ANKARA YILDIRIM BEYAZIT UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

EXPERIMENTAL STUDY OF AVAILABILITY OF USING OF CO$_2$ COMING FROM EXHAUST IN HYDROGEN PRODUCTION TECHNOLOGY OF NaBH$_4$

M.Sc. Thesis by

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We have read the thesis entitled **"EXPERIMENTAL STUDY OF AVAILABILITY OF USING OF CO₂ COMING FROM EXHAUST IN HYDROGEN PRODUCTION TECHNOLOGY OF NaBH₄"** completed by **ERSİN KİLCİ** under the supervision of **ASSIST. PROF. DR. KEMAL BİLEN** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

It has been extensively studied over the last years on hydrogen-containing chemical compounds to produce hydrogen on demand, and in the amount needed. Especially, sodium borohydride is a preferred compound because of its excellent characteristics for hydrogen production. Aqueous alkaline sodium borohydride solution is safely stored and transported as it is stable at room temperature.

Expensive compounds such as containing, nickel, ruthenium and cobalt are generally used to produce hydrogen from aqueous alkaline sodium borohydride solution as catalysts. But, some studies have shown that there is a direct correlation between pH value and stability of sodium borohydride solutions. Carbon dioxide gas having acidic effect has potential to easily change pH value of solutions.

In this study, hydrogen was obtained from alkaline sodium borohydride solutions by using the new method described above. Hydrolysis experiments were carried out at different temperatures by sending carbon dioxide gas to sodium borohydride solution containing potassium hydroxide for one minute. Solution concentration, solution temperature, amount of sodium borohydride, and flow rate of carbon dioxide gas were selected as variable. Thus, the effects of solution concentration, solution temperature, amount of sodium borohydride, flow rate of carbon dioxide gas and pH value of solution to rate of obtained hydrogen were investigated experimentally.

As a result of this study, it has been considered that a system can be designed that allows to be produced hydrogen without using of expensive catalysts by changing pH value of solutions through carbon dioxide gas generated at the end of combustion in systems where fossil fuels are used. It has been thought that combustion efficiency will increase, and fuel consumption and amount of waste gas will decrease by transferring the obtained hydrogen to combustion system.

Keywords: Hydrogen production, sodium borohydride solution, carbon dioxide gas, pH value, fuel saving.

EGZOZDAN GELEN CO_2'İN $NaBH_4$'DEN HİDROJEN ÜRETİM TEKNOLOJİSİNDE KULLANILABİLİRLİĞİNİN DENEYSEL ARAŞTIRILMASI

ÖZ

Hidrojeni ihtiyaç anında ve ihtiyaç miktarı kadar üretmek için son yıllarda hidrojen içeren kimyasal bileşikler üzerinde yoğun olarak çalışılmaktadır. Sahip olduğu mükemmel özelliklerinden dolayı özellikle sodyum bor hidrür hidrojen üretimi için tercih edilen bir bileşiktir. Sulu bazik sodyum bor hidrür çözeltisi oda sıcaklığında kararlı olduğu için emniyetli bir şekilde depolanabilmekte ve taşınabilmektedir.

Bazik sodyum bor hidrür çözeltisinden hidrojen üretmek için genellikle nikel, rutenyum ve kobalt içeren bileşikler gibi pahalı katalizörler kullanılmaktadır. Ancak, yapılan bazı çalışmalar pH değeri ile sodyum bor hidrür çözeltilerinin kararlılığı arasında doğru bir orantı olduğunu göstermiştir. Asidik etkiye sahip karbon dioksit gazı, çözeltilerin pH değerini kolaylıkla değiştirme potansiyeline sahiptir.

Bu çalışmada; potasyum hidroksit içeren sodyum bor hidrür çözeltilerine bir dakikalık süreyle karbon dioksit gazı gönderilerek farklı sıcaklıklarda hidroliz deneyleri yapılmıştır. Çözelti derişimi, çözelti sıcaklığı, sodyum bor hidrür miktarı ve karbon dioksit gazının debisi değişken olarak seçilmiştir. Böylece; çözelti derişiminin, çözelti sıcaklığının, sodyum bor hidrür miktarının, karbon dioksit gazı debisinin ve çözeltinin pH değerinin hidrojen elde etme hızına etkileri deneysel olarak incelenmiştir.

Bu çalışma sonucunda; fosil yakıtların kullanıldığı sistemlerde, yanma sonunda oluşan karbon dioksit gazı kullanılarak ilgili çözeltilerin pH değerinin değiştirilmesi ve böylece pahalı katalizörler kullanılmadan da hidrojen üretilebilmesine imkân veren bir sistemin tasarlanabileceği değerlendirilmektedir. Elde edilecek hidrojenin yakma sistemine gönderilmesiyle de yanma veriminde artış sağlanarak yakıt tüketiminde ve atık gaz miktarında azalma sağlanacağı düşünülmektedir.

Anahtar Kelimeler: Hidrojen üretimi, sodyum bor hidrür çözeltisi, karbon dioksit gazı, pH değeri, yakıt tasarrufu.

CONTENTS

NOMENCLATURE

AFC	Alkaline fuel cell
$B(OCH_3)_3$	Trimethyl borate
$B(OH)_3$	Boric acid
CB & H	Carbon black & hydrogen
CH_3OH	Methanol
CH_3COOH	Acetic acid
CH_4	Methane
CNT	Carbon nanotube
Co	Cobalt
CO	Carbon monoxide
CO_2	Carbon dioxide
CoO	Cobalt oxide
DAFC	Phosphoric acid fuel cell
DMFC	Direct methanol fuel cell
FeO	Iron oxide
H_2	Hydrogen
HCl	Hydrochloric acid
H_2O	Water
H_2S	Hydrogen sulfide
HGMS	Hollow glass microspheres
KOH	Potassium hydroxide
MCFC	Molten carbonate fuel cell
MgH_2	Magnesium hydride
$NaBH_4$	Sodium borohydride
$NaBO_2$	Sodium metaborate
NaH	Sodium hydride
$NaHCO_3$	Sodium bicarbonate
NaOH	Sodium hydroxide
Ni	Nickel
NO_x	Nitrogen oxides
O_2	Oxygen
PEM	Proton exchange membrane

PEMFC	Proton exchange membrane fuel cell
POX	Partial oxidation
Rh	Rhodium
Ru	Ruthenium
SMR	Steam methane reforming
SOFC	Solid oxide fuel cell
SO_x	Sulfide oxides
TGA	Thermo gravimetric analysis
UHC	Unburned hydrocarbon
XRD	X-ray diffraction
WGS	Water gas shift

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CHAPTER 1

INTRODUCTION

Many subjects such as economic growth, prosperity and the quality of life are based on energy. The requirement for energy increases in parallel with developments in technology, the population growth in the world and the diversity of basic human needs. It is not difficult to foresee that our need for energy will continue to increase for the progression.

Hydrocarbon fossil fuels such as coal, fuel oil, natural gas and petroleum are used as the primary energy source to meet energy needs. According to the data given by International Energy Agency, if current energy production and consumption habits are maintained, it is estimated that the world's need for energy will increase by 21.5% from 2015 to 2035 and about 73.7% of this need for energy will be met from fossil fuels [1].

But on the other hand, the main cause of climate change is carbon dioxide (CO_2) gas formed when fossil fuels are burned. The quantity of CO_2 in the atmosphere will continue to increase if the use of fossil fuels commonly continues to meet the need for energy. Lackner [2] stated that the CO_2 content of the atmosphere has now risen by more than a third since the beginning of the industrial revolution, from 280 parts per million by volume (ppm) to 385 ppm today and rising by 2 ppm per year. The CO_2 content of the atmosphere will reach 450 ppm, the critical threshold for global warming, after about 30 years with current rates of increase.

Therefore, there are a great number of studies about on the use of alternative energy sources, such as renewable energy sources, can be replaced fossil fuels in order to reduce CO_2 emissions in the literature. According to the Ministry of Energy and Natural Resources Directorate General of Renewable Energy, the development and utilization of renewable energy sources such as bioenergy, solar energy, geothermal energy, hydroelectricity, wave energy and wind energy, which have gained momentum in recent years, will reduce CO_2 emissions [3].

Also, there are many studies evaluated that hydrogen could be an alternative energy source to be replaced fossil fuels such as renewable energy sources in the literature. Shasby [4] expressed in his M.Sc. thesis that hydrogen is almost the perfect fuel. It has the highest energy content by weigh of any fuel. It has no emissions when burned and used in a fuel cell the only by-product is water. Hydrogen is very abundant and is found readily in many compounds on earth. It is also the only viable fuel identified for the future when current stores of fossil fuels run out.

There are in large quantities studies on the methods of hydrogen production. According to these studies, almost all of the hydrogen is produced from hydrocarbon that consist of hydrogen and carbon (natural gas, coal, oil and its derivatives) and the most commonly used method is steam reforming. Roussiere [5] is stated in his Ph.D. thesis that steam methane reforming (SMR) process performs in the range of 500-900 °C, above 20 bar and in two steps. He explained that the first step is the reforming reaction, which is strongly endothermic ($\Delta h=+206.16$ kJ/mole), the second step is the water gas shift (WGS) reaction, which is slightly exothermic ($\Delta h=-41$ kJ/mole).

Another method of producing hydrogen from hydrocarbon is partial oxidation (POX) of methane (CH_4). The studies show that POX process could be replaced the SMR process at producing of syngas, which a kind of a gas that consists of H_2 and carbon monoxide (CO), due to its advantages. Yaying et al. [6] expressed that when air is used instead of oxygen (O_2) as oxidant and rhodium (Rh)-coated monolith catalysts in auto thermal reactors, the conversion of CH_4 to CO and H_2 is above 90%, the air-separation process for O_2 production is not required, which can greatly reduce the investment for the POX and can avoid an explosion danger at low methane to oxygen ratios, in particular, under high pressures.

Gasification process is another method used to obtain hydrogen from hydrocarbons. Higman and Burgt [7] put forward in their studies that gasification might be played an important role in the transition from fossil fuels to a fully renewable world. According to them, polygeneration energy systems, producing both power and hydrogen used at gasification process could be transformed to hydrogen production units with low cost. Also, they expressed that gasification process is a key

technology to generate more efficient energy from coal and heavy oils with the best environmentally friendly method.

Kvaerner method [8], a process began using recently, is the newest way of obtaining hydrogen from hydrocarbon. Hydrogen has been produced without CO_2 emissions through this concept (also known Kvaerner Carbon Black and Hydrogen Process) developed by Kvaerner Engineering S. A. of Norway since the early 1980s. A pilot plant that has been operating in Canada since 1992 uses $1\,000\ m_N^3/h$ natural gas and $2\,100\ kW_{el}$ electrical energy to generate $1\,000\ kW$ hot steam, about $500\ kg/h$ activated carbon and $2\,000\ m_N^3/h$ of hydrogen. Taking into consideration all the useable products, the plant achieves an efficiency of 93%.

All hydrogen production methods based on hydrocarbons adversely affect the environment as they use fossil fuels. The electrolysis of water, producing hydrogen from water by using appropriate catalysts and electric power, is a completely environmental method. However, this method has a very little share in hydrogen production methods since catalysts (platinum, ruthenium etc.) as well as electric power are expensive. Recently, a great number of studies have been researched to reduce the costs of electrolysis. The Grid-Shift Process developed by Dopp [9] has been promising hope most of all. Dopp made the metallic electrodes to three-dimensional (3D) shape by coating all their surfaces with nano powders, which has excellent electrical conductivity in his experimental study. He observed that nano-coated 3D electrodes have high rate per surface area and so they can be smaller for the same hydrogen output. Also, he expressed that the costs of catalyst will reduce remarkable since no need to use expensive material like platinum as catalyst.

The other way to generate hydrogen without using fossil fuel source is thermolysis (the thermal splitting of water). Water is split into its components which form itself, hydrogen and oxygen, when it heats over 1400°C. But, this is very expensive method because of the heating of water to these degrees needs very huge energy. Therefore, there are various studies in literature about the thermal splitting of water at lower degrees. Agrafiotis et al. [10] achieved to decrease the heat of thermolysis to 800°C and split the eighty percent of water used, by using an iron-oxide-based redox pair

system in their experimental studies. So, the amount of energy needed to split water decreased, as well as was obtained much hydrogen due to rising system efficiency.

One of the main cause of not to widespread of utilizing hydrogen adequately is storage problems since the storing of hydrogen is hard because of its chemistry and physical characteristics, as well as high costs. The most commonly used storage technique of hydrogen is to store it in pressured tanks as gas. Hydrogen is generally filled in tanks between 150 and 300 bar. The obligation of the tanks to be made from highly resistant materials to withstand such high pressures, the tanks become very heavy as a result of this and the use of some of the energy to be taken from the hydrogen in the pressurization of the gas are the biggest obstacles of this method. Klebanoff [11] stated in his theoretical study that when the compression pressure rises up, the amount of stored hydrogen in the tank increases. For example, at 350 bar, the molar volume of hydrogen is 22% larger than predicted by the ideal behavior due to intermolecular repulsion of the hydrogen molecules. But, it means that a heavier tank and much more energy need for compression.

There are many studies in the literature that hydrogen can also be stored in the pressured tanks as liquid. Hirscher [12] expressed that hydrogen liquefies at -253°C and higher storage densities are possible with liquid hydrogen according to gas form of hydrogen in his theatrical study. He is also stated that its very low boiling point at -253°C means that the generation of liquid hydrogen is complex and requires 20% to 30% of its energy content, the storage of liquid hydrogen is technically challenging and containers with high levels of insulation are used, expensive and consisting of an inner tank and an outer container with an insulating vacuum between them.

A great number of studies have been conducted on new hydrogen storage techniques in recent times since storage of hydrogen in pressurized tanks brings many challenges such as cost, safety and weight. One of them is to store the hydrogen in micro-sized glass spheres (HGMS - Hollow Glass Microspheres). This method is based on to be stored of hydrogen under high pressure and temperature into glass spheres of very small size. When the glass sphere is cooled, the hydrogen is trapped in the sphere. To be reheated of the glass sphere is sufficient to recover the hydrogen. Shelby [13] used glass spheres made of FeO and CoO in an experiment and filled

them with hydrogen gas under the pressure of 35 MPa and 69 MPa. He achieved to recover the hydrogen in the glass spheres by using a light source with a wavelength of 1 500-2 300 nm as a heater. As a result of the experiment; he determined that the amount of hydrogen stored in the glass spheres is proportional to the pressure, the amount of hydrogen recovered is equal to about 2.2% of the glass spheres, and that glass spheres can be used repeatedly for this process.

Carbonaceous materials, which are one of the most suitable materials for gas storage due to its physical and chemical properties, have been recently begun to be used as hydrogen storage material. Especially, many researches have been made on carbon nanotubes (CNT) discovered by Iijima in 1991. Züttel et al. [14] showed in a study they conducted that the amount of hydrogen to be stored in carbon nanotubes and retrieved later depends on temperature and pressure. They found that a mass of 5.5% hydrogen could be stored at -196°C in a nanotube, while it dropped to 0.6% at room temperature (25°C). In addition, they determined that only 2% of the hydrogen stored at room temperature could be recovered because the carbon and hydrogen atoms forms a covalent bond between them, and the temperature has to be increased above 77°C in order to get more hydrogen.

Some metals and alloys can be absorbed hydrogen like sponges. These materials, called metal hydrides, have been begun to be used for hydrogen storage in recent times. Heat must be supplied for storage. During the recovery of hydrogen, heat is spread in the environment. Sherif et al. [15] stated in their study that the metal hydride method could be compared with the liquid hydrogen storage method as the amount of stored hydrogen and with the pressurized gas hydrogen method as total weight. In addition, they expressed that the best metal hydrides are MgH_2 with a H_2/kg hydrogen storage rate of 7%.

Due to the heavy weight of metal hydrides, great deals of researches have been carried out in recent years on the method of obtaining hydrogen from chemical hydrides. The greatest advantage of systems using chemical hydrides for hydrogen production is that hydrogen is not stored but produced when needed. All the risks and difficulties of hydrogen storage and transportation are eliminated with this system.

Studies have been focused on borohydrides, especially on sodium borohydride ($NaBH_4$), because it has a promising potential of using hydrogen energy in vehicles.

The pure $NaBH_4$ contains 10.8% by weight of hydrogen. Studies on which the hydrogen is obtained from the aqueous alkaline $NaBH_4$ solution by using catalyst are the majority in literature. In an experimental study, Sim and Kim [16] generated hydrogen from solid-state $NaBH_4$ existing in a reacting chamber by using sodium bicarbonate ($NaHCO_3$) solution as a catalytic. They injected the $NaHCO_3$ solution into the reactor when the hydrogen was needed. They measured the hydrogen generation rate according as various conditions such as temperature, the concentration and injection speed of $NaHCO_3$ solution. They noticed that the hydrogen generation initiated immediately when the $NaHCO_3$ solution was injected. They observed that the hydrogen generation rate and $NaBH_4$ conversion increased with increasing the $NaHCO_3$ concentration but decreased with increasing the injection speed of $NaHCO_3$ solution. They concluded that $NaBO_2$ forming the result of hydrolysis, covers on the catalyst surface and it causes the loss of catalytic properties.

Aiello et al. [17] aimed to develop a new method producing H_2 for using in hand-portable fuel cells. They obtained pure H_2 by reacting the water in the liquid or vapor phase with $NaBH_4$ in an experimental study. The reaction was carried out in an isothermal semi-batch reactor. They worked between 110 and 180 °C and compared the measured hydrogen yield with the theoretical efficiency. While the theoretical yield was 100% at 110 °C, it fell below 50% after 140 °C. Experimentally, they reached a hydrogen production rate of 0.33 L H_2/min and a yield of 99% at 110 °C. They observed that while the hydrogen yield strongly depends on the temperature, the steam flow rate has little effect. They also found that insoluble layer on the surface of the reactant prevented the reaction by constituting a film between water vapor and $NaBH_4$.

Marrero-Alfonso et al. [18] have carried out an experimental study and reported that when sodium borohydride reacts with vapor, H_2 gas and $NaBO_2$ form. They filled the reactor with solid $NaBH_4$ and reacted it with steam. They detected H_2 at the outlet of the reactor. They performed thermo gravimetric analysis (TGA) and x-ray diffraction

(XRD) analysis to detect water loss and formed solid products. Unlike the reaction in liquid water, they produced hydrogen from the reaction of sodium borohydride with steam without a catalyst with about a yield of 95% at 140 °C. They noticed that the addition of 1% mole of methanol and acetic acid (liquid regulator) did not enhance the reaction rate, although acetic acid improved the reaction yield of slightly. As a result of this study, they emphasized that hydrolysis efficiency is high in acidic medium.

Marrero-Alfonso et al. [19] investigated the effect of water on $NaBO_2$ in the hydrolysis of $NaBH_4$ with steam by changing the amount of water in another experimental study. The gravimetric and volumetric energy densities that can be obtained from the hydrolysis of chemical hydrides largely depend on the amount of water required for the process. They investigated this situation for steam hydrolysis of $NaBH_4$. They also investigated the thermal stability of commercial $NaBO_2.2H_2O$ and $NaBO_2.4H_2O$. The standard $NaBO_2.2H_2O$ was stable up to 100 °C, although it leaved all the crystal water in its structure between 100 °C and 350 °C. The standard $NaBO_2.4H_2O$ started to decay continuously from 40 °C, although it leaved all of the crystal water in its structure above 400 °C.

Beaird et al. [20] investigated the hydrolysis of $NaBH_4$ with water vapor in different humidity ranges at 110 °C with visual technic. For this, they placed a borescope video camera on a glass reactor and used the nitrogen (N_2) gas as a humidifier. They found that the hydrolysis reaction did not start above the humidity value of 21.7% in studies conducted at 19-40% humidity range. In study, they observed that solid $NaBH_4$ firstly absorbed the moisture at low humidity, then it passed to the saturated liquid phase, and hydrolysis reaction initiated as foaming when it passed completely to the liquid phase. They reported that the H_2 output ended in 22th minutes at 110 °C and was reached the 90% conversion with 32% humidity. They also observed that $NaBO_2$, formed by foaming in the reaction, covered on the walls of the reactor as a thin film.

Minkina et al. [21] did experiments on the stability of $NaBH_4$. In their experiments, they prepared an alkaline aqueous solution by adding sodium hydroxide (NaOH) into the water. Then, they observed the reaction rate at 25 °C, 40 °C and 80 °C and at

different concentrations by adding $NaBH_4$ into this alkaline solution. They found that when the concentration of NaOH increases (the alkalinity of the solution increases, in other words the pH value of concentration increases) and the temperature decreases, the hydrolysis rate slows down, so the hydrogen production decreases. They came up with that the hydrolysis rate of $NaBH_4$ is very small such as 0.01% per hour at room temperature (25 °C) and in the NAOH alkaline aqueous of 1.0N, so that $NaBH_4$ is very good hydrogen storage and can be safely transported even at room temperature.

Akdim et al. [22] investigated the effect of acetic acid (CH_3COOH) and hydrochloric acid (HCl) on the hydrolysis of $NaBH_4$. They put $NaBH_4$ into a reactor, and then added acid solution. They worked at reactor temperatures between 20 °C and 80 °C. The experiment did with the HCl solution ended in a shorter time than the experiment did with the CH_3COOH. They stated that the efficiency of hydrogen production was 100% at all temperatures which mole ratio of $HCl/NaBH_4$ was 1 and 2. It was also determined that the hydrolysis yield was 100% at all temperatures which mole ratio of $CH_3COOH/NaBH_4$ was 2.

Javed and Subramanian [23] investigated the effect of physicochemical parameters on hydrogen production at the hydrolysis of $NaBH_4$ with acid solution. They investigated the effect of the temperature (0-60 °C), the acid concentration, the amount of $NaBH_4$ and the flow rate on hydrogen production in experiments carried out in a reactor. The obtained results indicated that 80% of theoretical hydrogen might be generated from 2 mg (0.053 mM) of $NaBH_4$ by using a 6 N HCl solution at a flow rate of 1 μL/min at 60 °C as the most highly efficiently. It was stated that the hydrolysis by-products were $NaBO_2$ and NaCl. One of the critical importance of this work was that it was emphasized that the ratio of $acid/NaBH_4/H_2O$ was effective in the composition of by-products. They carried out the characterization processes in XRD and SEM.

Prosini and Gislon [24] carried out a study on obtaining hydrogen from $NaBH_4$ in acidic medium. They designed a prototype reactor to provide hydrogen for the fuel cell. They obtained hydrogen from solid $NaBH_4$ with the aid of HCl acid solution at room temperature. They observed that the reaction stopped when the acid solution was removed. The hydrogen capacity of the system was 2.5% by weight and

hydrogen was produced up to 92% of the theoretical hydrogen production. They were obtained about 720 Wh/kg of energy in a fuel cell operating at 0.8 V with this amount of hydrogen. This means that it is 4 times more energy than commercial high energy density lithium-ion batteries.

