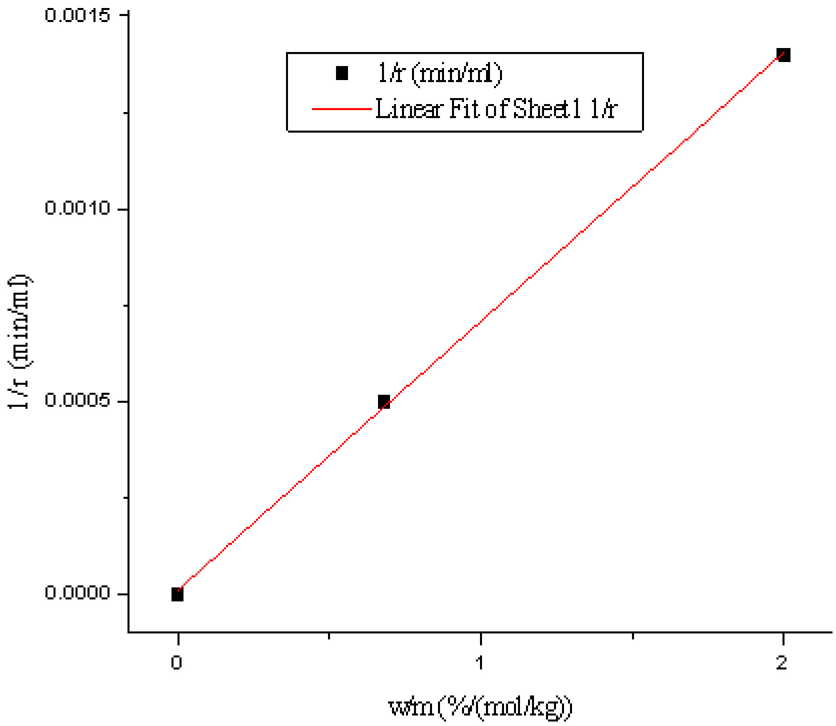


Figure 5.3: Regression at $63^{o}C$ and 1.71 mol/kg of $NaBH_4$.

CHAPTER 6
CONCLUSION

The hydrogen gas generation experiments are carried out during the research work. The following conclusions drawn are as follows:

1. Hydrogen gas is generated from the Sodium Borohydride with Cobalt Chloride as catalyst.

2. Hydrolysis reaction of Sodium Borohydride is a first order reaction.

3. The amount of hydrogen generated is 1300 ml for 0.45 gm of Sodium Borohydride and 0.05 gm of Cobalt Chloride.

4. As a result from experiment performed with Cobalt Chloride as a catalyst Hydrogen Generation Rate increases with increase in temperature, Sodium Borohydride ($NaBH_4$) concentration and decreases with Sodium Hydroxide (NaOH) Concentration.

5. Calculations for Activation energy shows that Activation Energy Calculated with Cobalt Chloride as catalyst is same as compared with the Ruthenium based catalyst from literature study.

6. The rate constant '*k'* with respect to sodium Borohydride increased significantly from 555.50 to 1666.40 min^{-1} when the temperature increased from 45 to 63 °C. However, rate constant with respect to Sodium Borohydride k_1 did not change significantly with $NaBH_4$ concentration and temperature.

7. From the above study, the empirical relationship describing the relation between rate of hydrogen generation and molality of sodium borohydride is good enough to describe the effect of NaOH concentrations, temperatures, and $NaBH_4$ concentration.

8. According to Gas Chromatography for Hydrogen Gas Analysis, the Hydrogen gas purity is 85% and rest being Nitrogen.

9. The tendency of sodium borohydride to store and release hydrogen is more effective and favorable.

10. From the SEM analysis for the residual substance metals with low atomic number and more atomic numbers are not uniformly distributed in this composition. Therefore, they get aggregated and form clusters. The morphology of the residue is not uniform.

11. The EDAX analysis signifies that Atomic percentage of Sodium (Na) is 12.09 %, Cobalt is 32.20%, Chlorine is 0.66% and Oxygen is 55.05%, thus the residue content contains more percentage of Cobalt excluding oxygen.

FUTURE SCOPE OF WORK

1. Study the role of water in hydrolysis reaction of Sodium Borohydride and further carry out the kinetic study.

2. Studies on various methods of recycling sodium metaborate residue left after the hydrolysis reaction.

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Annexure- 1

RATE KINETICS CALCULATIONS

1) Calculation of rate constants k and k_1 for Sodium Borohydride hydrolysis reaction.

$$r_{H_2} = \frac{k m^{\alpha}_{NaBH_4}}{1 + k_1 w_{NaOH}} \qquad (1)$$

According to Equation (1), (k / (1+k_1 w $_{NaOH}$) was assumed to be constant K, and m $^{\alpha}$ $_{NaBH4}$ was assumed M. By Regression analysis using power function calculations were carried out as under:

$$r = K M^{\alpha} \qquad (2)$$

$$\ln r = \ln K + \alpha \ln M \qquad (3)$$

$$R = C + \alpha N \qquad (4)$$

According to regression Analysis:

$$\Sigma R = n C + \alpha \Sigma N \qquad (5)$$

$$\Sigma R*N = C \Sigma N + \alpha \Sigma N^2 \qquad (6)$$

1. For 0% NaOH at 25°C:

r	m	ln r = R	ln m = N	R*N
160	1.19	5.07	0.17	0.86
200	1.45	5.29	0.37	1.95
260	1.71	5.56	0.53	2.94
320	1.98	5.76	0.68	3.91

$\Sigma N^2 = 0.9091$, $\Sigma R = 21.68$, $\Sigma M = 1.75$, $\Sigma R*N = 9.66$, $\Sigma N = 1.75$

Putting the above calculated values in Equation (5) and (6)

$21.68 = 4 C + 1.75 \alpha$

$9.66 = 1.75 C + 0.9091 \alpha$

Therefore, Order of reaction $\alpha = 1.2$, (k / (1+k_1 w $_{NaOH}$) = C = 133.62.

2. For 0 % NaOH at 35°C

r	m	ln r = R	ln m = N	R*N
260	1.19	5.56	0.17	0.95
300	1.45	5.70	0.37	2.11
440	1.71	6.08	0.53	3.22
400	1.98	5.99	0.68	4.07

$23.33 = 4\,C + 1.75\,\alpha$

$10.34 = 1.75\,C + 0.909\,\alpha$

Therefore, order of reaction $\alpha = 0.94$, $(k/(1+k_1\,w_{NaOH}) = C = 226.16$.

*Rest of the calculations was carried in similar way as above and the results are given in Table 5.3.

2) Calculation of Rate Constants k, k_1:

$$\frac{1}{r_{H_2}} = \frac{1}{k} m_{NaBH_4} + \frac{k_1}{k} \frac{w_{NaOH}}{m_{NaBH_4}} \qquad (1)$$

As shown in Figure 4.3 which would yield a linear fit and according to equation-1, a plot of $(1 / r_{H2})$ and (w_{NaOH} / m_{NaBH4}) should yield a straight line, where intercept on y axis give (1/k) and slope will give k_1/k. Therefore, k and k_1 are calculated.

For m = 1.19 (mol/kg) at 45°C

NaOH %	rate (r) (ml/min)	1/ r_{H2} (min/ml)	w/m (%/(mol/kg))
0	300	.0033	0
1	500	.002	0.840
3	420	.0024	2.52

Slope = $2.38 * 10^{-4}$, *k = 555.5*, $k_1 = 0.13$

For m = 1.19(mol/kg) at 63°C

NaOH	rate (r) (ml/min)	1/ r_{H2} (min/ml)	w/m (%/(mol/kg))
0	340	0	0
1	1000	0.001	0.84
3	560	0.00178	2.52

Slope = 4.64×10^{-4}, k = 1666.6 min^{-1} and $k_1 = 0.7\ min^{-1}$.

*Rest of the calculations was carried in similar way as above and the results are given in Table 5.4.

3) Calculation of Activation Energy:

$$k = Ae^{\frac{-E}{RT}} \qquad (1)$$

$$\frac{k}{A} = e^{\frac{-E}{RT}} \qquad (2)$$

$$\ln\frac{k}{A} = \frac{-E}{RT} \qquad (3)$$

$$\ln k - \ln A = \frac{-E}{RT} \qquad (4)$$

Calculating activation energy at two temperatures i.e. 45^{o}C and 63^{o}C and putting the value of ‘k’ according to the temperature in equation-4.