Murugesan et al. [25] conducted experimental studies on hydrogen production for small portable applications. They were carried out hydrogen production with the reaction of solid $NaBH_4$ and HCl acid solution. They also investigated the effect of horizontal and vertical position of 5 mm^3 volume reactor on hydrogen production. In the hydrolysis of $NaBH_4$, they examined the effect of several mineral and organic weak acids on hydrogen yield by using them. Among the mineral acids examined, HCl generated a maximum hydrogen yield of 97% of the theoretical yield at 3N concentration at the vertical position of reactor Formic acid gave 87% of the hydrogen yield at 12N concentration. Characterization of the reaction products was carried out in SEM and XRD.

Liu et al. [26] examined the parameters affecting the reaction efficiency at high temperature (150 °C, 180 °C and 200 °C) and pressure (30 psi) in the hydrolysis of $NaBH_4$ with steam. They have designed a batch reactor for this purpose. Solid $NaBH_4$ was put into the inner compartment of the reactor and water was put into the outer compartment. TGA and XRD analyzes were performed in the characterization process. They reached the conclusion that it needs to the low temperature or increased the amount of water fed for increasing the hydrolysis rate of $NaBH_4$.

Amendola et al. [27] carried out experiments to obtain hydrogen from alkaline $NaBH_4$ solution by using Ru catalyst. They examined the effect of the concentrations of NaOH and NaBH4, and temperature on hydrogen production. Hydrolysis experiments of 30 mL of $NaBH_4$ solution, containing 1, 5 and 10% by weight NaOH and 1% $NaBH_4$, with 5% by weight resin, containing Ru, were carried out at 25 °C. They observed that when the concentration of the NaOH solution decreases, the hydrolysis rate of the hydrolysis reaction increases. They explained that; free OH^- ions present in the medium strongly complex with water. This reduces the amount of water and so the reaction rate reduces. They have also examined the solubility of $NaBO_2$ in NaOH solutions at different concentrations. They observed that if the

concentration of NaOH increases, the solubility of $NaBO_2$ decreases. They emphasized that this situation is effective on the decreasing of hydrogen production.

Hua et al. [28] tried a nickel boride catalyst (Ni_xB) at the catalytic hydrolysis of the alkaline $NaBH_4$ solution. They chose the temperature and NaOH concentration as variable parameters. At room temperature (25°C), they realized the hydrolysis of 20 ml of $NaBH_4$ solution (1.5% by weight) at by weight of 0%, 10% and 20% NaOH concentrations used 0.1 g of catalyst. They observed that when the concentration of NaOH increases, the duration of the hydrolysis reaction increases. Water is stoichiometrically consumed during hydrolysis. The reaction time is prolonged because if the amount of NaOH increases, the amount of water decreases. This situation also reduces the hydrolysis efficiency. They found that the hydrogen storage capacities of $NaBH_4$ solutions containing 0%, 10% and 20% NaOH by weight as 7.1%, 6.75% and 6% respectively.

Ye et al. [29] tested the γ-Al_2O_3 supported Co catalyst in catalytic hydrolysis of the alkaline $NaBH_4$ solution. Hydrolysis experiments were studied from 5% $NaBH_4$ + x%NaOH solutions (x=1, 5, 10, 15) at 303K using 50 mg of catalyst by measuring the cumulative volumes of hydrogen periodically. Fluctuation was observed at the reaction rate during the hydrolysis reaction. They observed that when the NaOH concentration decreases, the reaction rate increases. The highest hydrolysis yield was obtained with 85% in the solution containing by weight of 5% $NaBH_4$ and 5% by weight of NaOH.

Ingersoll et al. [30] tested the Ni-Co-B catalyst they prepared in the catalytic hydrolysis of the alkaline $NaBH_4$ solution. They investigated the effect of the parameters such as the concentration of NaOH and $NaBH_4$ and temperature on hydrogen production in the hydrolysis of the alkaline $NaBH_4$ solution with Ni-Co-B catalyst. They hydrolyzed the 5 mL of alkaline $NaBH_4$ solution containing 1, 5, 8, 10, 15, 20 and 25% by weight of NaOH and 0.16 g of $NaBH_4$ using 0.1 g of catalyst at 28 °C. They reached the highest hydrogen production in the $NaBH_4$ solution containing 15% NaOH and observed the anomalies based on catalyst under and above this concentration. They explained the reason of this that catalysts containing Ni-Co interact with OH^- ions. They stressed that the hydrogen production efficiency

in the $NaBH_4$ solutions containing NaOH at high concentration is low because of the low water solubility of $NaBO_2$ and low water activity.

Walter et al. [31] performed catheteric hydrolysis experiments of the alkaline $NaBH_4$ solution with Ni_3B, Co_3B and Ru catalysts at 60 °C. They selected $NaBH_4$ concentration (2.5-30% by weight) and NaOH concentration (2.5-30% by weight) as variable parameters. They expressed that when the NaOH concentration increased, the reaction rate of the Ru catalyst decreased while the reaction rate of the boron catalysts increased. They observed that the catalysts formed a strong bond with hydrogen. When the concentration of the hydroxide increased, some catalysts (such as Ni_3B, Co_3B) released the hydrogen quickly. This situation reflected as an increase in hydrogen production rate. The maximum hydrogen production rate at hydrolysis of by weight of 5% NaOH and 5% $NaBH_4$ solution was found as 18.6, 6 and 1.3 L/min for Ru, Co_3B and Ni_3B catalysts, respectively at 60°C.

The studies, worked on fuel cell, have a significant share at studies on hydrogen energy in the literature. Fuel cells convert the chemical energy in hydrogen directly into electricity and heat. As a result of this cycle, only water comes out as a by-product. A conventional combustion-based power plant typically generates electricity at efficiencies of 33 to 35%, while fuel cell systems can generate electricity at efficiencies of up to 60%. In normal driving, 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. Hydrogen fuel cell vehicles, which use electric motors, are much more energy efficient and use up to 60% of the fuel's energy [32].

Recently, studies have been made on the use of hydrogen in internal combustion engines as a fuel. Ganesh et al. [33] conducted an empirical study comparing gasoline and hydrogen as fuels at the Madras Institute of Technology. For this purpose, a single-cylinder spark ignition engine was adapted that it would inject hydrogen from the intake manifold. At the end of the study; it was observed that the emissions of unburned hydrocarbons (UHC) was almost zero when hydrogen was used as fuels, but that emissions formed over the 2500 rpm when gasoline was used as fuels. However, emissions of nitrogen oxides (NO_x) have been found to be higher in hydrogen burning (8000 ppm at hydrogen burning, 2000 ppm at gasoline burning).

In addition, since hydrogen has low ignition energy and a wide range of flammability, lower air/fuel mixture ratio (0.85) is required, while gasoline requires higher mixture ratio (1.03). It has been also found that hydrogen could be reached about 80% of the power of gasoline as engine output power.

Escalante et al. [34] linked the high NO_x values, forming as a result of combustion of air/hydrogen mixtures in internal combustion engines, to high temperatures and high flame velocities that hydrogen has compared to other fuels such as gasoline in their studies. They stated that if the sprays time decreases and the spark ignition delays, NO_x emissions forming in hydrogen engines could be reduced. They emphasized that three points should be taken into consideration when hydrogen is used as fuel in internal combustion engines working with gasoline. Initially, injectors having higher volumetric capacity should be used because of the lower density of hydrogen. It has been determined at studies carried out that natural gas injectors are suitable for this purpose. Secondly, temperature control needs to be improved because of the high burning rate of hydrogen according to other fuels. New cooling techniques have to be developed for the valve, spark plug and cylinder heads. Finally, the initial combustion should be started with a mixture of hydrocarbon (gasoline, diesel, natural gas) with poor hydrogenation (5-10%).

In recent years, studies have been made to use hydrogen in combination together existing hydrocarbon fuels at a certain mix ratio. Akansu et al., [35] made a study on a hydrogen/natural gas mixture at an internal combustion engine with spark ignition in Erciyes University. Different mixing ratios and ignition times were taken as criteria at the study. They obtained about 50% efficiency in the mixture containing 40% hydrogen at 0.8 air/fuel mixture ratios. They also compared NO_x emissions, forming from the combustion of the hydrogen/nature gas mixture and only the resulting from the natural gas combustion. They found that the emissions of combustion of the hydrogen/natural gas mixture were significantly lower.

Another experimental study on the hydrogen/natural gas mixture was carried out at the Norwegian University of Science and Technology. Bysveen [36] used an engine that it was three-cylinder, 2.7 L volume, compression ratio 11:1, spark plug ignition and operating with natural gas. He located thermocouples to the intake manifold, the

cooling system and the exhaust. He compared the values of emissions, power and efficiencies of natural gas (99.5% methane) and hydrogen/natural gas mixtures (29% hydrogen). As a result of the study, he obtained the lower NO_x emission values, 30% efficiency and 20 kW power in the hydrogen/natural gas mixture. He observed that the yield and power values obtained combustion of hydrogen/natural gas mixture were higher than the values obtained combustion of only from natural gas.

Another study used hydrogen as a fuel mixture was carried out in a single-cylinder and direct-injection diesel engine at Anna University in India. In this experimental work done by Saravanan [37], it was found that the yield of hydrogen/ diesel mixture reached 27.5%. While the high NO_x emission values were achieved in the hydrogen/diesel mixture above 2500 rpm, it was observed that when diesel was used a 25% reduction in the unburned hydrocarbon emission values.

Greenwood et al. [38] conducted a research to determine the effect of hydrogen enrichment on ethanol. For his purpose, they modified a 2-cylinder, spark-ignition internal combustion engine with a volume of 0.745 L to operate with both ethanol and hydrogen. They obtained data on emission quantities, power, exhaust gas temperature, thermal efficiency, volumetric efficiency, fuel consumption by carrying out experiments at stable engine ratios and fuel mixtures containing 0%, 15% and 30% hydrogen. According to these data, when ethanol is enriched with hydrogen, NO_x emission decreases and combustion process accelerates. Particularly, in mixtures with a hydrogen content of 15% and 30%, they found that NO_x emissions decreased more than 95% compared with stoichiometric gasoline combustion, but power, thermal efficiency and volumetric efficiency did not change at these mixture ratios.

In this study; it has been aimed to be produced when hydrogen is needed by reducing the pH value of the aqueous alkaline solution of $NaBH_4$ that is a good storage agent for hydrogen and can be carried safely. To reduce the pH value of the alkaline solution, CO_2 gas, which has acidic effect, will be used. When the pH-value drops, the stability of the solution will decrease and the hydrogen stored in $NaBH_4$ will be released and produced hydrogen. Thus, it is estimated that hydrogen production costs

will be reduced, as there is no need to use expensive catalysts used to obtain hydrogen from $NaBH_4$.

Especially, it has been evaluating that the pH value could be decreased by sending the CO_2 gas, forming the result of the burning of the fossil fuels, into the aqueous alkaline $NaBH_4$ stored in a tank at the time of need, so that the stored hydrogen in the $NaBH_4$ can be released. So, the efficiency of the fuel used will increase and fuel consumption will decrease by sending this hydrogen into the combustion system.

CHAPTER 2

ENERGY

Energy that has vital importance for survival of living beings is one of the indispensable elements for people and states. Especially, it has strategic importance in many areas such as heating, defense, transportation, lighting, communication, etc. In other words, human beings can't produce, travel, and defend himself without energy, in short, can't live. For these reasons, the addiction to energy for mankind will never end.

The environment is affected by each result, which occurs during the production and use of the energy. Because of the influence of energy on the environment, the living world is also affected by this situation. Increased energy production and utilization have caused to environmental issues, such as air pollution, global warming and climate changes, directly affect people's lives. The main reason for this is that nowadays most of the energy needed have been met from fossil fuels.

The first thing to do to deal with these problems is to get rid of fossil fuel dependence. So, different energy sources such as renewable energy sources should be used. It is known that fossil fuels will run out in the very short period of time because their reserves are limited. For this reason, human beings will have to turn to different energy sources for their needs in the near future even if they do not want.

2.1 The Demand for Energy

With increasing world population and developing technology, the need for energy has been continuously increasing. For example, between 1850 and 1970, the number of living on Earth more than tripled [39] and so the amount of the energy required increased naturally. As can be seen from Table 2.1, it is foreseen that global energy consumption will increase by 21.5% from 2015 to 2035, and assumed that the energy demand will increase from 13 776 Mtoe to 16 748 Mtoe [1].

Table 2.1 World primary energy demand by fuel in the New Policies Scenario (Mtoe) [1].

Fuel kind	1980	2008	2015	2020	2030	2035	2008-2035[*]
Coal	1 792	3 315	3 892	3 966	3 984	3 934	0.6%
Oil	3 107	4 059	4 252	4 346	4 550	4 662	0.5%
Gas	1 234	2 596	2 919	3 132	3 550	3 748	1.4%
Nuclear	186	712	818	968	1 178	1 273	2.2%
Hydro	148	276	331	376	450	476	2.0%
Biomass and waste	749	1 225	1 385	1 501	1 780	1 957	1.7%
Other renewables	12	89	178	268	521	699	7.9%
Total	**7 229**	**12 271**	**13 776**	**14 556**	**16 014**	**16 748**	**1.2%**

[*]Compound average annual growth rate.

The differences in population growth, economic growth and living standards of the countries cause different energy needs. Table 2.2 shows the global distribution of annual energy demand [40].

Table 2.2 The increase in energy need [40].

Countries	The annual demand increase (%)
The world average	2.4
Developed countries average	<2.0
In emerging countries average	4.1
Turkey	6-8

2.2 Today's Energy Sources

Energy resources used today are classified according to whether they are renewable or not. While fossil fuels such as coal, oil and gas, with nuclear energy are classified as non-renewable energy sources, solar energy, wind energy, wave energy, bioenergy and geothermal energy are classified as renewable energy sources.

As can be seen in Figure 2.1, when it is looked at the distribution of energy consumption according to sources in the world in 2014, it is seen that the consumption is met from fossil sources at a great rate of (86.3%) [41].
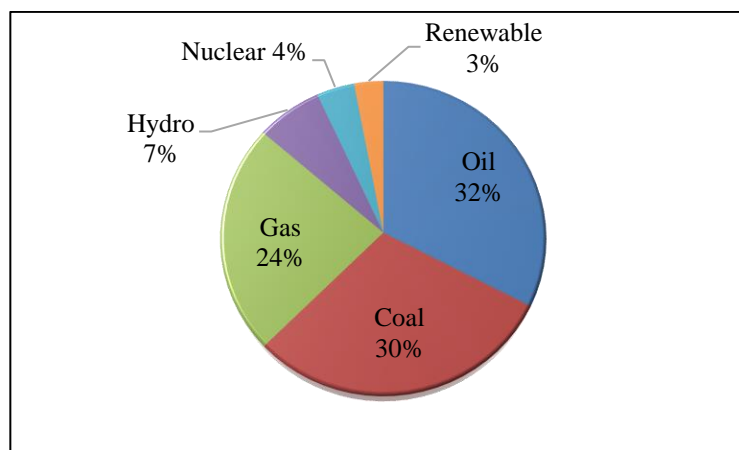
Figure 2.1 The world energy consumption according to resources [41].

2.3 The Environmental Impacts of Energy Usage

According to Table 2.1, it has been predicted that fossil fuels will continue to meet the vast majority of energy consumption between 2015 and 2035. Even the share of fossil fuels in energy production in 2035 is estimated to decrease from 86.3% to 73.7% compared to 2014; they will continue to remain a dominant energy source.

However, fossil fuels, which have limited reserves, are the greatest source of CO_2 gases that cause greenhouse gases. Because, when carbon-based fossil fuels burn, CO_2 and water form. This reaction for methane is as in Eq. 2.1 [42];

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 55.5 \text{ MJ/kg} \tag{2.1}$$
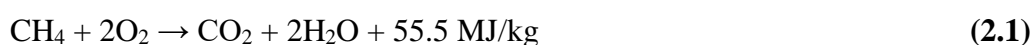
As long as dependence on fossil fuels continues, greenhouse gas levels will continue to increase and the world will continue to warm up. Therefore, the greatest problem of the 21st century is global warming according to many scientists. It is very important to move to alternative energy sources in order to solve this problem.

CHAPTER 3

HYDROGEN

3.1 Characteristics

Hydrogen, constituting 80% by mass of the universe, is the most abundant element. For this reason, it can be said that hydrogen is the main energy source of the universe. Hydrogen, which is placed 1st element of the periodic table, is also the simplest element. Because the hydrogen atom has a proton and an electron as shown in Figure 3.1 and it does not contain neutron except isotopes. These isotopes are; deuterium, which founds small amount of quantity (one proton and one neutron), and tritium that are produced as synthetic since it does naturally not found (one proton and two neutron) [43].
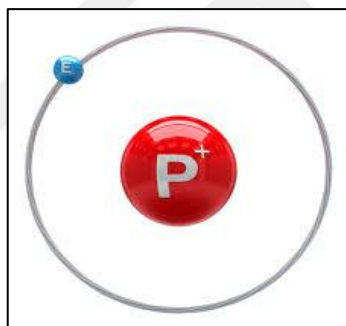
Figure 3.1 The hydrogen atom [44].

Hydrogen is found as molecule (compound) form in nature, not free form. As known, a molecule is formed by the combination of two atoms. The hydrogen molecule is also composed of two hydrogen atoms having one electron (H_2). However, hydrogen molecule is found extremely rare in nature because it reacts with oxygen atom very easily. As seen in Eq. 3.1, as a result of this reaction water is formed [45].

$$2H^+ + O^{-2} \rightarrow 2H_2O \tag{3.1}$$

Hydrogen was described as "Hydrogéne" by the French chemist Lavoisier in 1782, since it is formed water together with the oxygen atom. Because, hydror is means water and génes is means constituent in Latin.

Hydrogen, existing in the state of gaseous form at room conditions (at 25 °C temperature and 1 atm pressure conditions), is colorless, odorless, non-poison and the lightest gas (14.4 times lighter than air). Hydrogen, which has a very low boiling temperature, turns into liquid form from gaseous form at -253°C. Helium is the only gas that boiling point is lower than hydrogen (-270 °C). The volume of liquid hydrogen is 1/700 times the volume of the state of gas. Table 3.1 shows some chemical and physical properties of hydrogen [46].

Table 3.1 Some physical and chemical properties of hydrogen [46].

	Symbol	H
	Atomic number	1
	Atomic mass	1.00794 g/mole
	Under normal room conditions (25 °C – 298 K)	Known, colorless and the lightest gas
	Non-metal	
Chemical properties	Electronic configuration	1s1
	Shell structure	1
	Electronic interest	72.8 kJ/mole
	Electronegativity	2.20
	Atomic radius	25 pm
	Ionization energy	1 312 kJ/mole
	Oxidation number	1
	Density	0.0899 kg/m^3
	Melting point	-259.14 °C (14.01 K)
	Boiling point	-252.87 °C (20.28 K)
Physical properties	Molar volume	11.42 mL/mole
	Thermal conductivity (at 300 K)	0.1815 W/(m·K)
	Specific heat	14.314 J g-1 K^{-1}
	Evaporation enthalpy	0.452 kJmol^{-1}
	Atomization enthalpy	218 kJmol^{-1}

Hydrogen has the highest energy content per unit mass in all fuels (140.9 MJ/kg). 1 kg hydrogen gas contains as much energy as 2.1 kg natural gas or 2.8 kg gasoline. The energy content per unit mass of known fuels is compared with the energy content per unit mass of hydrogen at Figure 3.2 [47].
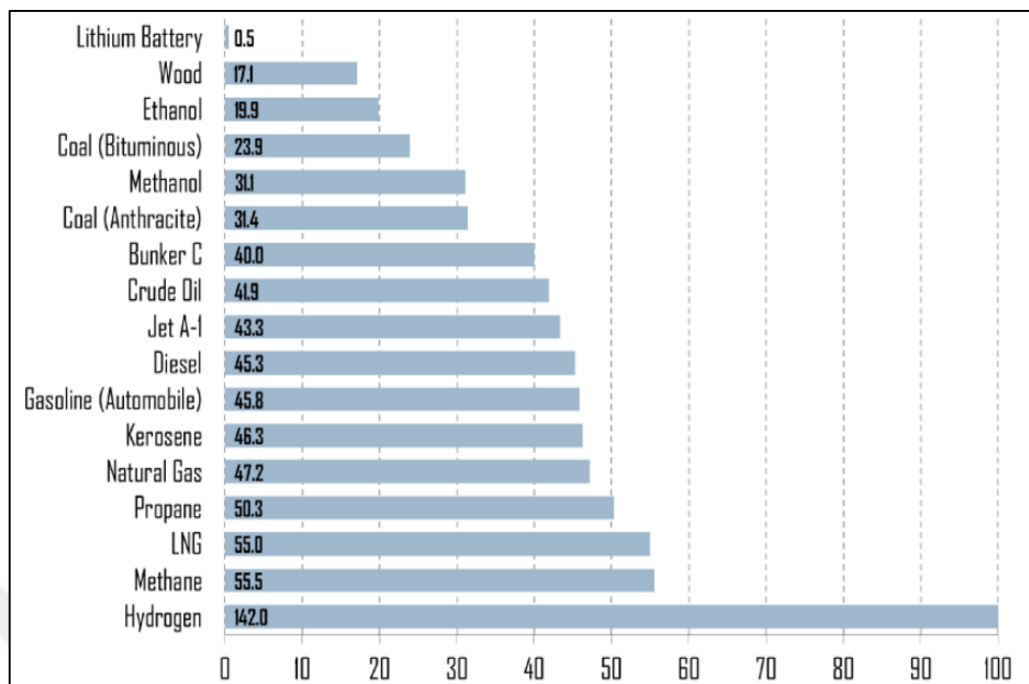
Figure 3.2 The energy content per unit mass of some combustibles (MJ/kg) [47].

When hydrogen is used as fuel, emission gas is not emitted to the environment because only water is generated at the end of combustion. This makes hydrogen a serious alternative fuel to fossil fuels.

3.2 Production

Since hydrogen does not exist as pure state in nature, there is need an external energy, which will be produced from primary energy sources, to generate hydrogen. Today, almost all of this external energy is derived from carbon-based fossil fuels for economic reasons. However, the use of fossil fuels, which is known the damages to the environment, is illogical to produce hydrogen, which is harmless to the environment. Because, the use of hydrogen as a clean energy source will not contribute to the prevention of environmental disasters in this case. For this reason, it is imperative to develop new economic methods to reduce the share of fossil fuels in hydrogen production.