$$\ln 555.5 - \ln A = \frac{-E}{8.314 \times 318} \quad \&$$

$$\ln 1666.6 - \ln A = \frac{-E}{8.314 \times 336}$$

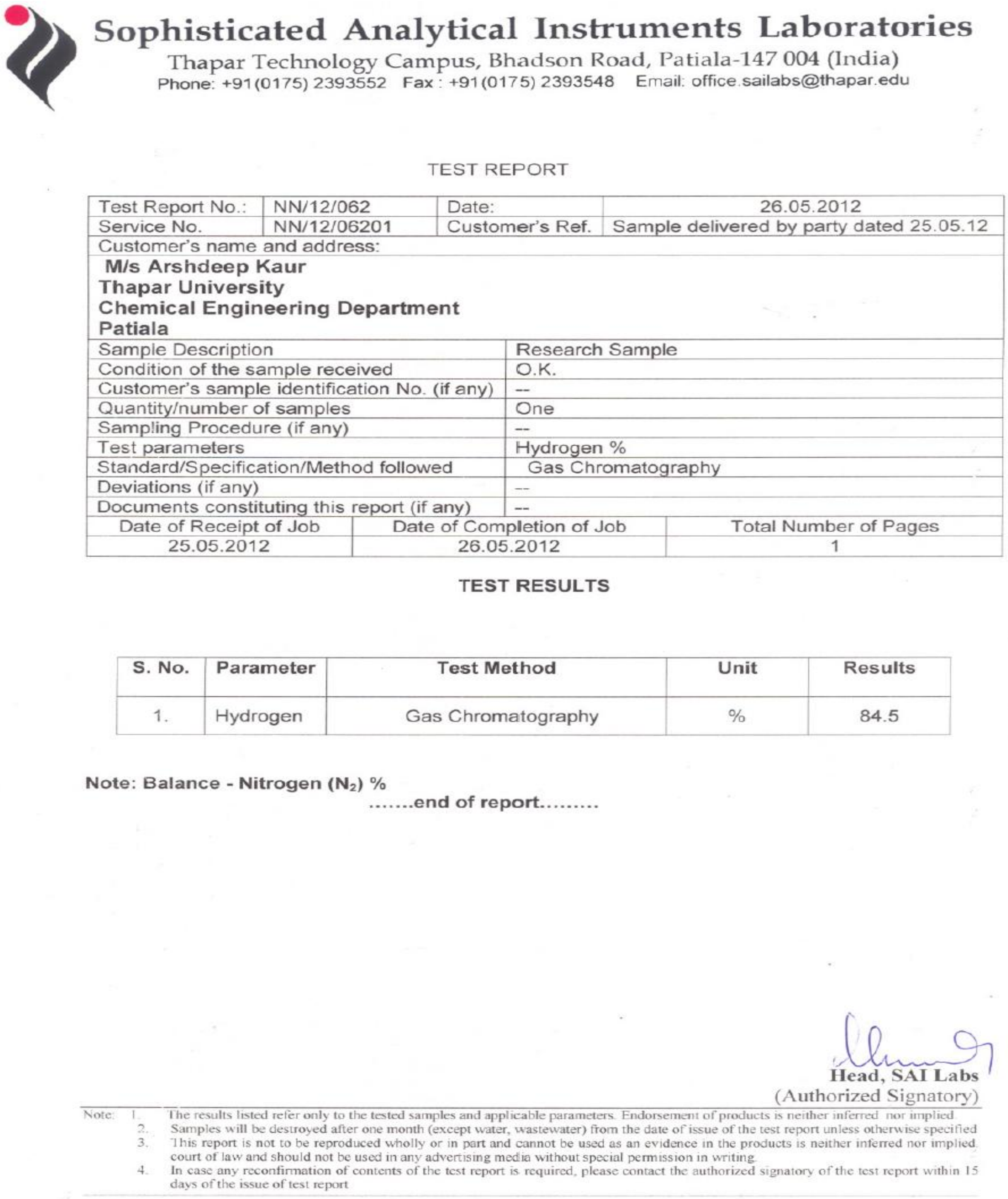
Therefore, *E = 37931.03 J/mol, 37.931 KJ/mol*

*A=1.2*10^{9} sec^{-1}*

Annexure – II

ANALYSIS REPORTS

1. Purity of Hydrogen by Gas Chromatograph



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TEST REPORT

Test Report No.:	NN/12/062	Date:	26.05.2012
Service No.	NN/12/06201	Customer's Ref.	Sample delivered by party dated 25.05.12

Customer's name and address:
M/s Arshdeep Kaur
Thapar University
Chemical Engineering Department
Patiala

Sample Description	Research Sample
Condition of the sample received	O.K.
Customer's sample identification No. (if any)	--
Quantity/number of samples	One
Sampling Procedure (if any)	--
Test parameters	Hydrogen %
Standard/Specification/Method followed	Gas Chromatography
Deviations (if any)	--
Documents constituting this report (if any)	--

Date of Receipt of Job	Date of Completion of Job	Total Number of Pages
25.05.2012	26.05.2012	1