3.2.1 Hydrogen Production from Fossil Fuels

As shown in Figure 3.3, at the present time, global crude hydrogen production relies almost exclusively on processes that extract hydrogen from fossil fuel feedstock [48]. But, this situation increases the dependence on fossil resources and causes air pollution at the same time.
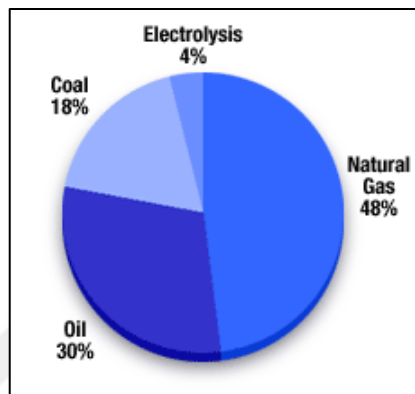
Figure 3.3 Feedstocks used in the current global production of hydrogen [48].

3.2.1.1 Steam Methane Reforming (SMR)

Among the hydrogen production methods, SMR is the most preferred and economical method with a 50% share. Basically, this method, having 80% efficiency, is based on the reaction of natural gas (CH_4), a fossil fuel based on carbon, with steam at high temperature [45]. A typical steam reforming method, shown in Figure 3.4, consists of four main steps [49];

- The removing of sulfur from CH_4,
- The production of the synthesis gas (H_2 and CO),
- The conversion of CO to CO_2,
- The purification of hydrogen.
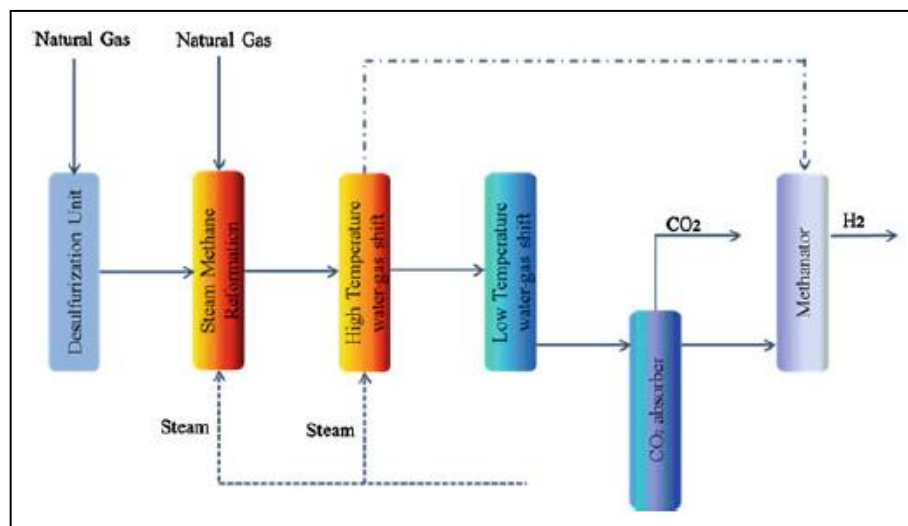
Figure 3.4 A schematic of hydrogen production by SMR [50].

Firstly, the sulfur in methane gas is removed from the system thanks to the nickel wires used as the catalyst. Then, this gas is reacted with steam at high temperature (700-1000 °C). The equation of this reaction is the same as in Eq. 3.2.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{3.2}$$

The synthesis gas (H_2 and CO) formed in the result of reaction is reacted again with steam (shift reaction) at a lower temperature to obtain additional hydrogen and convert CO to CO_2. The equation of the reaction is given in Eq. 3.3.

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{3.3}$$
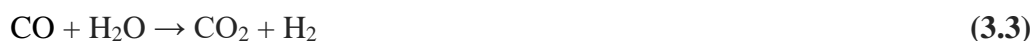
These two reactions can be generalized as in Eq. 3.4;

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \tag{3.4}$$

In the last step, the obtained hydrogen is purified by applying pressure change and so, hydrogen is separated from the undesired components [50].

3.2.1.2 Partial Oxidation (POX)

In this method, it is provided that partial combustion of hydrocarbon-based fossil fuel by water vapor with the limited quantities of O_2 in a closed combustion chamber. The flame temperature is between 1300 °C and 1500 °C. At the end of the reaction, synthesis gas (H and CO mixture) is produced. The advantage of the partial oxidation process according to the steam reforming is that it allows the use of even low quality fossil fuels containing sulfur as it does not require catalyst [51]. In other words, this method has great flexibility because there is no need for desulfurization. However, since 95-99% pure O_2 is used in this method, providing this is a challenge.

Partial oxidation of methane carried out through the following reactions [52]. The reaction is not catalytic and the total reaction is exothermic.

The reaction steps;

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \text{ (exothermic)} \tag{3.5}$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \text{ (endothermic)} \tag{3.6}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2O \text{ (endothermic)} \tag{3.7}$$

The total reaction;

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \text{ (exothermic)} \tag{3.8}$$
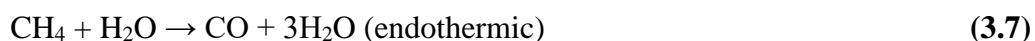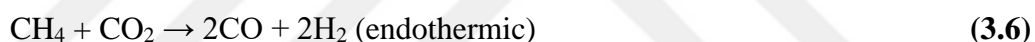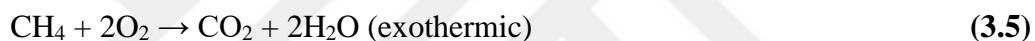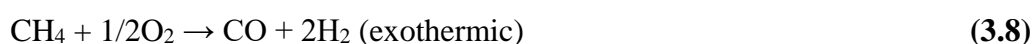
The reactions in Eq. 3.6 and 3.7 are endothermic and the heat required for these reactions comes from the heat generated in the reaction in Eq. 3.5. The compound of the obtained gas depends on the ratio of C/H in the starting material and the amount of water vapor added.

Approximately, 25% of the total hydrogen production is made with this method and a schematic picture of the partial oxidation method, having 70% yields, is shown in Figure 3.5.
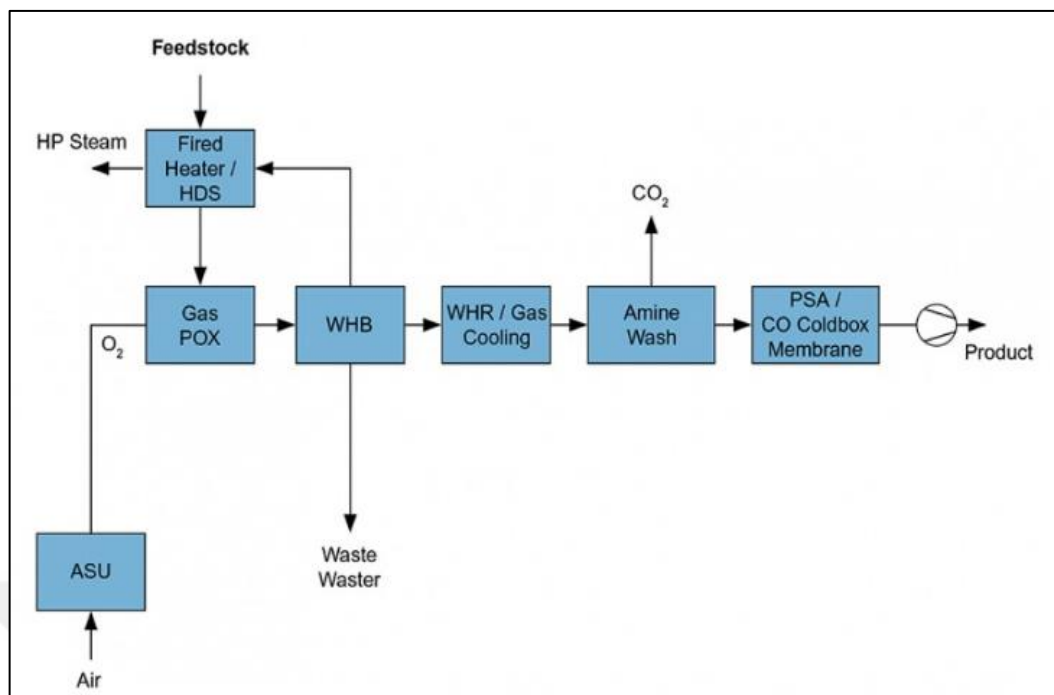
Figure 3.5 The general diagram of the partial oxidation process [53].

3.2.1.3 Gasification

Gasification is a flexible, reliable, and commercial technology that can turn a variety of low-value feed stocks into high-value products, help reduce a country's dependence on imported oil and natural gas, and can provide a clean alternative source of baseload electricity, fertilizers, fuels, and chemicals [54].

Coal (especially, low-calorie coals), fuel oil containing high sulfur, biomasses and wastes (hazardous wastes, domestic wastes etc.) are generally used as feedstock in gasification. These feed stocks are processed with steam and oxygen in a gasifier which has high temperature (1000-1400°C) and low oxygen content. Synthetic gas containing CO, H_2, CH_4 and CO_2 is obtained at the end of the process. The synthetic gas obtained can be used to generate electric by sending direct to a turbine, either to produce chemicals such as hydrogen and fertilizer after some processes. As a result of the gasification process, non-gasificated substances are taken as slag under the gasifier and this slag is used as an additive in the construction industry.

Gasification has been used more and more in recent years, because of innovations in gasification technology, limited reserves of fossil fuels and their negative effects on the environment and gasification is an environmentally friendly way of producing energy [55]. Figure 3.6 shows the process of gasification system.
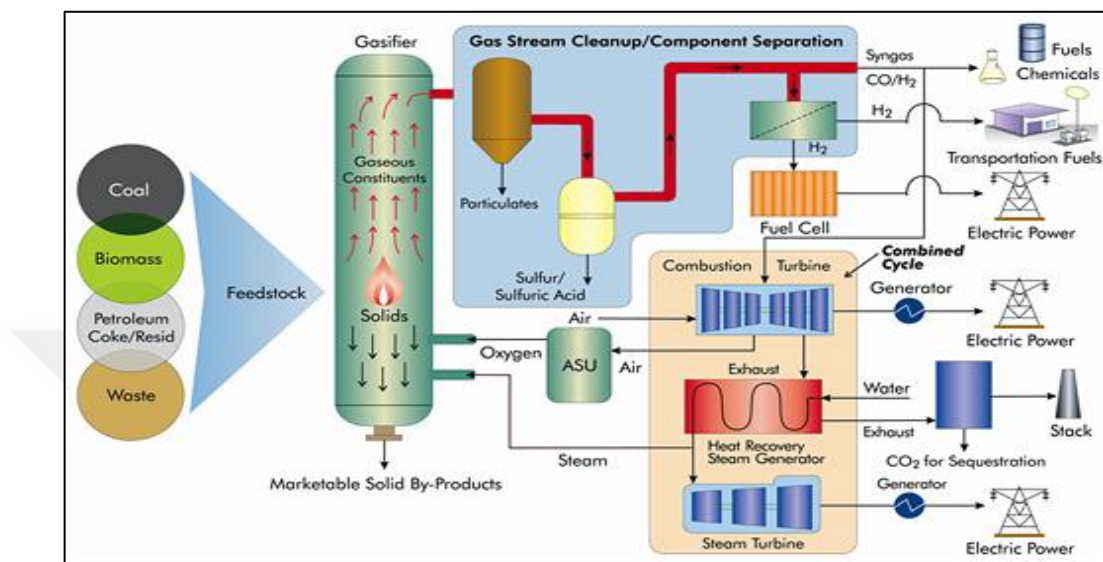
Figure 3.6 The process of gasification system [56].

3.2.1.4 Kvaerner Process

This method is called Kvaerner Process or Kvaerner Carbon Black & Hydrogen Process (CB & H), which is named after Kvaerner, a Norwegian company. The company started to work on the process in 1990 and the first plant was established working with this process in 1992 [57].

Kvaerner process is a method of producing activated carbon and hydrogen from hydrocarbons such as natural gas and oil by using electric current. The process is a completely endothermic reaction and takes place in an oxygen-free medium. Because the process, which carries out at about $1600\,°C$, does not have oxygen, it does not occur a combustion. Therefore, CO_2 gas does not form in the reaction (Eq. 3.9) and hydrocarbons used as raw materials are separated to carbon and hydrogen.

$$C_nH_m + energy \rightarrow nC + m/2\ H_2\ (endothermic) \tag{3.9}$$

The energy required to initiate the reaction is provided by the use of hydrogen, obtained from the process, as the plasma gas. As a result, Kvaerner method is a process that does not require anything other than hydrocarbons used as raw materials and electric current that will ignite the plasma gas. The process has the following advantages according to other hydrogen production methods (steam reforming, partial oxidation and gasification;

- The yield of the process is close to 100% (48% hydrogen, 10% hot steam, 40% activated carbon).
- The purity of the obtained hydrogen is very high.
- The cost of hydrogen production is lower.
- All hydrocarbon-containing materials, from light gasses to heavy petroleum products, can be used as raw materials [57].

3.2.2 Hydrogen Production from Electrolysis of Water

The richest materials in terms of hydrogen content are fossil fuels such as natural gas, coal, oil, biomass and water. Hydrogen production from water is the most promising method because the reserves of other materials are limited and their damages to the environment, also water will never end and there is no harm to the environment.

The water molecule consists of two hydrogen atoms and one oxygen atom. As shown in Figure 3.7, two electrons in the outer orbital of the oxygen atom fill the positions of electrons that are empty in the outer orbits of the two hydrogen atoms.
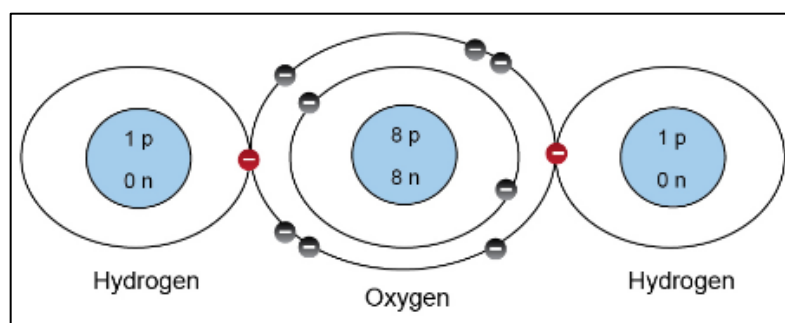
Figure 3.7 Covalent bonds between hydrogen and oxygen in a H_2O molecule [58].

The bond forming by using the electrons of each other jointly is called covalent bond. The molecules consisting of covalent bonds such as water are highly stable and strong. For this reason, the covalent bonds do not break away from themselves, required a high energy of 50-110 kcal/mole for breaking [59].

Water electrolysis is the process of separating water into its basic constituents, hydrogen and oxygen, by using electric current. The reaction is given in Eq. 3.10;

$$H_2O + electrical\ current \rightarrow H_2 + 1/2\ O_2 \hspace{2cm} \textbf{(3.10)}$$
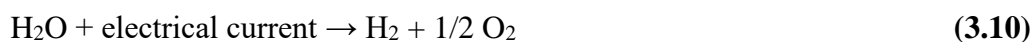
Simple electrolysis system consists of two electrodes, called anodes and cathodes, which do not enter the reaction, a conductive liquid which these electrodes are immersed in it and referred to as electrolyte, and a direct current source. When current is applied to the electrodes, there will be a flow from the positive electrode (anode) to the negative electrode (cathode). As a result, the water is separated into its basic components and oxygen gas is accumulated at the positive electrode and hydrogen gas is accumulated at the negative electrode [60]. Figure 3.8 shows an electrolysis system.
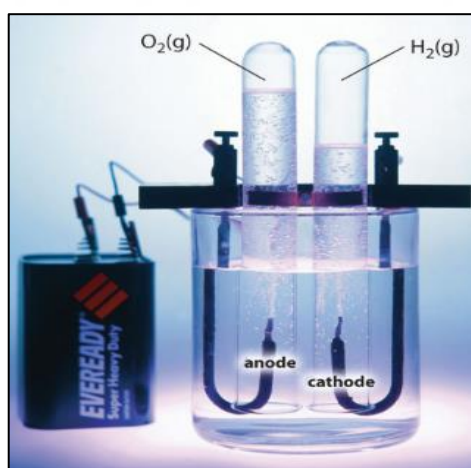
Figure 3.8 The electrolysis of water [61].

Since pure water has a high electrical resistance (100 ohm/cm), a great deal of current is required for the electrolysis process to carry out. This causes to the fact that the electrolysis process is very expensive and has only 4% a share of in hydrogen production as seen in Figure 3.3. The required voltage is 1.24 volts at 25°C

and 1 atm of pressure for the electrolysis of water. The minimum amount of energy required for electrolysis of one mole of water is 65.3 watts-hour and the minimum amount of energy required to produce 1 m^3 of hydrogen is 4.8 kWh. Accordingly, the yield of the electrolysis process is about 70%. In order to reduce the cost of the method, it is necessary to reduce the electrical resistance of the water, in other words to increase the conductivity. For this, the water temperature should be increased to 700-1000°C, or substances increasing the conductivity for the water such as salt and potassium hydroxide (KOH) and nickel-coated steel electrodes should be used [62].

3.2.3 Thermal Decomposition of Water (Thermolysis)

The breakdown of molecules into atoms, forming themselves, by heat is called thermal decomposition. When the water vapor is heated above 1 400 °C, the water molecule decomposes into its basic constituents, hydrogen and oxygen atoms. If the temperature increases, the decomposing of the rate of water vapor molecules increases. A system called heliostat is used to raise the water vapor to these extents. This system consists of a mirror, that directs the incoming sun rays to a specific target and keeps it at a target, and a setting system that allows the sun rays to always be directed to a fixed target by moving this mirror according to the movement of the sun [63]. After the water vapor is decomposed, the gases formed by a ceramic membrane are separated from each other. The disadvantage of this system is that the materials used in the system can't withstand such high temperatures for a long time. Figure 3.9 shows a heliostat system.

Figure 3.9 The heliostat system.

Since very high temperatures are needed for thermal decomposing of water, this situation increases both costs and some material problems arise. For this reason, various chemicals are used for thermal decomposition of water at lower temperatures. According to the investigations made, the most suitable chemicals to be used in the thermolysis process are sulfur and iodine. The thermochemical cycle is called that the thermolysis process in which the chemical substances are used, and the sulfur-iodine thermochemical cycle is called that the cycle used the sulfur-iodine as the chemical substance [64].
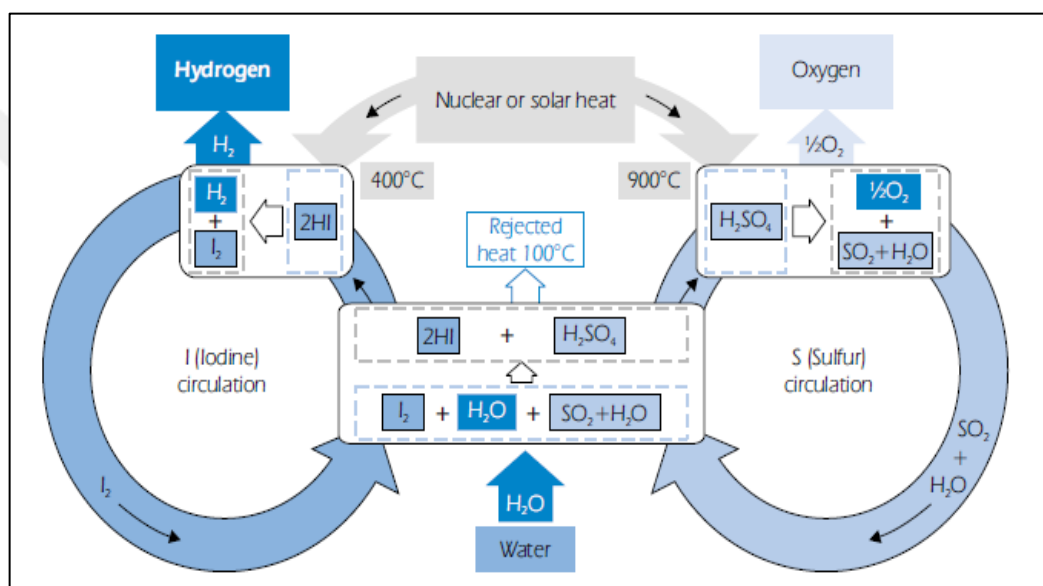
Figure 3.10 Overview of the sulfur-iodine process.

The sulfur-iodine cycle shown in Figure 3.10 consists of a three-stage reaction;

1. At this stage, sulfuric acid and hydrogen iodide, required for the cycle, are produced and the obtained oxygen gas is separated as product. The reaction at this stage is a totally exothermic and a heat is given to medium about $100\,°C$.

$$2H_2O + SO_2 + I_2 \rightarrow 2HI + H_2SO_4 \text{ (exothermic)} \tag{3.11}$$

2. The step at which the sulfuric acid components are separated. At this stage, the reaction is endothermic and heat is given to the cycle about $900\,°C$ from outside. The equation of the reaction is as follows;

$$H_2SO_4 \rightarrow SO_2 + H_2O + 1/2O_2 \text{ (endothermic)} \qquad \textbf{(3.12)}$$

3. The step at which the hydrogen iodide is separated into the own components. Also at this stage, the reaction is endothermic and the temperature is about $400\,°C$. The equation of the reaction is as follows;

$$2HI \rightarrow I_2 + H_2 \text{ (endothermic)} \qquad \textbf{(3.13)}$$

3.2.4 Hydrogen Production by Biochemical Methods

The puppy bacteria belonging to rodospirillum rumrum, which live in the deep parts of the lakes in the forest, can produce about $3m^3$ hydrogen per kilogram per day. Some of the bubbles that form on the surface of lakes are arisen from this hydrogen that is formed. These bacteria release hydrogen as a result of an equilibrium reaction in their cells after they have taken as much nutrients as needed through the sunlight and have met their nitrogen needs [45].

It does not have a large share at hydrogen production, because it can't allow the production hydrogen at large quantities and complex systems and devices needed for production that are quite expensive.

3.3 Storage

Although hydrogen has very high energy content by weight (it has more energy about three times than the same weight of gasoline), it has very low energy content by volume. Hydrogen in the form of gas takes up $3\,000$ times more space than a gas, which has the same amount of energy content, at room temperature and pressure. Consequently, the physical and chemical properties of the hydrogen gas create great difficulties in its storage [65].

As shown in Figure 3.11, the main hydrogen storage methods are as follows;

- Gas phase,
- Liquid phase,
- Metal hydrides
- Carbon nanotubes,

- Glass microspheres,

- Chemical hydrides.
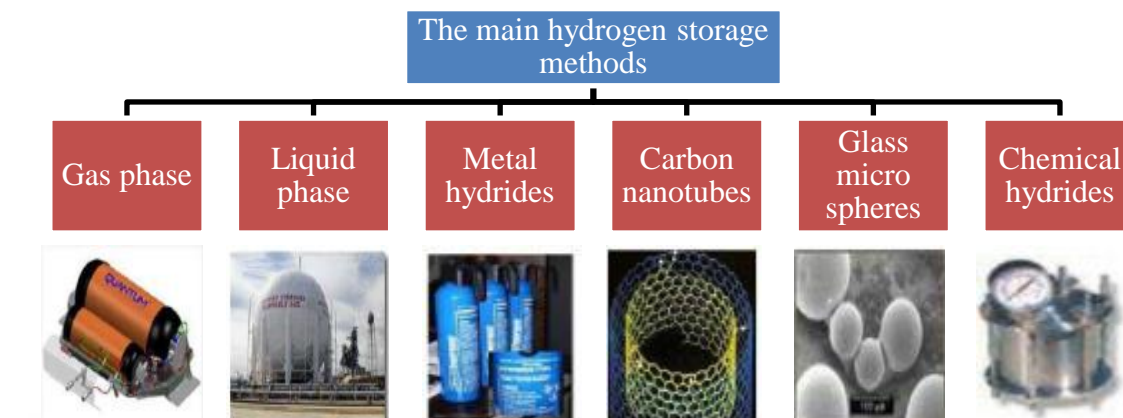
Figure 3.11 The main hydrogen storage methods [65].

Table 3.2 shows the energy amounts and energy densities of hydrogen storage methods.

Table 3.2 Energy amounts and energy densities of hydrogen storage methods [65].

Storage medium	Amount of hydrogen (mass %)	Volumetric density* (H/l) (x10^{25})	Energy density	
			MJ/kg	MJ/l
Gas phase	100	0.50	141.9	1.20
Liquid H$_2$ (-253°C)	100	4.20	141.9	9.92
MgH$_2$	7.65	6.70	9.92	14.32
VH$_2$	2.10	11.4	-	-
Mg$_2$NiH$_4$	3.60	5.90	4.48	11.49
TiFeH$_{1.95}$	1.95	5.50	2.47	13.56
LaNi$_5$H$_{6.7}$	1.50	7.60	1.94	12.77
NaAlH$_4$	7.40	-	-	8.25
NaBH$_4$ (solid)	10.6	6.80	-	-
NaBH$_4$ -20 solution	4.40	-	44.0	-
NaBH$_4$ -35 solution	7.70	-	77.0	-
Nanotubes	1–10	-	-	-
Gasoline	-	-	47.27	6.6–9.9
Methanol	-	-	22.69	5.9–8.9
* Tank weight is not included in these values.				

3.3.1 Storage at Gas Phase

The most common and simplest method of hydrogen storage is compression of the gas phase at high pressure (> 200 bar) [66].

The only equipment it requires is a compressor and a pressure vessel. The main problem with gaseous hydrogen is that it has poor energy density by volume and therefore it needs larger tank for storage. The capital and operating costs are directly proportional to the storage pressure. Thus, higher the storage pressure, higher is the capital and operational costs. Also, one of the major concerns with large storage vessels is the cushion gas that remains in the empty vessel at the end of the discharge cycle. A large variety of vessels are in operation today. The size of these vessels is limited by its materialistic characteristic to withstand high pressure as the thickness of the walls increases with increase in volume of the vessel [67].

Hydrogen is stored 1-7% by weight depending on the weight and the type of tank at compressed gas storage. About 20% of the energy content of the hydrogen is spent to compress the hydrogen gas [68].

The disadvantages of the storage tank for compressed hydrogen gas, shown in Figure 3.12, can be listed as follows;

- The high energy requirement for the pressurization of H_2 gas,
- Heating of the gas due to the inverse Joule-Thomson effect at fast compression and to be compressed less hydrogen gas at the presumed pressure [69],
- The penetrating possibility of gas hydrogen into the composite materials,
- High material costs,
- They must be kept at 200 times the pressure of the atmosphere and present danger [70].

Figure 3.12 Storage tank for compressed hydrogen gas [66].

Storage of hydrogen in gas is also carried out in underground caverns, where natural gas is depleted, other than pressure vessels. These caves allow hydrogen gas to be stored cheaply and easily in large quantities. The hydrogen gas pressures in underground caverns are between 80 and 160 bar. Despite the fact that hydrogen is leakier than other gases, leakage is not a big problem with this technique. Approximately 1-3% of stored hydrogen in caves disappears every year due to leakage. (It has been storing significant amounts of hydrogen in a cave, at a depth of 1330 m, since 1971 in Kiel, Germany [69].

3.3.2 Storage at Liquid Phase

This method, which base on passing hydrogen from gas phase to liquid phase at -253 °C (20K), requires very well insulated tanks for storage. The liquid hydrogen contains 3 times more energy than equivalent amount of oil by weight, but requires 2.7 times more volume at equivalent amount of energy [69]. The most important issue is the thermal insulation of the tank (LH_2) on storing hydrogen in the liquid phase. Since the storage of hydrogen in tanks is carried out at low temperatures, the fuel tanks to be used must have good thermal insulation. In this technique, hydrogen can be stored up to 16% of the total tank weight. In addition, 28% of the energy content of the fuel is used for fluidization. Hydrogen is used extensively in the space

and aeronautical space, where liquidation costs in space crafts and rockets are ignored, even though the energy used for liquefaction is excess because hydrogen consists of much higher energy than other known fuels per unit weight.

Due to the heat transfer in the tank despite the isolation, some of the hydrogen evaporates when it passes from gas state to liquid state. For this reason, the phase change must be taken place rapidly [71]. Also, if liquid hydrogen is stored in large tanks, approximately 0.06 percent of hydrogen, if it is stored in small tanks, approximately three percent of hydrogen is lost by evaporating per day. Reduction of these rates depends on the insulation [65]. Figure 3.13 shows the internal structure of a liquid hydrogen tank.
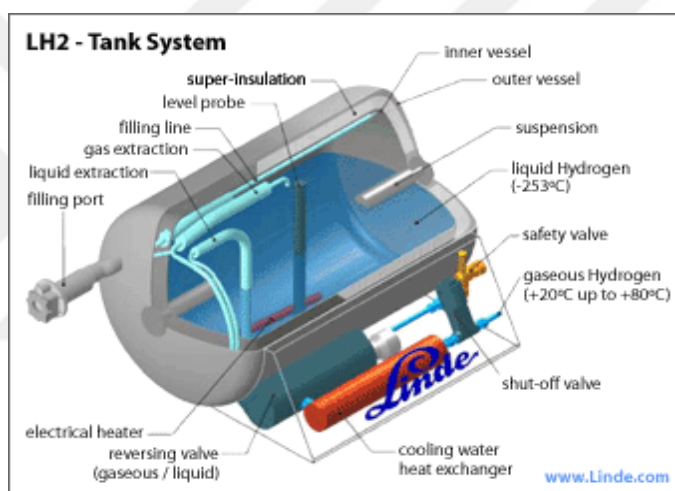
Figure 3.13 Liquid hydrogen storage tank.

3.3.3 Storage in Glass Micro Spheres

In this method, glass spheres, which are small, hollow and have ~1 μm wall thicknesses and in diameter between 25 and 500 μm, are used in hydrogen storage. The glass microspheres, shown in Figure 3.14, are filled with hydrogen gas at high pressures and high temperatures such as 200-400°C. At high temperatures, the glass walls become permeable and hydrogen begins into fill the micro spheres. When the glass is cooled to room temperature, the hydrogen is trapped in the spheres. When the hydrogen is used, the spheres are reheated to release the hydrogen gas. The

storage capacity of the glass spheres is around 5-6% under 200-490 bar pressure [65].
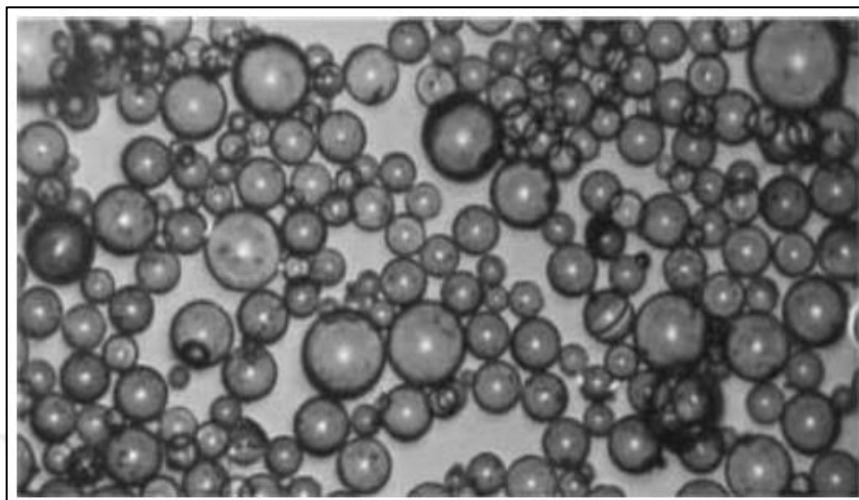
Figure 3.14 Hydrogen storage in glass micro spheres [65].

The main disadvantages of this system can be listed as follows;

- Low volumetric density,
- Very high pressures required during filling,
- Very slowly gas leaks from spheres at room temperature,
- They can be broken during refilling,
- For the release of hydrogen gas is required higher temperatures (~ 300 °C) than operating temperatures of PEM fuel cells (70-80°C) [70].

3.3.4 Storage in Carbon Nanotubes

Carbon materials have recently been used as hydrogen absorbers because of their light weight, their high surface area, their chemical stability, and their attraction force between carbon atoms and gas molecules, making them one of the most convenient materials for gas storage. As can be seen in Figure 3.15, this method is based on to storage the hydrogen on highly porous, super-active carbon surface under pressure. Due to their reliability and their ability to store hydrogen at high levels, a great deal of study has been done in this area over the last years [72].
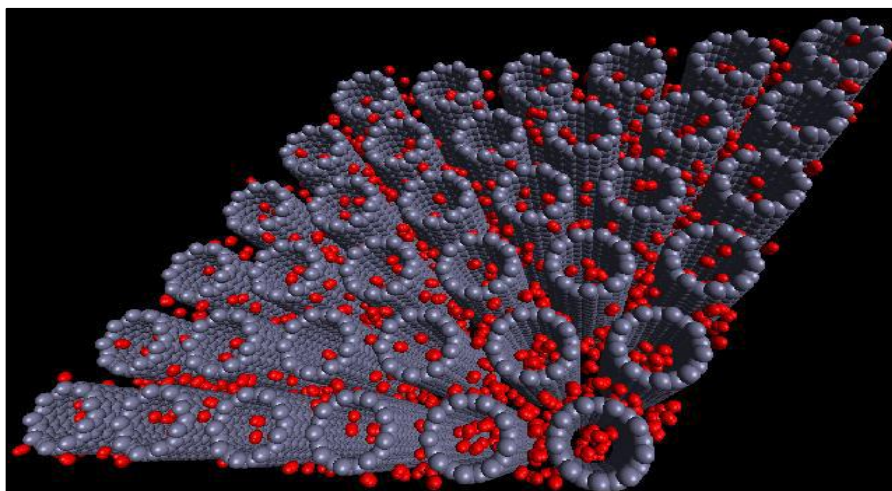
Figure 3.15 Hydrogen gas (red) adsorbed in an array of carbon nanotubes (grey) [66].

The carbon nanotubes, discovered by Dr. Sumio Iijima in 1991, are graphite sheets in tubular form as seen in Figure 3.16. Their diameters are between 20 nanometers and a few nanometers and their lengths are micron levels [73].
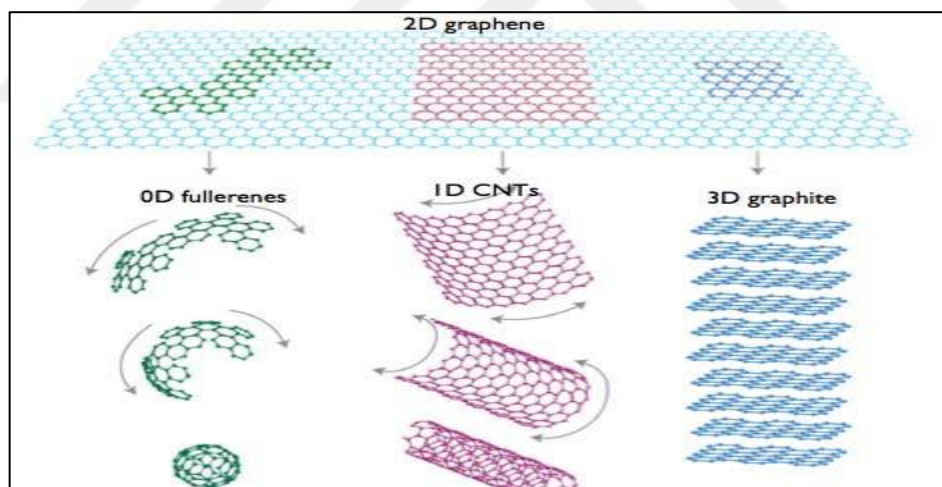
Figure 3.16 2D Graphene can be transformed into CNTs, graphite or fullerenes [66].

Hydrogen can be stored in nanotubes in two forms as physical and chemical;

- Physical storage is a storage, which weak Van der Waals forces are active, and stored hydrogen is recovered again by removing active forces. Storage and recovery operations can be repeated continuously.

- Covalent bonds are formed between atoms in chemical storage, in order to recover the loaded hydrogen is needed breaking these bonds, so high temperatures [74].

Nanotubes can be produced as single-walled or multi-walled tubes. Carbon nanotubes can store 4-14% by weight of hydrogen. Hydrogen storage capacity of carbon nanotubes depends on the kind of the nanotubes (single-walled, multi-walled), whether the tubes are closed or open, their dimensions (tube diameter and length etc.) and the activity of the tube surfaces [75].

3.3.5 Storage in Metal Hydrides

Some metals and alloys have absorbent properties to absorb the hydrogen such as a sponge at normal pressure and temperature. At the end of this absorption process, hydride compounds occur. In other words, hydrides are chemical substances containing hydrogen with one or more other elements. In the storage technique with the metal hydride system, hydrogen is stored in the space between the hydrogen metal atoms [43].

Hydrogen absorption in metals occurs in six stages as shown in Figure 3.17 [76].

- The first stage: Molecular hydrogen gas and metal are not yet interacting with each other.
- The second stage: Hydrogen molecules begin to physically adhere to the metal surface at normal temperature and pressure.
- The third stage: Hydrogen molecules are separated into their atoms and formed bonds with the atoms on the metal surface (chemical adhesion).
- The fourth stage: Hydrogen atoms begin to move between cavities in the metal.
- The fifth stage: Hydrogen atoms continue to diffuse through the voids in the metal until not the gap remains (alpha phase).
- The sixth stage: Hydrogen atoms fill all the gaps in the metal and hydride formation is completed.
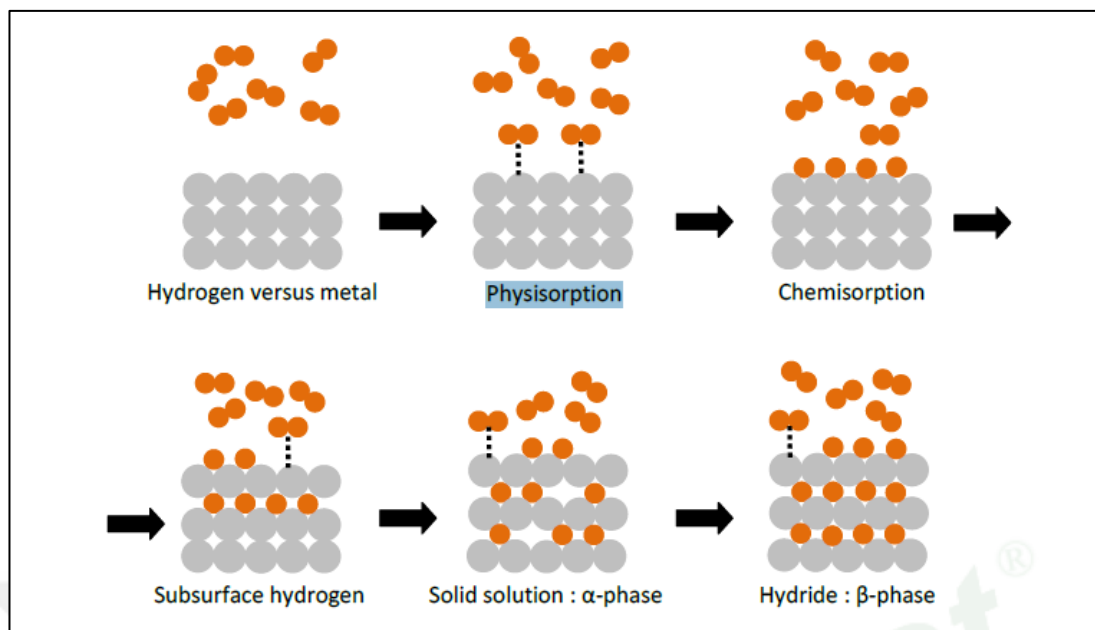
Figure 3.17 Hydrogen storage stages in metal hydrides [76].

In order to recover the hydrogen, it is necessary to give a heat, so to use energy. This means that metal hydrides can cool the heat of the medium during a fire and reduce the effect of fire. The hydrogen gas trapped in the structure is released by the following hydrolysis reactions [68];

$$MH_x + xH_2O \rightarrow M(OH)_x + xH_2 \tag{3.14}$$

$$MXH_4 + 4H_2O \rightarrow 4H_2 + MOH + H_3XO_3 \tag{3.15}$$
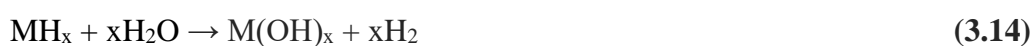
Metal hydrides are generally formed metals such as palladium, magnesium, tantalum, special compounds such as $ZrMn_2$, $LaNi_5$, Mg_2Ni, which form between metals, and multi-phase alloys such as $TiNi$-T_2Ni and Mg-Mg_2Ni. Metal hydride systems are reliable and take up little space, but they are heavy and expensive. According to the metal used, it can be stored 7% hydrogen by weight. In Figure 3.18, it can be seen that comparison of some metal hydrides frequently used with other hydrogen storage methods [77].
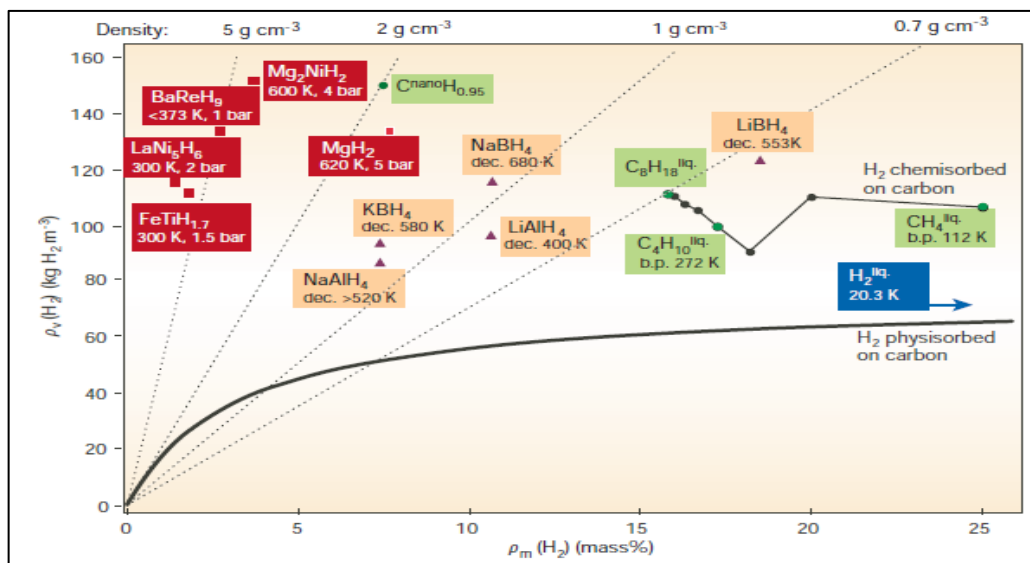
Figure 3.18 Comparison of metal hydrides, carbon nanotubes, petrol and other hydrocarbons [77].

The main advantages of metal hydrides are;

- The operating temperature and pressure are very low,
- It can be prepared in any desired way,
- It can be filled in repeatedly,
- The obtained hydrogen is quite pure,
- There is no loss of evaporation as in liquid hydrogen tanks.

Their disadvantages are;

- Low storage density by mass,
- The short range for vehicles,
- Filling time is long [45].

3.3.6 Boron Based Storage

Due to the importance of safety and lightness at the storage of hydrogen, to store hydrogen in the hydride structure comes forward. For this reason, in recent years instead of metal hydrides, which are quite heavy, the hydrogen production method from chemical hydrides has gained importance. The great advantage of this system is that hydrogen is not stored but produced when it needed [45].

Although there are various chemical hydrides such as $NaBH_4$, KBH_4, LiH, NaH which absorb and release hydrogen, boron hydrides are the most commonly used in this subject. The chemical and physical properties of some borohydrides are shown in Table 3.3. $NaBH_4$ is the most preferred borohydride. It is non-flammable, non-explosive and not an explosion risk even in the case of accumulation in the reactor [65].

Table 3.3 Properties of some boron hydrides [45].

Properties	$LiBH_4$	$NaBH_4$	KBH_4	$RbBh_4$	$CsBH_4$
Boiling point (°C)	268	505	585	-	-
Decomposition temperature (°C)	380	315	584	600	600
Density (g/cm^3)	0.68	1.03	1.17	1.71	1.71
Refractive index	-	1.547	1.490	1.487	1.498
Crystal energy (kJ/mole)	792	697.5	657	648	630.1
$\Delta H°$ (kJ/mole)	-184	-183	-243	-246	-264
$S°298$ (J/(mole·K))	-128.7	-126.3	-161	-179	-192

As can be seen in the following reaction equation, $NaBH_4$ is obtained by a method, known Schlesinger process, as a result of to be converted of boric acid ($B(OH)_3$) to trimethyl borate ($B(OCH_3)_3$) with methanol (CH_3OH) and then reduced with sodium hydride (NaH).

$$B(OH)_3 + CH_3OH \rightarrow B(OCH_3)_3 + 4NaH \rightarrow NaBH_4 + 3NaOCH_3 \qquad \textbf{(3.16)}$$

As can be seen from the equation, three moles of four moles of sodium (in other words, 75%) are converted into the by-product sodium meth oxide ($3NaOCH_3$) and only one mole of $NaBH_4$ is obtained. This low yield causes that the production cost of $NaBH_4$ is high.

Studies have shown that $NaBH_4$ can be used as a hydrogen storage medium due to its high H_2 content. $NaBH_4$ contains 10.6% H_2 by weight and this value is much higher than many of the hydrogen storage compounds as shown in Table 3.4 [45].