TEST RESULTS

S. No.	Parameter	Test Method	Unit	Results
1.	Hydrogen	Gas Chromatography	%	84.5

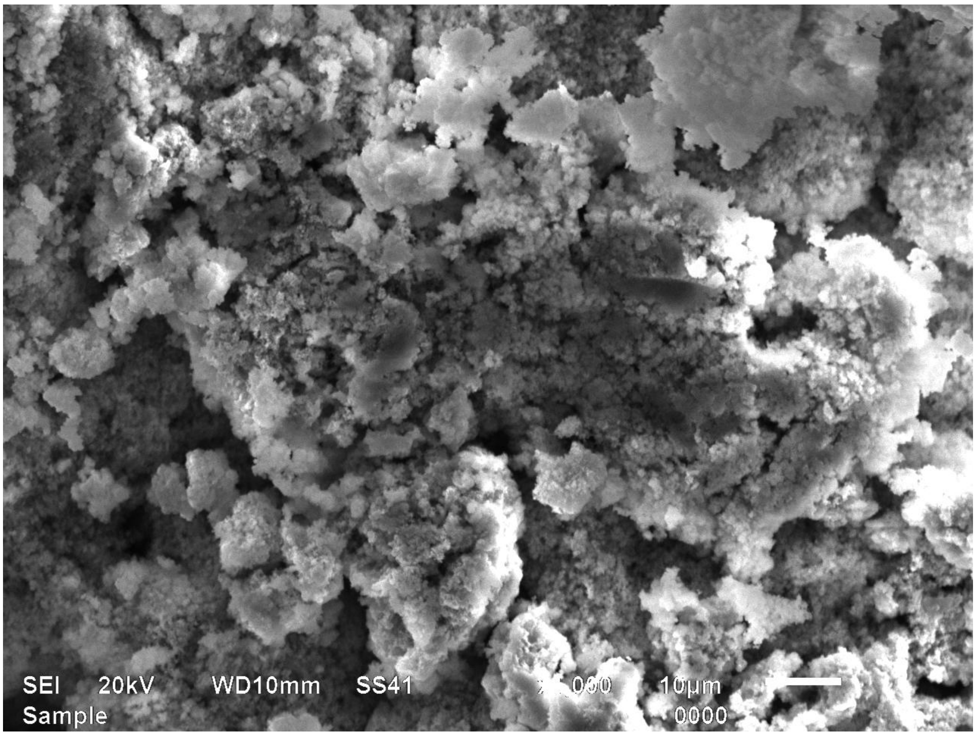
Note: Balance - Nitrogen (N_2) %

.......end of report.........

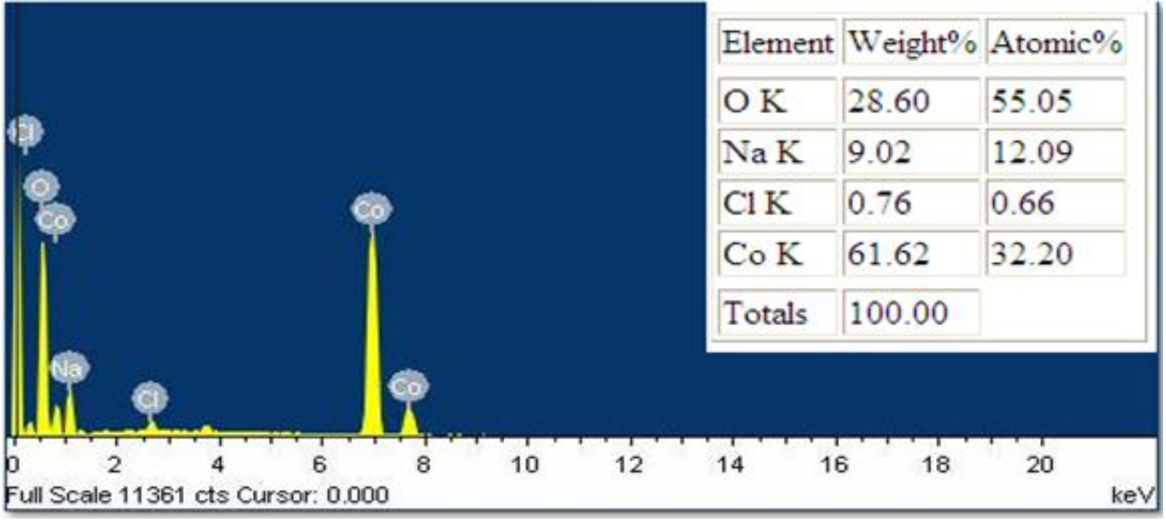
Head, SAI Labs
(Authorized Signatory)

Note:
1. The results listed refer only to the tested samples and applicable parameters. Endorsement of products is neither inferred nor implied.
2. Samples will be destroyed after one month (except water, wastewater) from the date of issue of the test report unless otherwise specified
3. This report is not to be reproduced wholly or in part and cannot be used as an evidence in the products is neither inferred nor implied. court of law and should not be used in any advertising media without special permission in writing.
4. In case any reconfirmation of contents of the test report is required, please contact the authorized signatory of the test report within 15 days of the issue of test report

2. Residue analysis by SEM:



3.Residue analysis by EDAX



Element	Weight%	Atomic%
O K	28.60	55.05
Na K	9.02	12.09
Cl K	0.76	0.66
Co K	61.62	32.20
Totals	100.00	