Table 3.4 Hydrogen storage capacities of some compounds [45].

Compound	Hydrogen (atom·10^{22}/cm^3)	Amount of hydrogen (mass %)
Gas H_2 (200 bar)	0.99	100
Liquid H_2 (-253 °C)	4.2	100
Solid H_2 (-269 °C)	5.3	100
MgH_2	6.5	7.6
Mg_2NiH_4	5.9	3.6
$FetiH_2$	6.0	1.89
$LaNi_5H_6$	5.5	1.37
$NaBH_4$	6.8	10.60

When a catalyst is added to the $NaBH_4$ solution even at room temperature, hydrogen gas is released according to the following reaction.

$$NaBH_4 + 2H_2O \longrightarrow 4H_2 + NaBO_2 + heat\ (300\ kJ) \qquad (3.17)$$
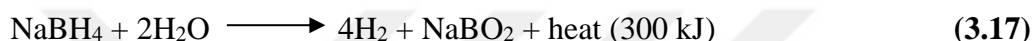
The reaction is very efficient as weight because 4 molar H_2 are released; its half comes from $NaBH_4$ and other half from water. In other words, water is also a source like $NaBH_4$ for hydrogen. The $NaBH_4$ solution is both a hydrogen carrier and a storage agent. In order to produce hydrogen at the using time, it is sufficient to ensure that the $NaBH_4$ solution is contacted with the catalyst. Thus, rapid and controllable hydrogen production is provided. The main advantage of this method is that hydrogen can be produced in a controlled manner (as needed and as required) in normal temperatures without any energy [65].

The nature and structure of the catalyst, used to increase the rate of reaction, is the focus of studies on this technology. The most commonly used catalysts in this field are metal hydrides, colloidal platinum, activated carbon, Raney nickel, fluoride magnesium based hydrides, nickel and cobalt borides. Highly hydrogen can be produced from $NaBH_4$ solution at high pH through catalysts such as platinum and ruthenium [78].

Recycling of $NaBO_2$, formed as byproduct result of the reaction of $NaBH_4$, to the main fuel is carried out by using coal or methane. However, the use of coal is recommended as a reducing agent, since the pyrolysis of methane according to the carbon is inefficient in terms of energy and economic.

$$NaBO_2 + C + 2H_2O \longrightarrow NaBH_4 + 2CO_2 \qquad \textbf{(3.18)}$$

$$NaBO_2 + CH_4 + 2H_2O \longrightarrow NaBH_4 + 2CO_2 + 4H_2 \qquad \textbf{(3.19)}$$
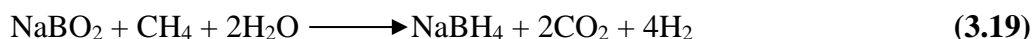
Since it is a stable structure under normal conditions, $NaBH_4$ has the possibility to move safely everywhere. Therefore, studies continue intensely to use $NaBH_4$ in the automotive sector. $NaBH_4$ has been using as hydrogen supplier and storage in a system shown in Figure 3.19, developed by Millennium Cell and named "Hydrogen on demand" [12].
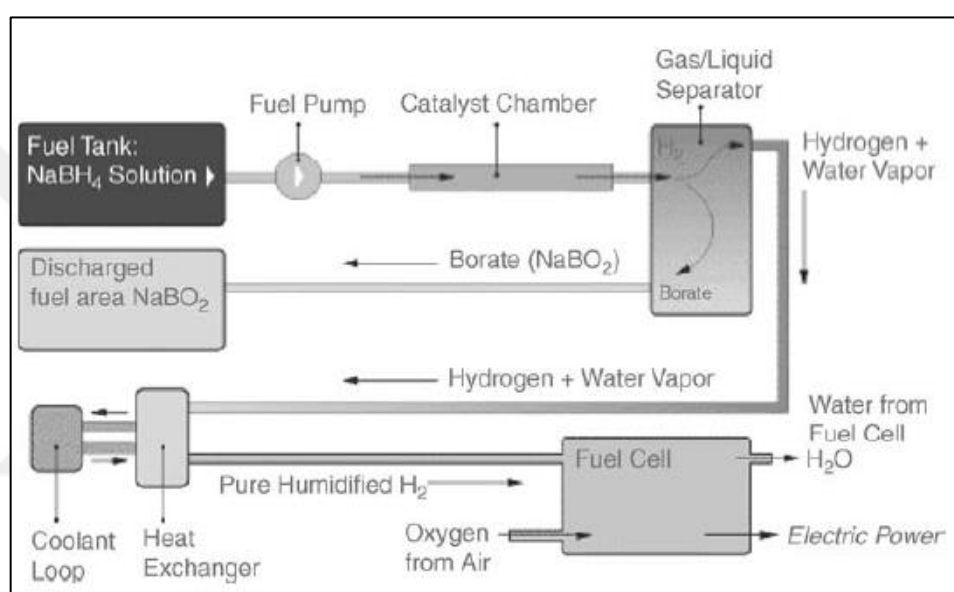
Figure 3.19 Hydrogen on demand system [12].

In this system; the $NaBH_4$ solution in the fuel tank is conveyed by fuel pump to the chamber where it will react with the catalyst that will initiate the hydrolysis reaction. The occurred humid H_2 gas and the $NaBO_2$ solution as a result of reaction are separated from each other and hydrogen gas is sent to the heat exchanger section where the amount of humidity is adjusted. The $NaBO_2$ solution is accumulated in a different tank. In the final stage, the pure hydrogen gas, adjusted humidity, is sent to a fuel cell or an internal combustion engine to use in energy production, while the $NaBO_2$ solution is taken back from the system to produce $NaBH_4$ again [79].

The advantages of using sodium borohydride in systems consuming hydrogen can be as follows;

- The controllability of the reaction is very high, since the reaction will terminate after removing of catalyst used from medium.
- Since, there is no need for additional energy for releasing of the hydrogen the reaction is even carry out at room temperature and pressure.
- When it is compared to other methods of obtaining hydrogen for the production of small quantities of hydrogen, it is a very economical and simple method.
- It is very convenient because it allows production at low pressure for applications where high pressure is harmful such as fuel cell.
- It is possible to increase the reaction rate by selecting suitable catalysts.
- Catalysts can be used many times.
- The reaction products are harmless to the environment. The by-products are water vapor and $NaBO_2$.
- $NaBO_2$, occurring result of reaction, can be used again in the production of $NaBH_4$.
- $NaBH_4$ solution is not flammable.
- $NaBH_4$ solution can wait months without degradation even outdoors [79].

3.4 Usage Areas of Hydrogen

Since hydrogen gas, used in many sectors, has high energy content and does not harm the environment, it is considered to be used as an energy carrier and storage as distinct from today's usage in the near future. Thus, non-stored wind, solar and electric energies can be stored thanks to hydrogen.

3.4.1 Utilization of Hydrogen at Present

Although the hydrogen energy system is new, hydrogen production is not new. Currently, 500 billion m^3 of hydrogen is produced, stored, transported and used every year in the world. The chemical industry, especially the petrochemical industry has the largest user sharing.

In our country, hydrogen production is made only for industrial utilization (artificial fertilizer industry (25 000 m^3), vegetable oil (margarine) production (16 000 m^3), petroleum refinery houses (refinery) (1 200 m^3) and petrochemical industry (30 000 m^3) hydrogenated animal oil production (200-300 m^3) and for using in various places (6 000 m^3)). Commercial size hydrogen production does not exist for energy production [80].

3.4.2. Utilization of Hydrogen in the Future

The storable characteristics of the hydrogen make it the most promising alternative on the fuel of the future. Hydrogen technologies of the future will either be direct use of hydrogen in internal combustion engines, or will be the generation of energy through the fuel cell [45].

3.4.2.1 Utilization of Hydrogen in Internal Combustion Engines (*HICE*)

Due to the hydrogen has chemical properties; it is superior to all known fuels. The remarkable features of hydrogen according to other fuels are shown in Table 3.5 [65].

Table 3.5 The characteristics that make hydrogen an alternative fuel [65].

Fuel	Hydrogen	Methane	Propane	Gasoline	Methanol
Self-ignition temperature (°C)	585	540	510	440	385
Min. ignition energy (MJ)	0.02	0.28	0.25	0.25	-
Ignition interval (% volume)	4-75	5-15	2.2-9.5	1.3-7.1	6.7-3.6
Max. laminar flame speed (cm/s)	270	38	40	30	-
Diffusion coefficient (cm^2/s)	0.63	0.2	-	0.08	-

One of the most important characteristics that will give advantage in the use of hydrogen as a fuel in engines is that the excess air coefficient for combustion range is very wide. In gasoline-air mixtures, ignition can be achieved between 0.3-1.7 of the excess air coefficient, while for hydrogen-air mixtures this limit is 0.14-4.35 [81].

One of the most important difficulties encountered in the use of hydrogen in internal combustion engines is the problem of pre-ignition. This problem is caused by low ignition limits of hydrogen-air mixtures and low ignition energy. The pre-ignition causes to start the burning event early so that more heat is transferred from the

surfaces. This causes to decrease of the engine efficiency. Another important problem encountered in hydrogen engines is knocking [82].

Due to its superior properties, a number of studies have been conducting on the use of hydrogen as fuel in internal combustion engines. However, in these studies, engines designed for gasoline are used and these engines have been modified to allow the use of hydrogen. The following results were obtained in the first studies on the use of hydrogen in internal combustion engines [83];

- The gasoline engines can start with hydrogen through some minor modifies. Their thermal efficiencies are closer to the gasoline engine.
- In stoichiometric operating conditions, high amounts of NO_x are produced in the hydrogen engine. However, the NO_x formation can be reduced by leaning the mixture sent to the cylinder.
- 20% power loss occurs in the hydrogen engine modified from the gasoline engine at the stoichiometric hydrogen-air mixture.
- The flareback on the intake manifold is a major problem in carburetor engines [83].

Advantages of using hydrogen in internal combustion engines;

- The great advantage of using hydrogen as fuel in internal combustion engines is that hydrogen engines produce less pollutant than gasoline engines.
- Basically, products formed by the combustion of hydrogen in air are only water vapor and nitrogen oxides in low amounts.
- Hydrogen has the ability for ignition in a wide range (from 5% to 75% by volume in air), so more air can be used more efficiently in high amounts.
- NO_x resulting from hydrogen-air combustion can be reduced by using excess air.
- NO_x emissions can also be reduced by cooling the combustion chamber periphery.
- NO_x emissions originated from hydrogen engines are one-fold less than NO_x emissions arisen from equivalent gasoline engines [83].

Disadvantages of using hydrogen in internal combustion engines;

- Irregular combustion.
- Knocking combustion during compression.
- The cool start that the cooling water system brings at the spark plugs.
- Loss of efficiency due to transport losses.
- The hydrogen is not slippery enough.
- The obligation to use high-durability materials.)
- Nitrogen emission values [45].

3.4.2.2 Utilization of Hydrogen in Fuel Cells

The energy, obtained from the main energy source (solar, wind, nuclear, etc.), and hydrogen, obtained by one of the methods of obtaining hydrogen described in the previous section, are used in the fuel cells. Hydrogen forms water by burning with oxygen in the air through fuel cell. The reaction is exothermic and the heat is formed after the reaction but the heat is thrown out of the fuel cell with water since it is not too high. The cooling may also be needed at the fuel cell, which produces high heat. In fact, it can be said that the events in fuel cells are reverse what happens in electrolysis. In other words, an electrochemical combustion reaction carries out in the fuel cells that electricity, water and heat occur by the reaction of oxygen with hydrogen. This reaction takes place in a structure consisting essentially of two electrodes (anode and cathode) separated by an electrolyte. The reaction can be carried out at a wide temperature range from 70°C to 1000°C. Another positive point of fuel cells is that they have high-yield energy conversion technologies as well as have features such as clean and non-environmental damage. There are also many other advantages such as obtaining water and heat as waste, usable of waste heat, small size, silent operation and the absence of solid waste problem. Fuel cells, that produce electrical energy by only electrochemical reaction and reach their total efficiency up to 80%, take various names according to the type of electrolyte used in their structures. The main fuel cell types and their properties are shown in Table 3.6 [45].

- Alkaline Fuel Cell (AFC)

- Direct Methanol Fuel Cell (DMFC)

- Proton Exchange Membrane Fuel Cell (PEMFC)

- Phosphoric Acid Fuel Cell (DAFC)

- Molten Carbonate Fuel Cell (MCFC)

- Solid Oxide Fuel Cell (SOFC)

Table 3.6 Features of fuel cells [45].

Fuel cell	Fuel	Working temperature (°C)	Electrical efficiency (%)	Power per surface
AFC	H_2	60-80	60	-
DMFC	CH_3OH	80	40-50	-
PEMFC	H_2	80-100	40-50	0.6 W/cm^2
PAFC	H_2	200	40-45	0.2 W/cm^2
MCFC	H_2CH_4	650	55-60	0.1 W/cm^2
SOFC	H_2CH_4	800-1 000	60	0.4 W/cm^2

Figure 3.20 shows the basic operating principle of the fuel cell. The basic principle of fuel cells is the same even the structure of their changes according to the material used, the working temperature, and the places of use. The most commonly used PEM fuel cell is shown here. The PEM is formed two electrodes that the anode connected to the positive terminal and the cathode connected to the negative terminal and a polymer membrane that provides the permeability of ions between the electrodes. This membrane to be used must be designed to have a thickness of 0.1 mm and not to pass through the gas and should not interact with electrons. It must only be permeable to protons, so be sensitive to hydrogen ions [45].
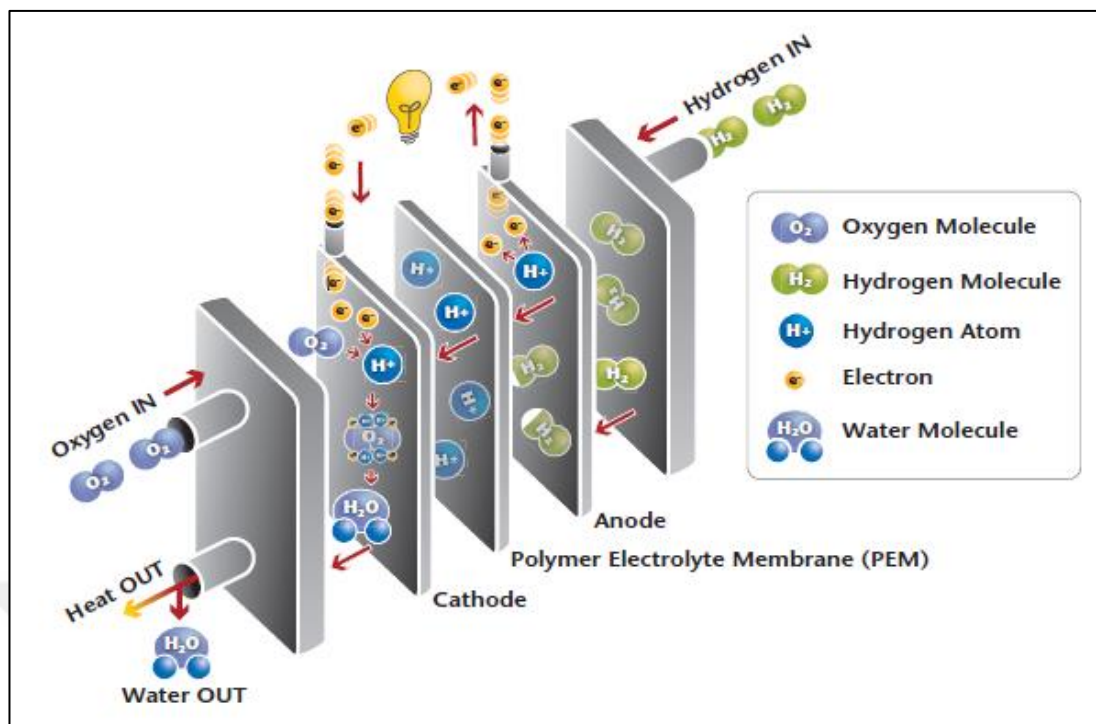
Figure 3.20 The working principle of PEM fuel cell [32].

Hydrogen transported to the anode compartment is separated into its electrons and protons by the help of catalyst. The released electrons are transmitted from the external circuit through the electrodes as electric current. The protons are diffused towards the cathode by the electrolyte membrane. Although electrons are smaller in size than proton, they can't pass through this membrane. The acidity of electrolyte designates that. The negatively charged electrolyte transports the ions to the proton. Electrons are pushed against it and are forced to pass from the external circuit. In the cathode, which is the other part of the cell, oxygen ions, transmitted from the air, generate water with ions that pass through from the external circuit and occur heat. In such a system, a certain voltage difference occurs between the cathode and the anode. If a user is connected between the two electrodes by an external circuit, the electricity generating from this potential difference can be used. The resulting heat can be used to heat the cell [45].

The number of materials to be used as electrolytes is very limited. While a small amount of acid or alkaline is used for fuel cell reactions at low temperatures, ceramic oxides and carbonates can be used for the fuel cell used in the high-temperature

region. Electrodes must have a large surface area to facilitate electrochemical conversion.

Platinum or platinum alloys have been usually using as catalysts. Membranes should contain low valence metal cations having strong acidic character. The fuel is supplied through graphite plates. These plates have two separate entrances. One opens to the area where hydrogen is to be sent and the other opens to the area where air containing oxygen is to be sent (Figure 3.20). The anode part of the membrane should be moistened and the water formed in the cathode part should be removed. The heat accumulated should be dissipated immediately and it should be ready to re-use [45].

It has to be overcame the cost and technology related issues to widespread of fuel cells and other hydrogen Technologies. Nowadays, fuel cell prices are very high. Large investments are needed from both the government and the industry to decrease the costs of hydrogen vehicles, to build the infrastructure needed, and to solve the technical problems associated with the efficient use of hydrogen as an energy carrier. The studies of R & D may have to be undertaken to solve technical problems and develop cheap parts for hydrogen fuel cell vehicles [81].

The fuel cells have advantages and disadvantages differ from one another.

The advantages of fuel cells;

- They are mechanically ideal and can be produced without moving parts.
- They can operate quietly.
- Harmful emissions such as NO_x and SO_x, or particulate emissions are virtually absent.
- It is possible to adjust the power and capacity as depending on size and tank size.
- They have high energy density.
- They are possible to charge easily.
- They covered less space than most energy sources.

The disadvantages of fuel cells;

- Production costs are high.
- They don't yet have sufficient power density for portable and automotive application areas.
- Fuel availability and storage of fuel are limited.
- Environmental effects such as temperature can affect operating conditions.
- They need improvement in terms of durability at the run-stop cycles [65].

3.5 Hydrogen and Turkey

The expansion of production volumes along with economic and social developments, and the increase of social demands and expectations have also increased steadily the energy demand. It can be said that the problems, resulting from the increase in the demand for energy, are more comprehensive and costly especially for the developing countries such as Turkey. Rapid industrialization, urbanization and population growth in developing countries directly affect energy consumption.

Figure 3.21 shows that the energy consumption of Turkey according to the sources in 2013. Natural gas has the most shares in consumption with 52%. This is followed by electricity (45% of electricity is also produced from natural gas) and 16% of fuel consumption (14% of diesel and 2% of gasoline). Total energy consumption is 80482 ktoe [84].
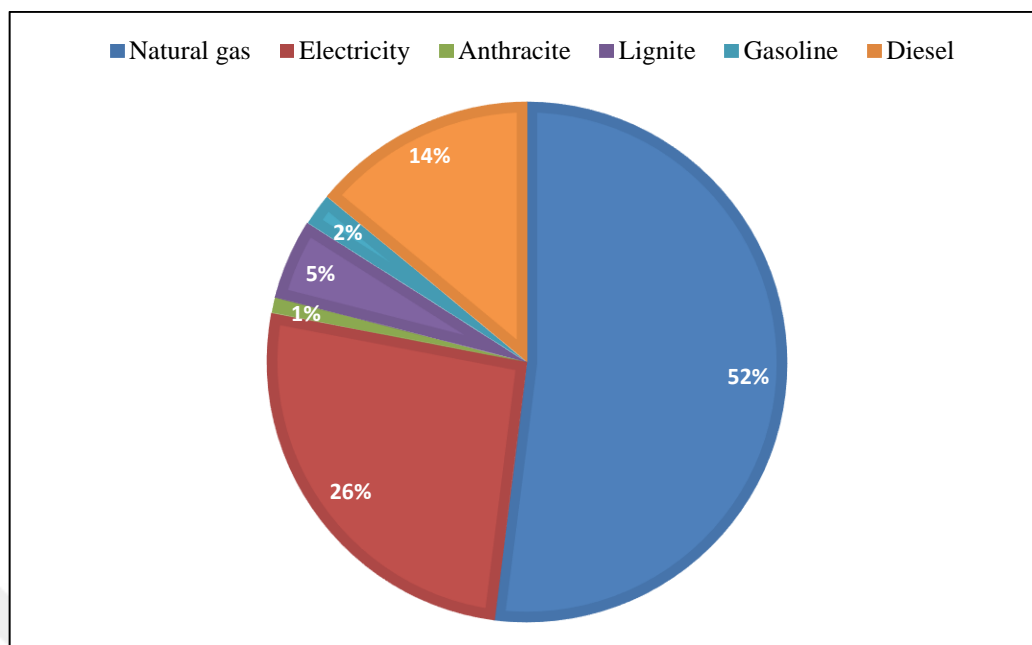
Figure. 3.21 Energy consumption according to the sources of Turkey in 2013 [84].

As it can be seen, Turkey supplies most of its energy needs from natural gas, electricity and oil (gasoline and diesel). Because the known reserves of these sources are very little, Turkey is an external dependence country. This external dependence causes a very negative impact on Turkey's current account deficit. $ 56 billion of Turkey's USD 65 billion current account deficits in 2013 result from energy imports [85].

In order to reduce the current account deficit due to high levels external dependence at energy, Turkey and the developing countries should turn to alternative energy sources that will increase domestic energy production, especially renewable energy sources.

One of the alternative energy sources is hydrogen because of its high energy content. However, production, storage and transportation costs are the biggest obstacle at the widespread of hydrogen nowadays. Despite all these negative factors, Turkey has two important advantages in both hydrogen production and storage.

3.5.1. Obtaining of Hydrogen from Hydrogen Sulfide (H₂S) in the Deep Waters of the Black Sea

Hydrogen sulfur (H_2S) in the Black Sea has been formed as a result of excessive pollution its deep waters. The deep waters including H_2S of the Black Sea are very poor in terms of oxygen. Since there is no oxygen in the parts where hydrogen sulfur is present, no living beings are found in these parts. The most important feature to be mentioned for hydrogen sulfur is that the hydrogen sulfur contains high toxic content and has a heavy odor. Hydrogen sulfur should be separated into its components to reduce environmental damage. The components resulting from the decomposition are sulfur and hydrogen in gaseous form [86].

Black Sea has been feeding with rivers coming from countries such as Bulgaria, Georgia, Romania, Russia, Turkey and Ukraine. In addition, the all effects of pollution, in which a large area of $2\,300\,000$ km^2 from 21 countries placed in river basins in Europe and Asia, is transported to the Black Sea. The Black Sea is isolated from other seas and is only opened to the Aegean Sea via the Marmara Sea. The absence of water circulation in the Black Sea caused the formation of an oxygen-free layer below about 150-200 meters deep (Figure 3.22).
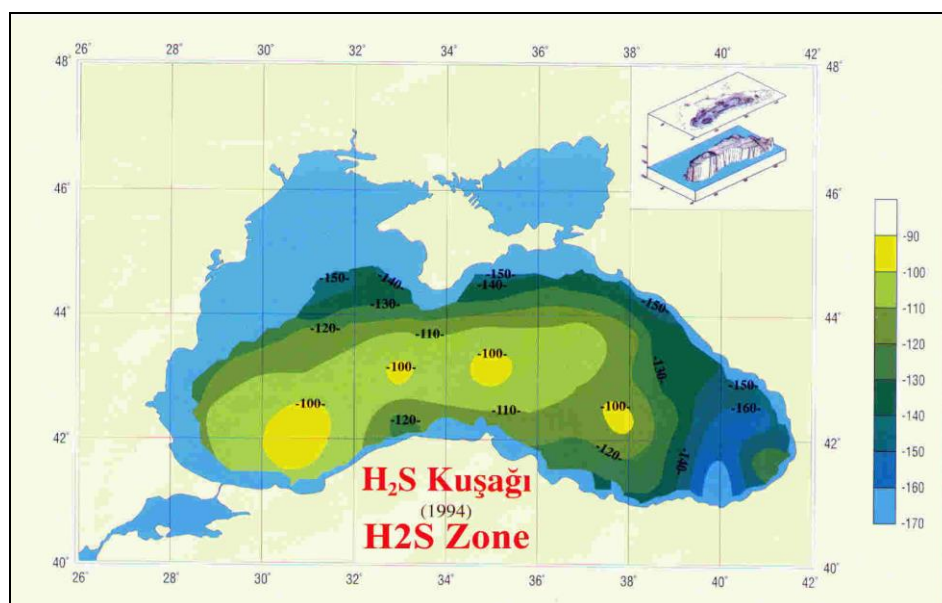
Figure 3.22 H₂S in the Black Sea [45].

In addition, the amount of salt in the Black Sea is less than the other seas and there is a water flow from the bottom of the Bosporus to the Black Sea. This situation causes the fishes and other sea creatures living in the Black Sea to die. As a result of accumulations of dying living creatures due to excessive pollution and of the salt density, it is possible that the concentration of H_2S in the bottom waters has increased. Also, the hydrogen sulfur layer will be found in the central regions of the Black Sea when it is lowered to a depth of about 100 m from the water surface. The depth of reaching to the H_2S on the coast is minimum 170 m. The platforms to be installed in the Black Sea will reduce the cost of removing H_2S to the surface. It is easier to reach to H_2S in Zonguldak, Samsun, Sinop and Giresun openings [86].

Considering the potential of total H_2S in the Black Sea deep waters, the amount of hydrogen to be obtained has a special importance for the region. It is possible to obtain $268\,823x10^6$ tons of hydrogen resulting from 100% decomposition of H_2S from the Black Sea deep waters. If it is considered that its annual energy requirement of a house is about $3\,600$ kWh and about 10 million people live in the Black Sea region, the total annual energy requirement for this people will be $3.6x10^{10}$ kWh. If all of this energy need is met only from hydrogen fuel obtained from the Black Sea deep waters, it is considered that this region will meet the energy requirement of approximately 180 years. If the fossil-based or renewable energy sources will meet the energy demand of the region in a certain share, it is estimated that the 350-year-old energy requirement of the Black Sea region can be met from the hydrogen obtained from the deep waters. If it is considered that the value of 1 KWh electric energy is USD 0.112 at today's conditions, it is estimated that the economic value of the hydrogen obtained from the Black Sea deep waters is approximately USD 715 billion depending on the H_2S reserves [65].

As it is known, hydrogen is present in both H_2O and H_2S. Hydrogen can also be obtained from these two compounds. The researches to obtain hydrogen from H_2S have been keep going on Earth. It is clear that existing techniques used to obtain hydrogen are costly. For example; the energy required to separate the hydrogen from the water in the following reaction by electrolysis of the water is proportional with the hydrogen-oxygen bond energy.

$$H_2O(s) + Energy \rightarrow H_2(g) + 1/2O_2(g) \hspace{2cm} \textbf{(3.20)}$$

As can be understood from this, a long process and high energy are required for hydrogen to be separated from water by electrolysis. However, the energy required to break up the H-S bond is lower than the electrolysis of water. It is possible to produce hydrogen from H_2S with less energy according to water through the following endothermic reaction.

$$H_2S(g) + Energy \rightarrow H_2(g) + 1/2 \; S_2(g) \hspace{2cm} \textbf{(3.21)}$$

While the amount of energy required for electrolysis of water is 237.1 kJ/mole under normal conditions, the amount of energy required for electrolysis of H_2S is 73.28 kJ/mole. As can be seen, hydrogen production is 3.235 times more profitable from hydrogen sulfur according to water. Also, the hydrogen energy obtained from H_2S is more profitable than the energy obtained from H_2O. Sulfur (S) releases as an additional product at obtaining hydrogen from H_2S. This released sulfur is used in industrial field [87].

3.5.2. Utilization of Boron Element in Storing and Transporting of H_2

Although hydrogen has the highest energy content in known fuels, its volumetric density is very small. For this reason, large volumes are needed to store hydrogen as gaseous. Figure 3.23 compares the energy capacities of existing hydrogen storage techniques for driving a distance of 500 km of a vehicle [45].
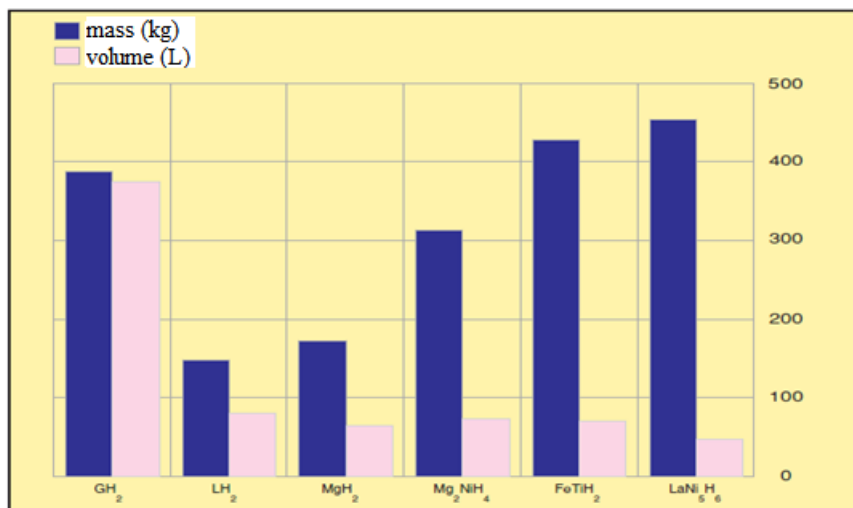
Figure 3.23 Comparison of storage requirements for hydrogen required for a distance of 500 km.

As can be seen, there is a need for huge storage tanks to store the hydrogen required for a range of 500 km with existing storage techniques. This increases both the weight and the cost of the tank. Therefore, existing hydrogen storage techniques are considered to be one of the biggest obstacles to the widespread use of hydrogen.

However, recent researches have shown that the boron element can be used as a hydrogen storage medium due to its high hydrogen storage capability. In particular, $NaBH_4$ contains 10.6% by weight hydrogen, which is much higher than the hydrogen storage component of many compounds. Turkey, which has the world's largest boron reserves according to Figure 3.24, has an important potential in the production of boron minerals and commercial borates [88]. Since the indispensable advantages of $NaBH_4$ as hydrogen storage agent has emerged, production systems have to be developed rapidly and fuel cell applications must be made at these field.
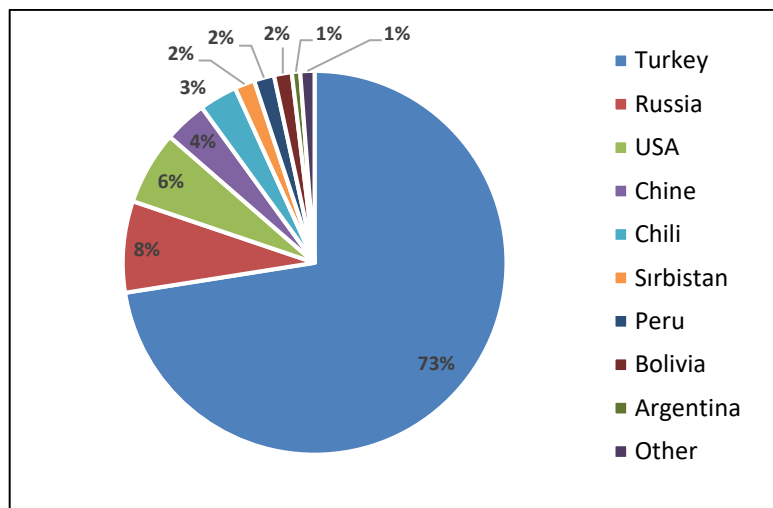
Figure 3.24 The world boron reserves [88].

CHAPTER 4

THE EXPERIMENTAL STUDIES

4.1 The Experimental Setup

Firstly, the parts of the experimental setup shown in Figure 4.1 and Figure 4.2 were established. Then, the regulator, to be used for sending the fixed CO_2 gas in the amount adjusted to the experiment apparatus, was connected to the CO_2 tank. A polyamide hose, 10 mm in diameter, was connected to the outlet of the regulator. Then, a 3-necked glass beaker, 500 mL, was placed in a balloon heater with temperature controlled the magnetic stirrer (the stirring mantle). The polyamide hose coming from the regulator of the CO_2 tube was connected one of these outlet nozzles. A glass thermometer was placed to the second outlet nozzle. A polyamide hose connection was made at the third outlet nozzle and the other side of the hose was connected to the inlet of the flowmeter, which will measure the hydrogen gas to be formed at the result of reaction. Another polyamide hose connection was made to the outlet of the flowmeter to remove the formed gas from the system. Sealing was attempted by using teflon tape in all hose connections.

Figure 4.1 The first part of the experimental setup.

Then, an alkaline KOH solution with a concentration of 5% was prepared. For this, 50 g of KOH compound was weighed by electronic balance and put into 1 liter (1000 mL) of water. The KOH was continuously mixed with the magnetic stirrer until it was completely dissolved in the water. Then, prepared 1 000 mL alkaline KOH solution was separated into 250 mL glass containers for to be used at 4 different temperature values.

Figure 4.2 The second part of the experimental setup.

The 1 g of NaBH$_4$ compound, which was measured by means of an electronic balance, was placed in the 250 mL alkaline KOH solution and mixed on the magnetic stirrer. This aqueous alkaline NaBH$_4$ solution was then put into the 3-necked glass beaker in the stirring mantle. The stirring mantle was switched on and its heater was turned off when the temperature of the solution was 20°C. Although the heater of the stirring mantle was automatically turned off at the set temperature, it was used on the value of the thermometer in the solution instead of on the value of the stirring mantle. The CO$_2$ gas was fed into the solution at a rate of 1 L/min with the heater closed. After 1 minute, the gassing process was finished and the flowmeter output

was closed with the setting valve on the flowmeter after reading the value on the flowmeter measuring the gas released. The solution was then taken out of the 3-necked glass beaker. After measuring the pH value of the solution with the pH meter, the solution was again placed into the 3-necked glass beaker. The same procedures were also carried out for mixing temperatures of 40°C, 60°C and 80°C, and the pH values of the solution and the rates of the gas releasing were measured.

Then, the other 250 mL of alkaline KOH solutions with a concentration of 5% were taken and the required solutions were prepared by adding 2 g, 3 g and 4 g $NaBH_4$ compounds, respectively, measured by electronic balance. The experiments were also carried out with these solutions at 20 °C, 40 °C, 60 °C and 80 °C in the same manner as described above and measured the pH values of the solutions and the rates of the gas releasing. Thus, experiments were completed for aqueous alkaline $NaBH_4$ solutions with concentration of 5% with CO_2 gas of 1 L/min.

Then, KOH mixtures with concentrations of 10% and 15% were prepared in the same manner and the above experiments were repeated with aqueous alkaline $NaBH_4$ solutions prepared by adding 1 g, 2 g, 3 g and 4 g of $NaBH_4$ compounds, respectively. So, all experiments were completed for CO_2 gas of 1 L/min.

The same experiments were repeated with CO_2 gas of 2 L/min and 3 L/min. The schematic view of the experimental setup is shown in Figure 4.3.

Figure 4.3 The schematic view of the experimental setup.

4.2 The Materials and Equipment Used in Experiments

The following equipment was used in the experiments;

- The compound of NaBH₄

  In the experiments, NaBH₄, bought by Merck, was used at approximately 99.5% pure. The characteristics of NaBH₄ are shown in Table 4.1 and the figure of NaBH₄ is given in Figure 4.4.

Table 4.1 Physicochemical information of NaBH₄.

Chemical formula	Molar mass (g/mole)	Boiling point (°C)	Density (g/cm³)	Purity	Ignition temp. (°C)	Vapor pressure (hPa)	Melting point (°C)
NaBH₄	37.83	500	1.07	≥ 98%	220	0.0001	>360
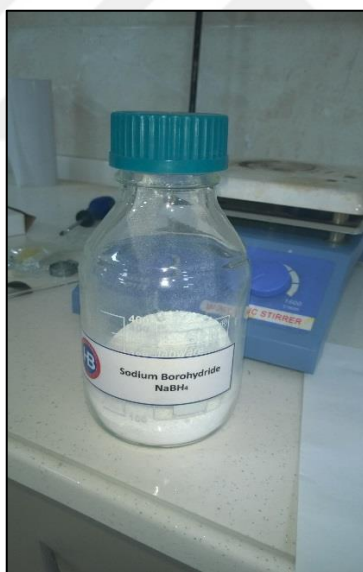
Figure 4.4 NaBH₄ used in the experiments.

- The solution of KOH

  In the experiments, 95% pure native KOH compound was used. This compound is put into pure water in desired amounts to prepare alkaline KOH solutions with concentration of 5%, 10%, and 15%. The characteristics of

KOH are given in Table 4.2 and the figure of KOH is given in Figure 4.5a and 4.5b.

Table 4.2 Physicochemical information of KOH.

Chemical Formula	Molar Mass (g/mole)	Boiling Point (°C)	Density (g/cm³)	Purity	Melting Point (°C)
KOH	56.11	1327	2.044	≥ 95%	406
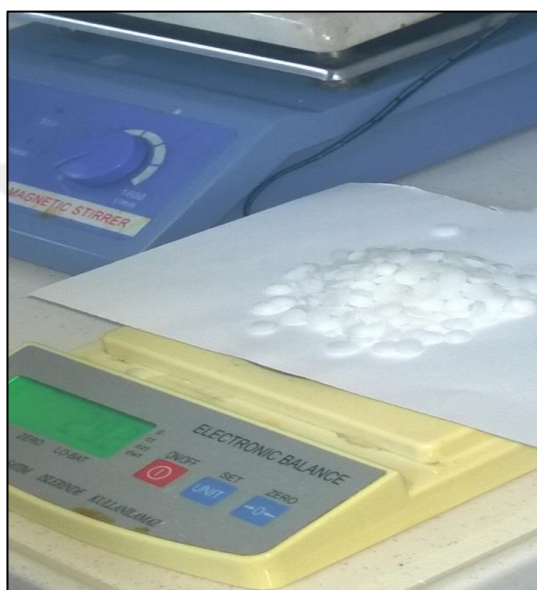
Figure 4.5a Weighing of KOH compound.

Figure 4.5b Preparing of KOH solution.

- CO_2 gas

99.5% pure CO_2 gas was used to initiate the reaction in the aqueous alkaline $NaBH_4$ solution. The characteristics of CO_2 gas are given in Table 4.3 and the figure of the tube of CO_2 is given in Figure 4.6.

Table 4.3 Physicochemical information of CO_2.

Chemical Formula	Molar Mass (g/mole)	Vapor Pressure (MPa)	Density (kg/m³)	Purity	Melting Point (°C)
CO_2	44.01	5.73	1.977	99.5%	-56.6

Figure 4.6 The tube of CO_2.

- Thermometer

A glass rod thermometer with a temperature range of 0~200 °C was used to measure the temperature of the aqueous alkaline $NaBH_4$ solution. The figure of the thermometer is given in Figure 4.7.

Figure 4.7 The mercury-in-glass thermometer.

- Single Stage Cylinder Regulator

It was used to provide the same rate regular CO_2 gas flow to the system. It was ensured that the desired CO_2 gas was sent to the system by using the adjustment valve of the regulator. The characteristics of the regulator are given in Table 4.4 and the figure of the regulator is given in Figure 4.8.

Table 4.4 The characteristics of the single stage cylinder regulator.

Model	Gas Type	Max. Inlet Pressure (bar)	Outlet Pressure (bar)	Max. Outlet Flow (m^3/h)
Harris 801	CO_2	230	0-10	155

Figure 4.8 The single stage cylinder regulator.

- Volumetric Flowmeter

A volumetric flowmeter, Gentek brand, has range of 0-7 L/min was used to measure the flow of hydrogen gas produced as a result of the reaction. The characteristics of the flowmeter are given in Table 4.5 and the figure of the flowmeter is given in Figure 4.9.

Table 4.5 The characteristics of the flowmeter.

Measuring range (L/min)	Operation pressure (bar)	Casing	Setting valve	Operation temperature (°C)
0-7	0-16	Polycarbonate	Yes	0-120
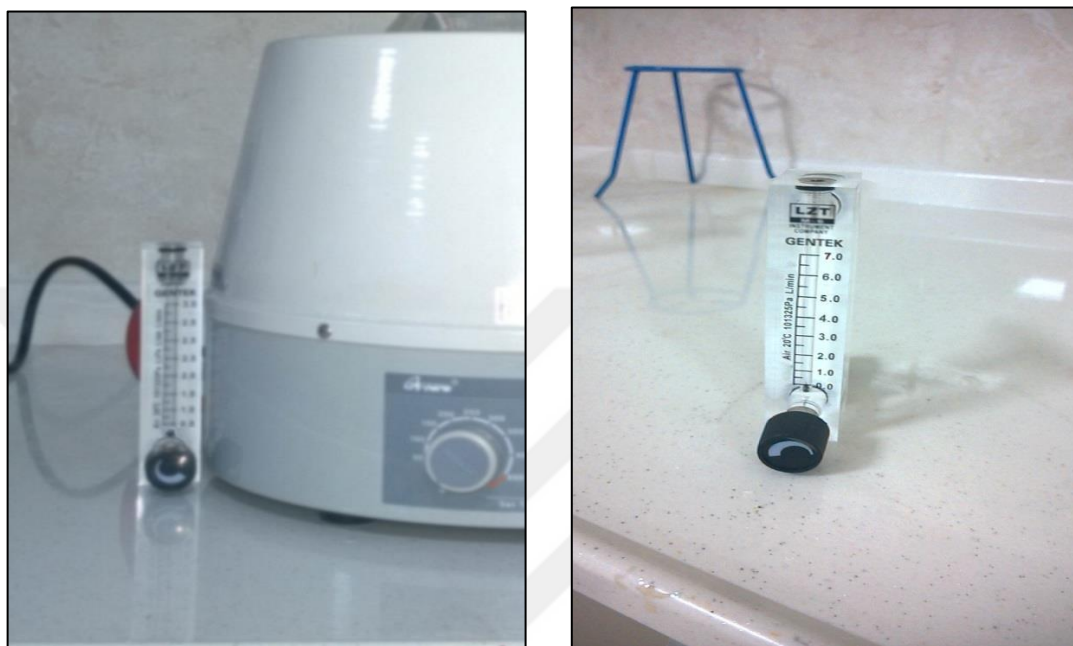
Figure 4.9 The flowmeter used to measure the flow of the resulted H_2 gas.

- The Stirring Mantle

A 2 000 L balloon heater with the magnetic stirrer was used to bring the solution to the desired temperature and ensure mixing of the $NaBH_4$ compound homogeneously in the solution. The properties of the stirring mantle are given in Table 4.6 and the figure of the stirring mantle is given in Figure 4.10.

Table 4.6 The specifications of the stirring mantle.

Model	Capacity (L)	Heating power (W)	Mixing speed (rpm)	Casing	Speed control	Operation temperature (°C)
ES 305	2000	500	100-1200	AISI 304	Yes	0-450

Figure 4.10 The stirring mantle.

- pH meter

A pH meter with ± 0.01 sensitivity, Hanna branded Edge model, was used to measure the changing pH value of the aqueous alkaline $NaBH_4$ solution the result of sending of CO_2 gas. The properties of the pH meter are given in Table 4.7 and the figure of the pH meter is given in Figure 4.11.

Table 4.7 The properties of the pH meter.

Range	basic mode: -2.00 to 16.00 pH, -2.000 to 16.000 pH; standard mode: ±1000.0 mV for pH
Resolution	0.01 pH; 0.001 pH; 0.1 mV
Accuracy (@25 ºC/77 ºF)	±0.01 pH; ±0.002 pH; ±0.2 mV
Calibration points	5 in standard mode; 3 in basic mode
Calibration buffers	standard mode: 1.68, 4.01, 6.86, 7.01, 9.18, 10.01, 12.45 and two custom buffers basic mode: 4.01, 6.86, 7.01, 9.18, 10.01
Temperature compensation	ATC (-20.0 to 120.0 ºC; -4.0 to 248.0 ºF)
Electrode diagnostics	standard mode: probe condition, response time and out of calibration range

Figure 4.11 The pH meter.

- Electronic Balance

An electronic balance, with ± 0.03 g sensitivity, was used to measure the mass of KOH and NaBH$_4$ compounds. The characteristics of the electronic balance are given in Table 4.8 and the figure of the electronic balance is given in Figure 4.12.

Table 4.8 The features of electronic balance.

Model	Measurement Range (g)	Accuracy (g)	The Smallest Indication (g)	Plate
SFE-300	0.2-300	±0.03	0.01	Stainless steel

Figure 4.12 The electronic balance.

- The Magnetic Stirrer

  To prepare alkaline KOH solution at the desired concentrations, the KOH compound was put into pure water. Isotex SH-4 the magnetic stirrer was used to dissolve the KOH compound in the pure water homogeneously. The properties of the magnetic stirrer are given in Table 4.9 and the figure of the magnetic stirrer is given in Figure 4.13.

Table 4.9 The specifications of the magnetic stirrer.

Model	Power (W)	Speed (r/min)	Max. Volume (ml)	Plate Max. Temperature (°C)
SH-4	600	100-2000	5000	380

Figure 4.13 The magnetic stirrer.

4.3 The Parameters Measured in the Experiments

The following parameters were measured in the experiments;

- The temperature of the aqueous alkaline $NaBH_4$ solution,
- The rate of the CO_2 gas sent to the aqueous alkaline $NaBH_4$ solution to initiate the reaction,
- The pH value of aqueous alkaline $NaBH_4$ solution,
- The rate of H_2 gas forming as a result of the reaction.

4.4 Theoretical Calculations for the Chemical Reaction

As shown in Eq.5.1, a total of 4 moles H_2 is obtained from the reaction of $NaBH_4$ with water.

$$NaBH_4 + 2H_2O \longrightarrow NaBO_2 + 4H_2 + heat\ (300\ kJ) \tag{5.1}$$
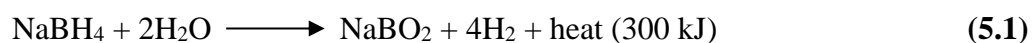
The molecular weight of $NaBH_4$ is 37.84 g/mole.

The amount of hydrogen that might be theoretically produced from 1 g of $NaBH_4$ is calculated as below.

According to the Eq. 5.1, 4 moles of H_2 is obtained from 1 mole of $NaBH_4$, i.e. 37.84 g of $NaBH_4$. So;

$4/37.84 = 0.11$ mole H_2 is obtained from 1 g of $NaBH_4$

Since 1 mole = 22.4 L,

$0.11 \times 22.4 = 2.46$ L hydrogen is theoretically obtained from 1 g of $NaBH_4$.

The amounts of hydrogen that can be theoretically obtained from the $NaBH_4$ compounds used in the experiments were calculated in a similar manner and are shown in Table 4.10.

Table 4.10 The amounts of hydrogen that can be theoretically obtained from the $NaBH_4$ compounds.

The amount of NaBH$_4$ (g)	The amount of hydrogen (L)
1	2.46
2	4.70
3	7.17
4	9.41

The amounts of hydrogen obtained from 1 g of $NaBH_4$ compound in the experiments are given in Tables 4.11, 4.12 and 4.13.

Table 4.11 The volumetric flow rates of H_2 obtained from 1 g of $NaBH_4$ compound ($\dot{m}_{CO_2} = 1$ L/min).

The concentration of solution	The volumetric flow rates of H$_2$ (L/min)			
	20 °C	40 °C	60 °C	80 °C
5% KOH	0.45	0.45	0.45	0.55
10% KOH	0.35	0.40	0.45	0.50
15% KOH	0.35	0.40	0.40	0.45

Table 4.12 The volumetric flow rates of H_2 obtained from 1 g of $NaBH_4$ compound ($\dot{m}_{CO_2}$ = 2 L/min).

The concentration of the solutions	The volumetric flow rates of H_2 (L/min)			
	20 °C	40 °C	60 °C	80 °C
5% KOH	0.45	0.45	0.50	0.60
10% KOH	0.40	0.40	0.45	0.55
15% KOH	0.35	0.40	0.45	0.50

Table 4.13 The volumetric flow rates of H_2 obtained from 1 g of $NaBH_4$ compound ($\dot{m}_{CO_2}$ = 3 L/min).

The concentration of the solutions	The volumetric flow rates of H_2 (L/min)			
	20 °C	40 °C	60 °C	80 °C
5% KOH	0.45	0.50	0.50	0.65
10% KOH	0.45	0.45	0.45	0.60
15% KOH	0.40	0.40	0.45	0.55

The value obtained by multiplying the total hydrolysis time by the volumetric flow rates of hydrogen could be compared with the amount of hydrogen that might be theoretically produced from compound containing 1 g of $NaBH_4$.

4.5 The Experimental Results

Table 4.14 The experimental results ($\dot{m}_{CO_2}$ = 1 L/min).

	20 °C								40 °C							
	NaBH$_4$								NaBH$_4$							
	1 g		2 g		3 g		4 g		1 g		2 g		3 g		4 g	
	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH
5% KOH	0.40	13.10	0.70	13.20	1.00	13.40	1.40	13.10	0.45	12.10	0.75	12.70	1.15	12.30	1.50	12.00
	60 °C								80 °C							
	NaBH$_4$								NaBH$_4$							
	1 g		2 g		3 g		4 g		1 g		2 g		3 g		4 g	
	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH
	0.45	10.50	0.85	10.30	1.35	10.50	1.65	10.70	0.55	9.60	1.00	9.80	1.50	9.30	1.95	9.50
	20 °C								40 °C							
	NaBH$_4$								NaBH$_4$							
	1 g		2 g		3 g		4 g		1 g		2 g		3 g		4 g	
	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH
10% KOH	0.35	13.20	0.65	13.40	0.90	13.70	1.30	13.50	0.40	12.40	0.70	13.10	1.10	12.60	1.40	12.30
	60 °C								80 °C							
	NaBH$_4$								NaBH$_4$							
	1 g		2 g		3 g		4 g		1 g		2 g		3 g		4 g	
	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH
	0.45	10.80	0.85	10.50	1.25	10.70	1.50	11.00	0.50	10.10	0.90	10.00	1.35	9.80	1.80	9.90
	20 °C								40 °C							
	NaBH$_4$								NaBH$_4$							
	1 g		2 g		3 g		4 g		1 g		2 g		3 g		4 g	
	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH
15% KOH	0.35	13.30	0.60	13.60	0.80	13.80	1.20	13.60	0.40	12.50	0.65	13.20	1.10	12.70	1.25	12.50
	60 °C								80 °C							
	NaBH$_4$								NaBH$_4$							
	1 g		2 g		3 g		4 g		1 g		2 g		3 g		4 g	
	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH
	0.40	11.00	0.80	10.60	1.15	10.80	1.35	11.20	0.45	10.30	0.90	10.20	1.25	10.00	1.60	10.10

Table 4.15 The experimental results ($\dot{m}_{CO_2}$ = 2 L/min).

5% KOH	20 °C								40 °C							
	NaBH$_4$								NaBH$_4$							
	1 g		2 g		3 g		4 g		1 g		2 g		3 g		4 g	
	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH
	0.45	12.70	0.75	12.50	1.10	12.60	1.50	12.70	0.45	11.30	0.80	11.20	1.25	11.10	1.65	11.20
	60 °C								80 °C							
	NaBH$_4$								NaBH$_4$							
	1 g		2 g		3 g		4 g		1 g		2 g		3 g		4 g	
	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH
	0.50	9.10	0.90	9.10	1.45	9.20	1.80	9.10	0.60	8.90	1.10	8.80	1.65	8.90	2.10	8.70

10% KOH	20 °C								40 °C							
	NaBH$_4$								NaBH$_4$							
	1 g		2 g		3 g		4 g		1 g		2 g		3 g		4 g	
	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH
	0.40	12.90	0.75	13.00	1.00	12.80	1.40	13.00	0.40	11.50	0.75	11.30	1.15	11.40	1.50	11.40
	60 °C								80 °C							
	NaBH$_4$								NaBH$_4$							
	1 g		2 g		3 g		4 g		1 g		2 g		3 g		4 g	
	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH
	0.45	9.20	0.85	9.40	1.35	9.40	1.65	9.50	0.55	9.20	1.00	9.00	1.50	9.10	1.90	9.00

15% KOH	20 °C								40 °C							
	NaBH$_4$								NaBH$_4$							
	1 g		2 g		3 g		4 g		1 g		2 g		3 g		4 g	
	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH
	0.35	13.30	0.70	13.40	0.85	13.40	1.20	13.50	0.40	12.20	0.70	12.00	1.10	12.40	1.40	12.30
	60 °C								80 °C							
	NaBH$_4$								NaBH$_4$							
	1 g		2 g		3 g		4 g		1 g		2 g		3 g		4 g	
	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH	H$_2$	pH
	0.45	9.70	0.85	9.70	1.25	9.60	1.50	9.60	0.50	9.40	0.95	9.30	1.40	9.40	1.70	9.30

Table 4.16 The experimental results ($\dot{m}_{CO_2}$ = 3 L/min).

	Temp	NaBH₄ 1 g H₂	pH	NaBH₄ 2 g H₂	pH	NaBH₄ 3 g H₂	pH	NaBH₄ 4 g H₂	pH
5% KOH	20 °C	0.45	9.90	0.85	9.80	1.20	9.70	1.65	9.90
	40 °C	0.50	8.90	0.90	9.00	1.30	9.20	1.85	9.10
	60 °C	0.50	8.00	0.95	8.10	1.60	8.10	2.00	8.20
	80 °C	0.65	8.20	1.15	8.10	1.90	8.30	2.20	8.10
10% KOH	20 °C	0.45	11.00	0.80	11.00	1.10	11.20	1.50	11.30
	40 °C	0.45	9.10	0.80	9.30	1.20	9.20	1.65	9.20
	60 °C	0.45	8.20	0.85	8.30	1.45	8.30	1.80	8.40
	80 °C	0.60	8.00	1.05	8.20	1.65	8.10	2.10	8.20
15% KOH	20 °C	0.40	11.20	0.75	11.40	1.00	11.50	1.40	11.50
	40 °C	0.40	9.30	0.75	9.50	1.15	9.40	1.50	9.60
	60 °C	0.45	8.10	0.80	8.20	1.35	8.40	1.65	8.40
	80 °C	0.55	8.50	1.00	8.40	1.50	8.40	1.95	8.30

CHAPTER 5

EVALUATION OF THE EXPERIMENTAL RESULTS

The hydrolysis of $NaBH_4$ through CO_2 gas was realized by adding CO_2 gas, which has acidic effect, to alkaline solution of $NaBH_4$ stabilized with KOH without using any catalyst. The main purpose of this study is; to obtain hydrogen from the aqueous alkaline solution of $NaBH_4$ without the use of metal catalysts such as Ru, Pt and Co, which is presently used, by changing the pH of the solution by supplying only CO_2 gas to the medium. The concentration of KOH in the solution which has alkaline effect, the temperature, the amount of $NaBH_4$, and the volumetric flow rate of CO_2 gas were taken as variable.

5.1. Graphs Obtained from the Experimental Results

The following graphs are drawn from the results obtained from the experiments. The graphs showing the variation of the volumetric flow rate of the obtained hydrogen with the temperature of the solution are shown in from Figure 5.1 to Figure 5.9.
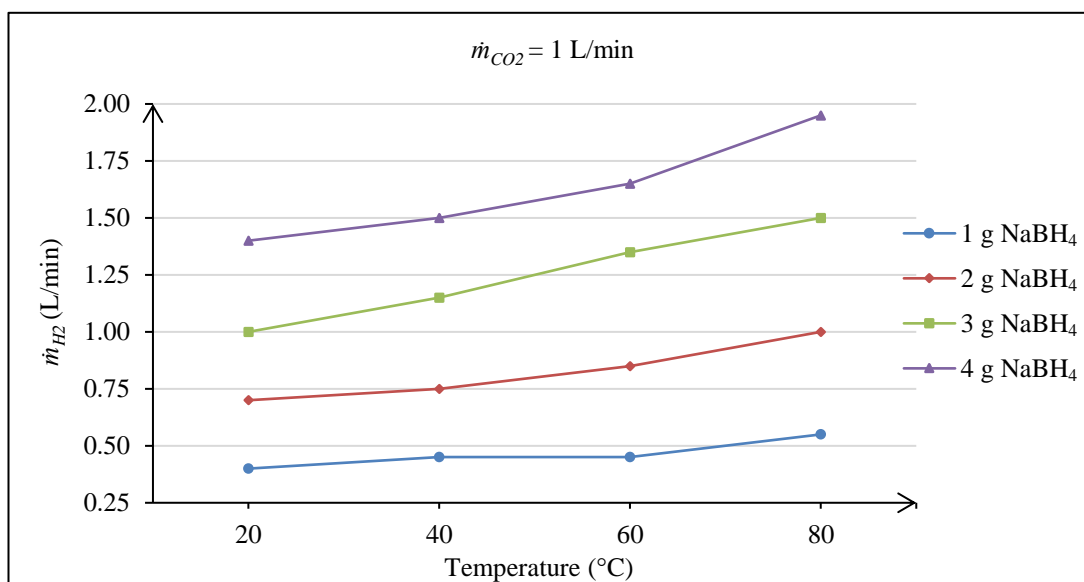

Figure 5.1 The volumetric flow rates of H_2 – Temperature ($\dot{m}_{CO_2}$ = 1 L/min, 5% KOH solution).

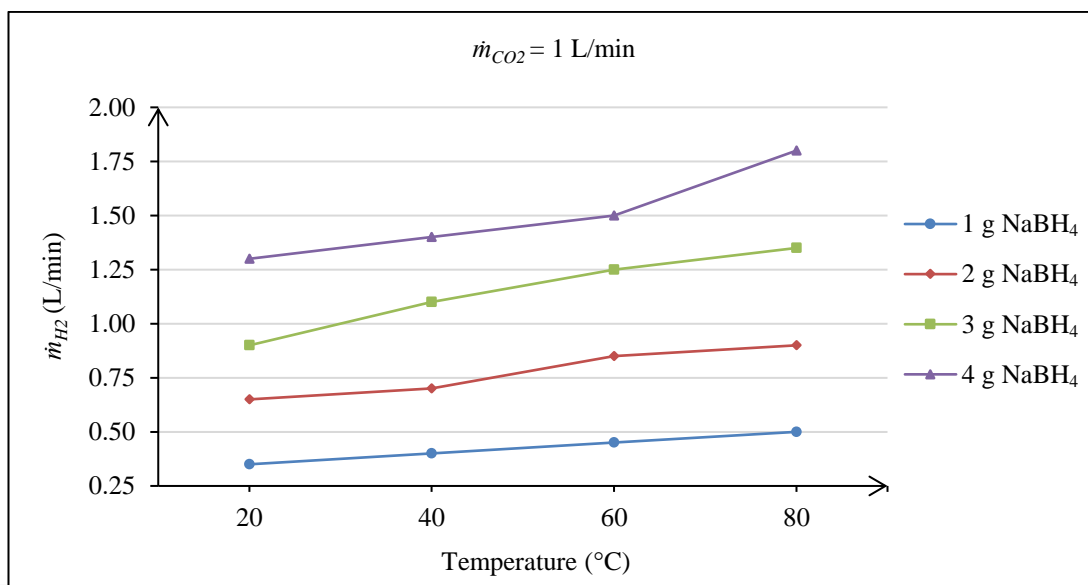**Figure 5.2** The volumetric flow rates of H_2 – Temperature ($\dot{m}_{CO_2}$ = 1 L/min, 10% KOH solution).

Figure 5.3 The volumetric flow rates of H_2 – Temperature ($\dot{m}_{CO_2}$ = 1 L/min, 15% KOH solution).

Figure 5.4 The volumetric flow rates of H$_2$ – Temperature ($\dot{m}_{CO_2}$ = 2 L/min, 5% KOH solution).

Figure 5.5 The volumetric flow rates of H$_2$ – Temperature ($\dot{m}_{CO_2}$ = 2 L/min, 10% KOH solution).
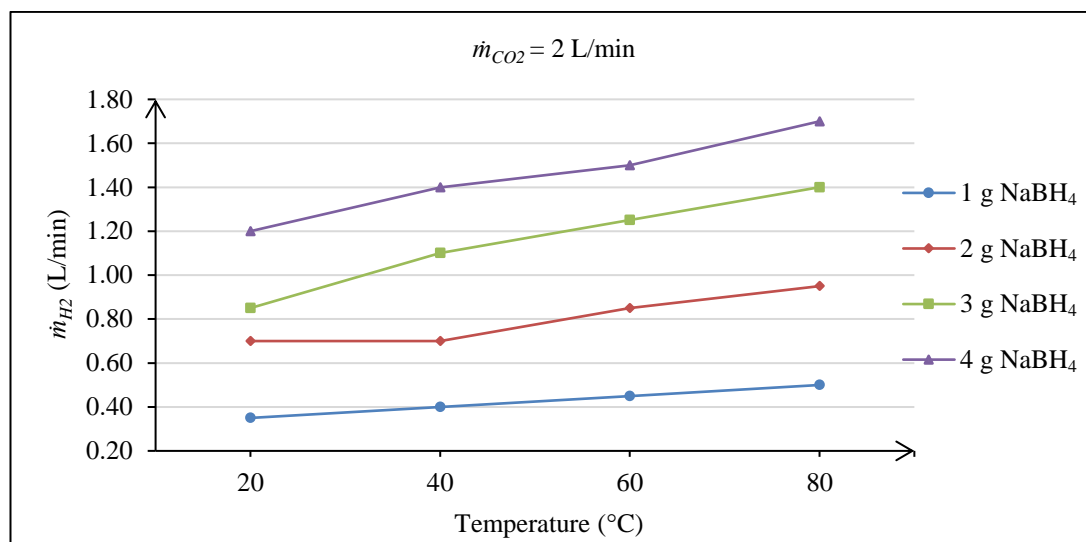
Figure 5.6 The volumetric flow rates of H_2 – Temperature ($\dot{m}_{CO_2}$ = 2 L/min, 15% KOH solution).
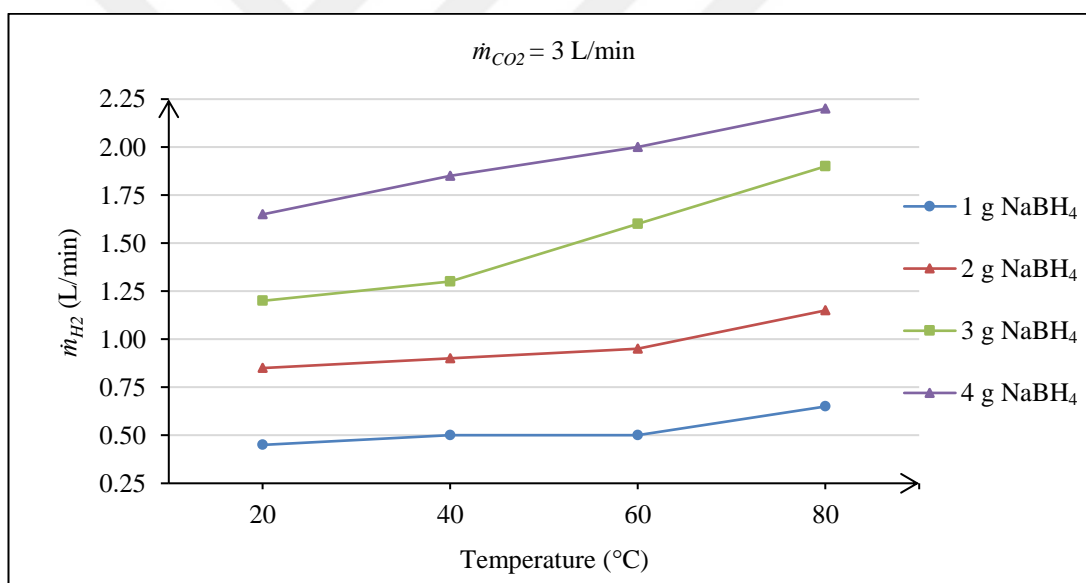
Figure 5.7 The volumetric flow rates of H_2 – Temperature ($\dot{m}_{CO_2}$ = 3 L/min, 5% KOH solution).
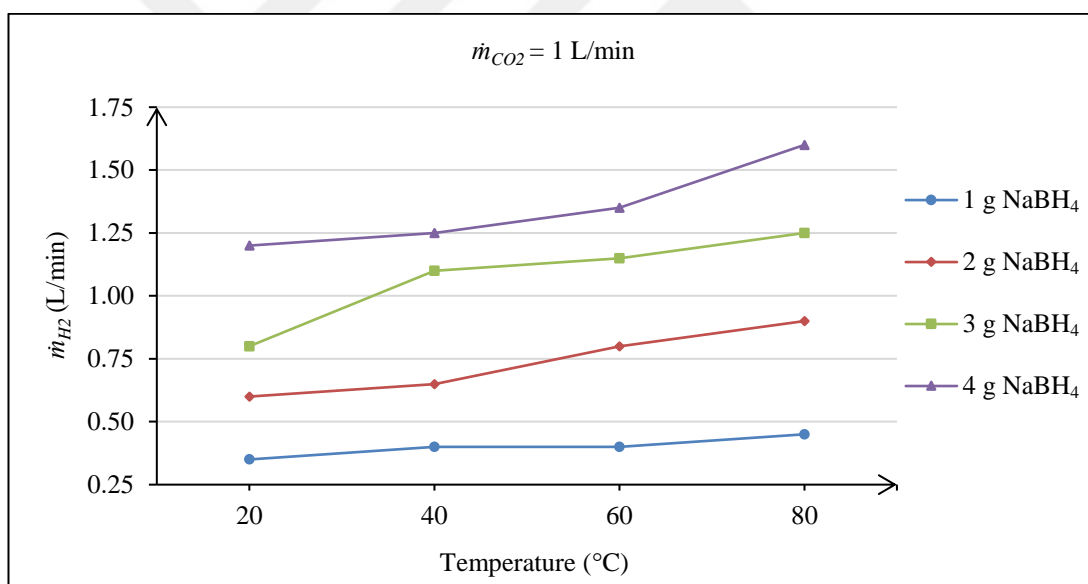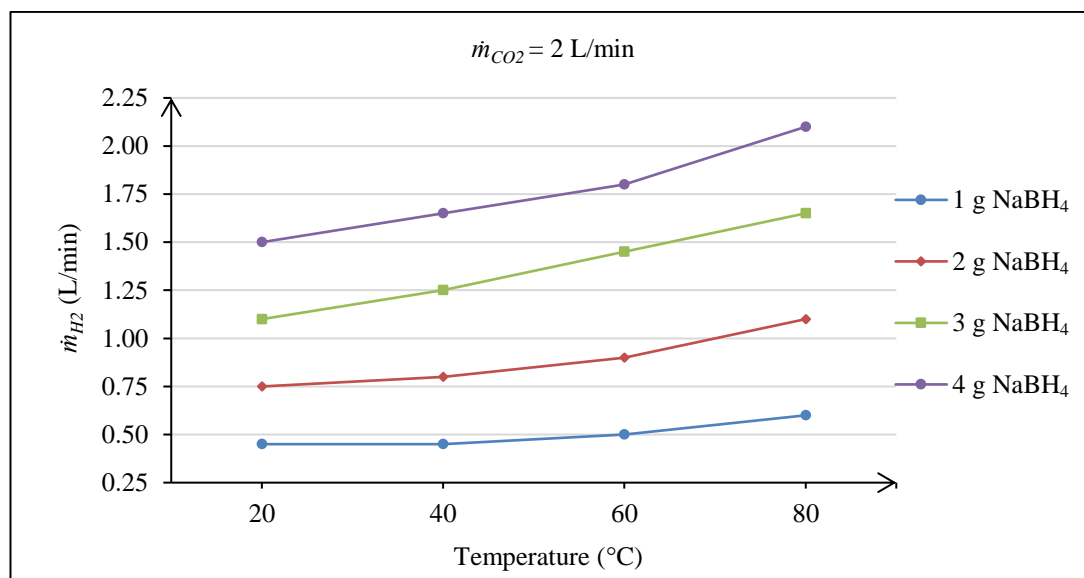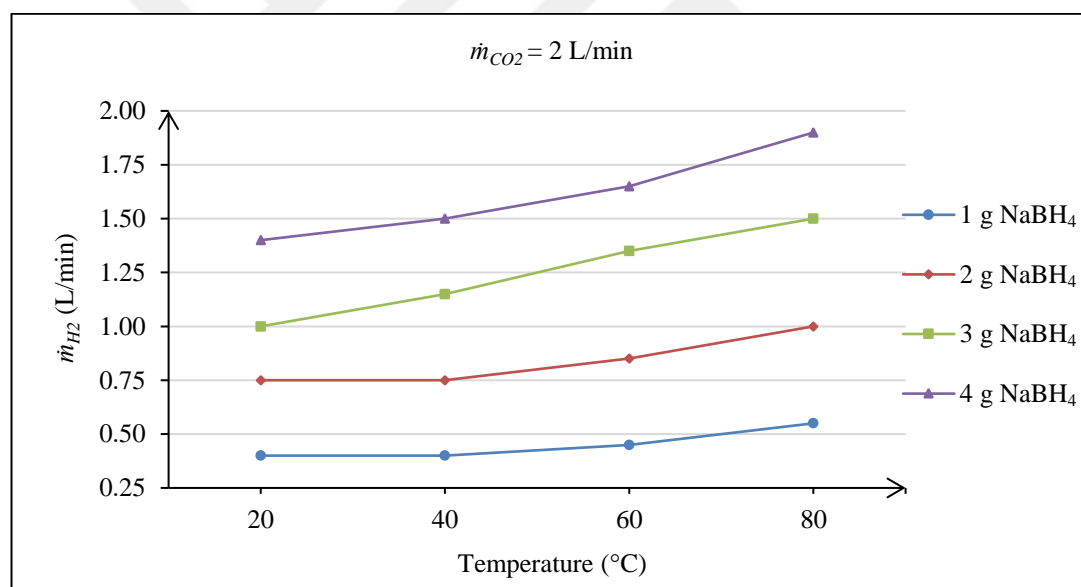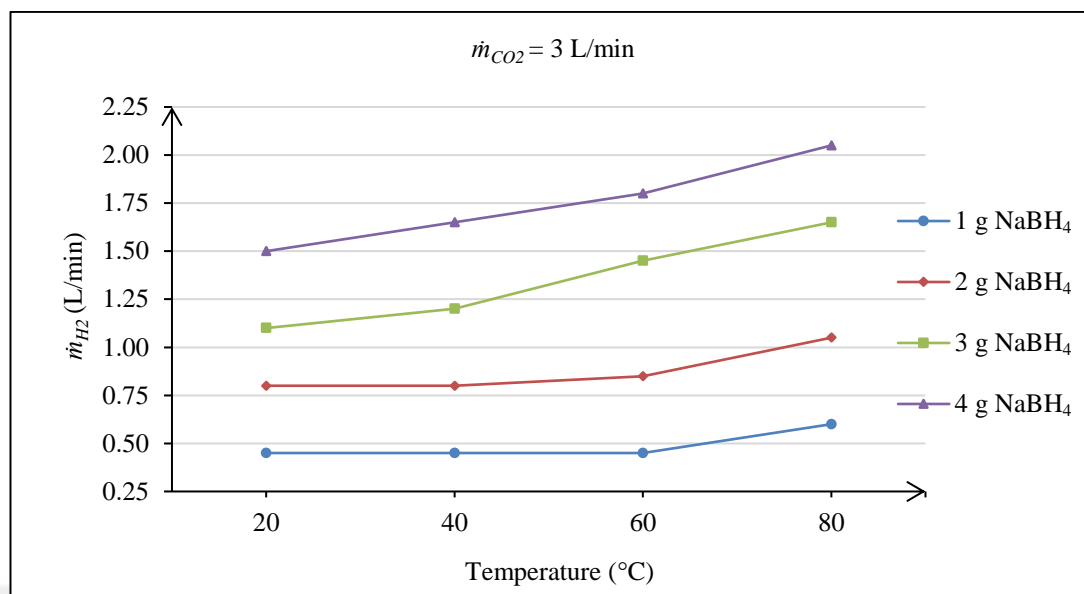
Figure 5.8 The volumetric flow rates of H_2 – Temperature ($\dot{m}_{CO_2}$ = 3 L/min, 10% KOH solution).

Figure 5.9 The volumetric flow rates of H_2 – Temperature ($\dot{m}_{CO_2}$ = 3 L/min, 15% KOH solution).

It can be seen from Figure 5.1 to Figure 5.9 that when temperature, flow rate of CO_2 gas and mass of NaBH$_4$ increase, the amount of generated hydrogen increases. But, the amount of generated hydrogen decreases while the amount of KOH in solution increases. The highest amount of hydrogen was obtained at $\dot{m}_{CO_2}$ = 3 L/min, 5% KOH solution and, 80 °C with 4 g of NaBH$_4$.

Graphs showing the change in solution pH with solution temperature are shown in from Figure 5.10 to Figure 5.18.

Figure 5.10 The pH value of solution – Temperature ($\dot{m}_{CO_2}$= 1 L/min, 5% KOH solution).
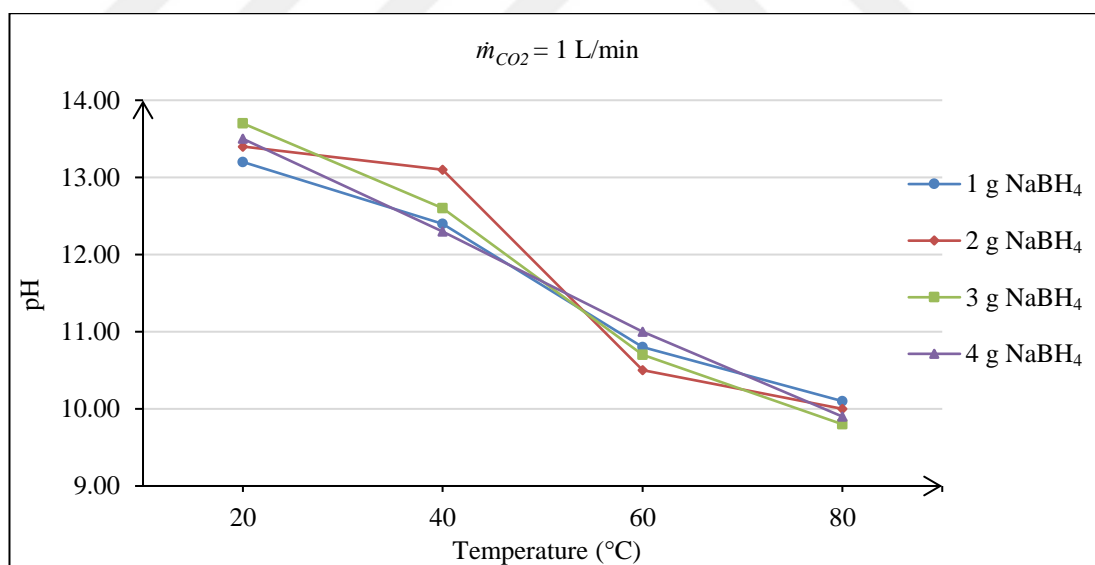
Figure 5.11 The pH value of solution – Temperature ($\dot{m}_{CO_2}$= 1 L/min, 10% KOH solution).
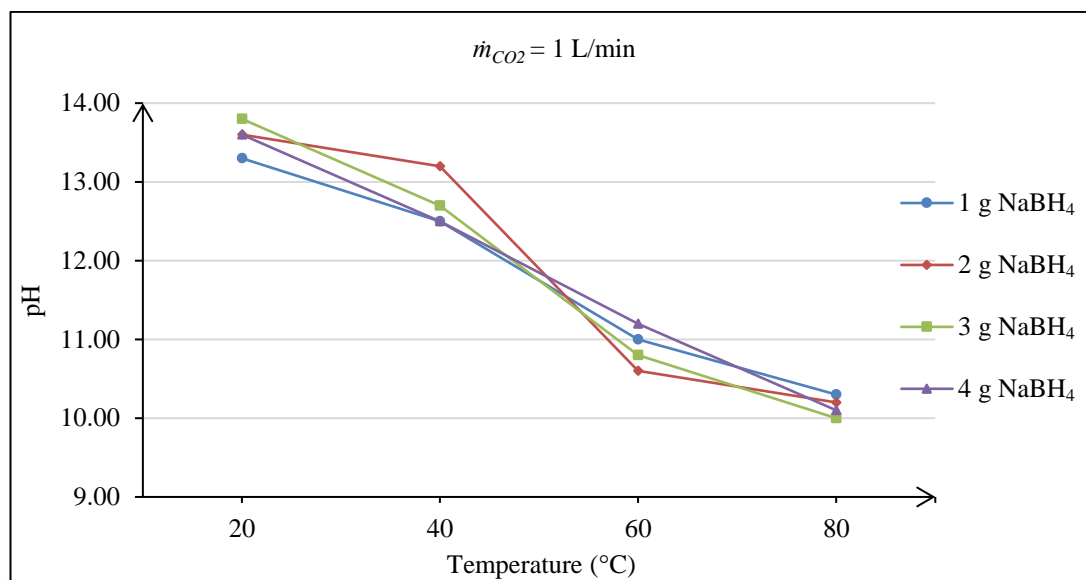
Figure 5.12 The pH value of solution – Temperature ($\dot{m}_{CO_2}$ = 1 L/min, 15% KOH solution).
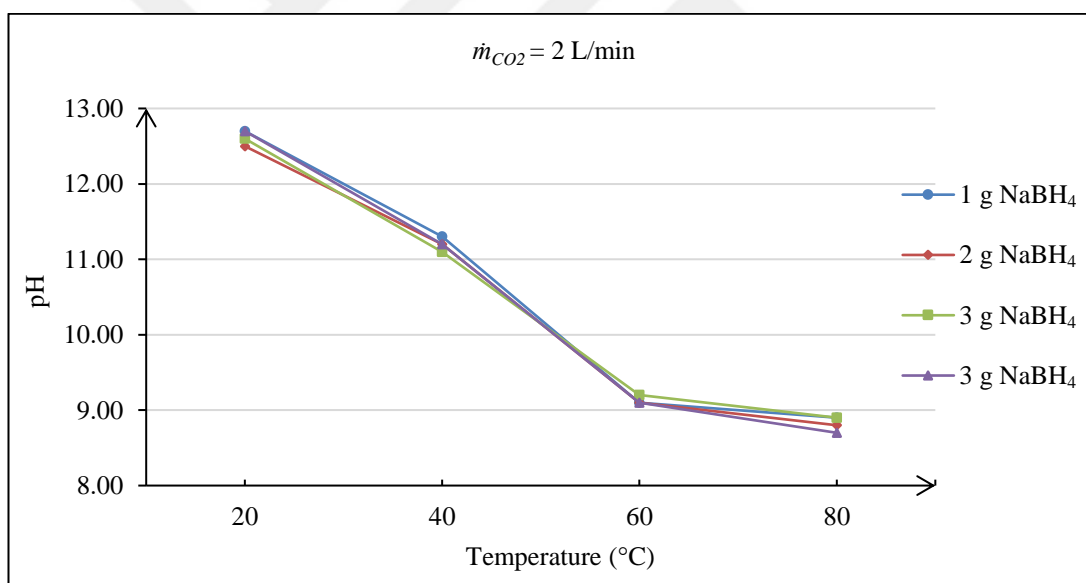
Figure 5.13 The pH value of solution – Temperature ($\dot{m}_{CO_2}$ = 2 L/min, 5% KOH solution).
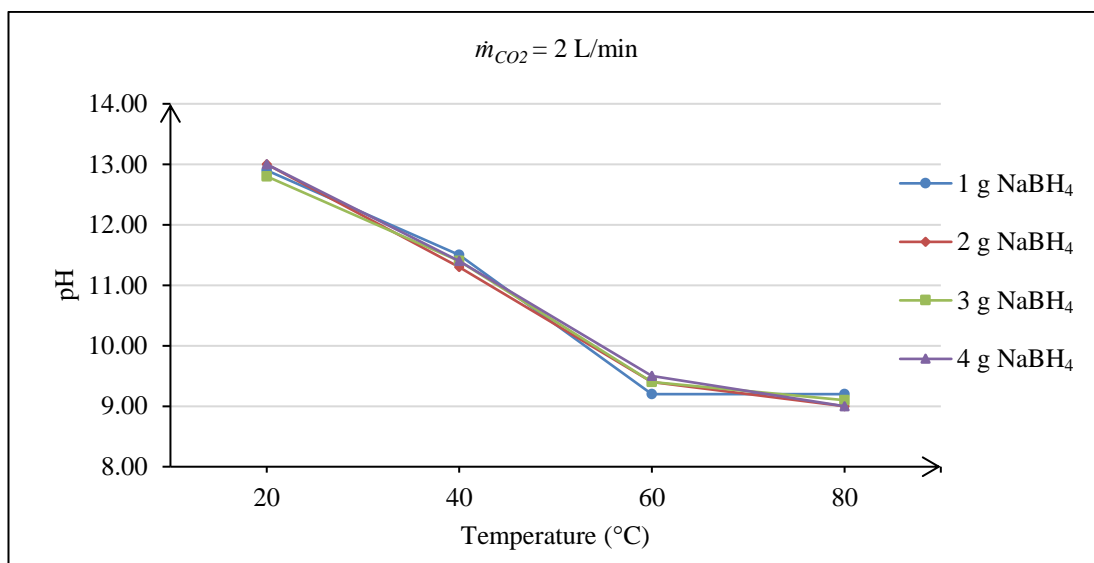
Figure 5.14 The pH value of solution – Temperature ($\dot{m}_{CO_2}$= 2 L/min, 10% KOH solution).
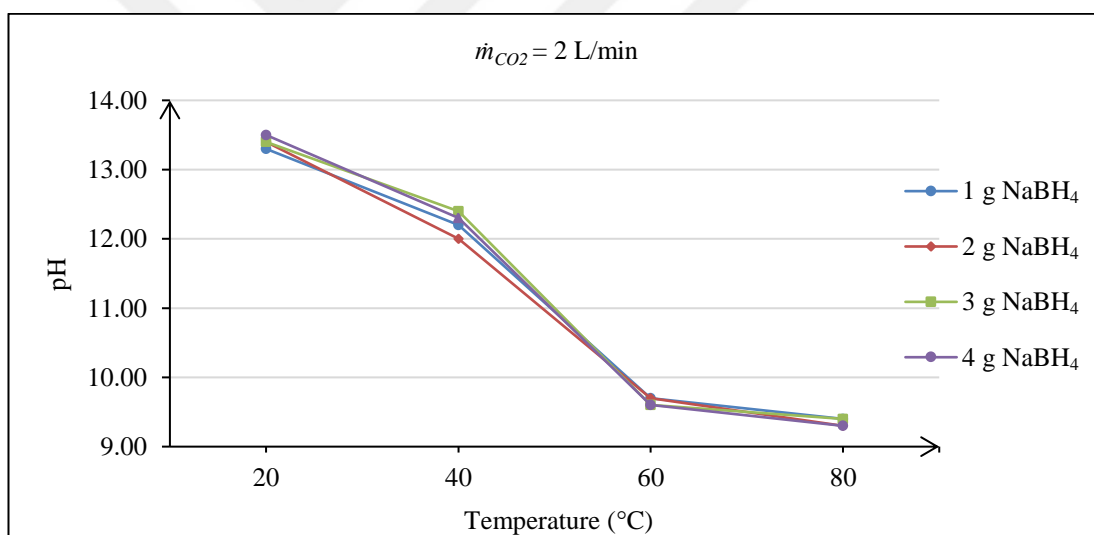
Figure 5.15 The pH value of solution – Temperature ($\dot{m}_{CO_2}$= 2 L/min, 15% KOH solution).
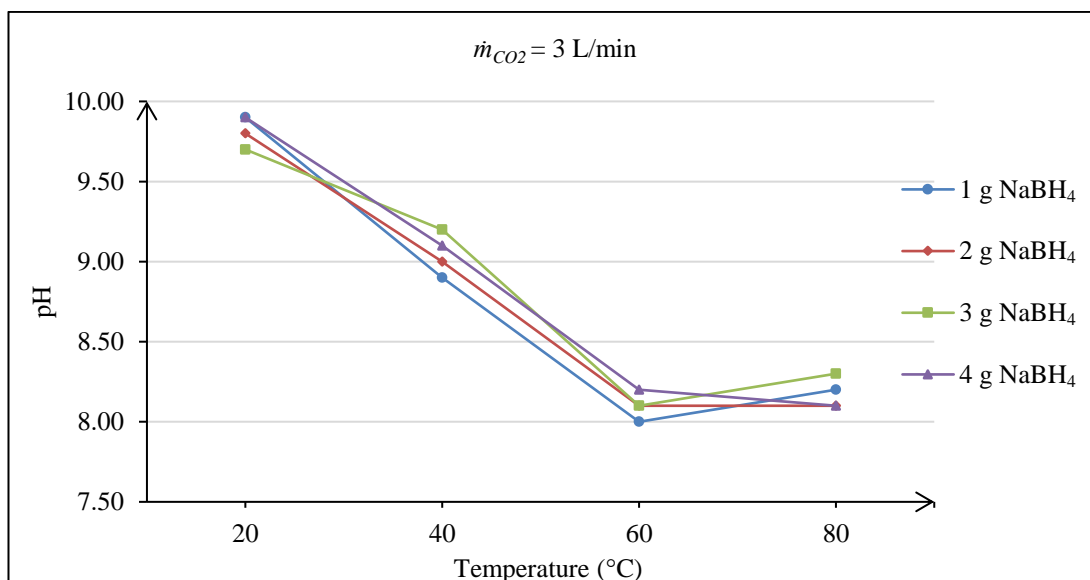
Figure 5.16 The pH value of solution – Temperature ($\dot{m}_{CO_2}$ = 3 L/min, 5% KOH solution).

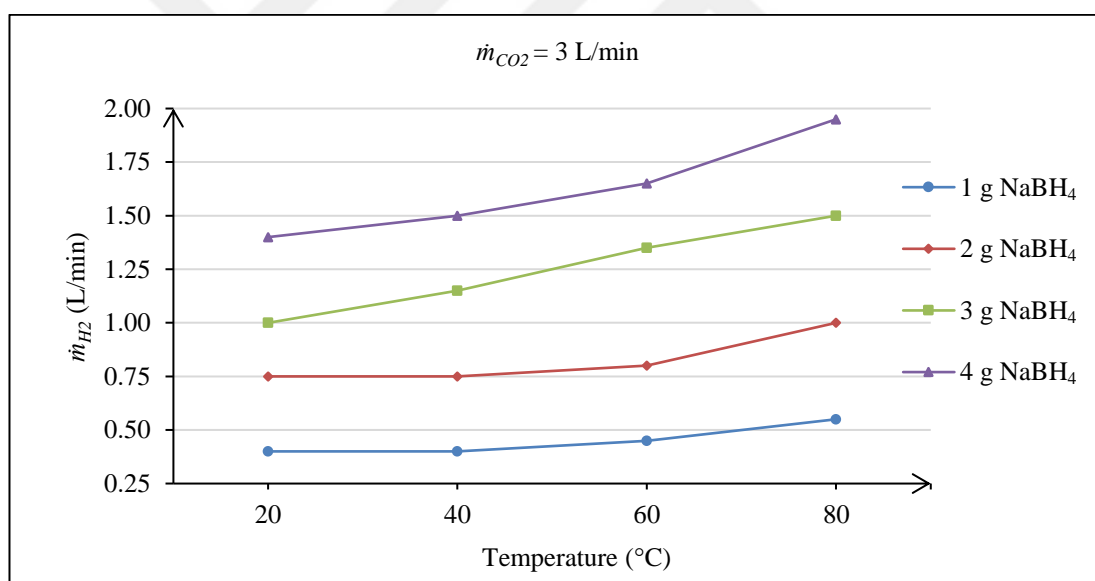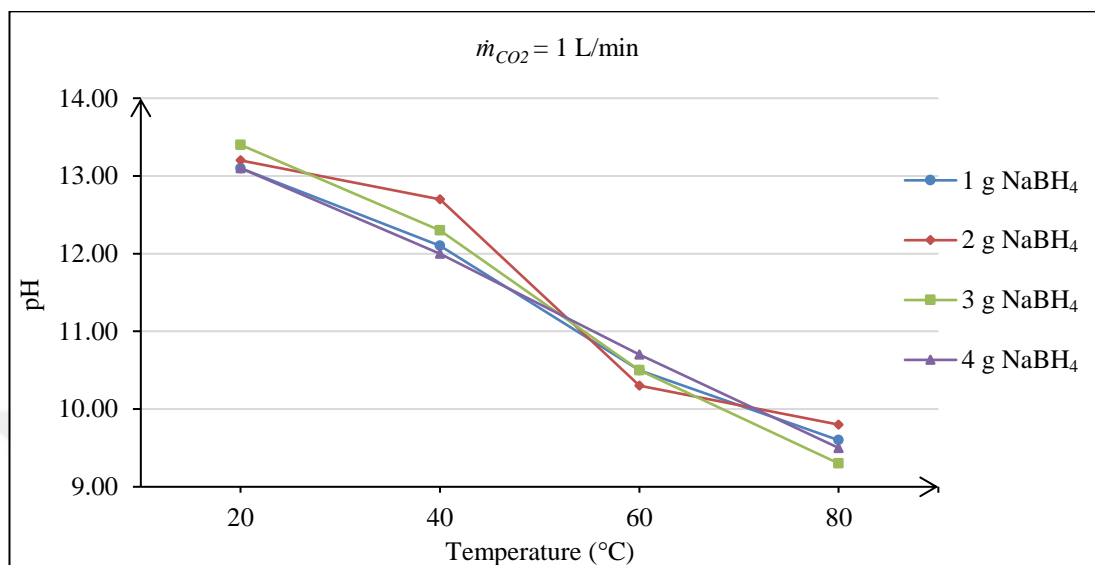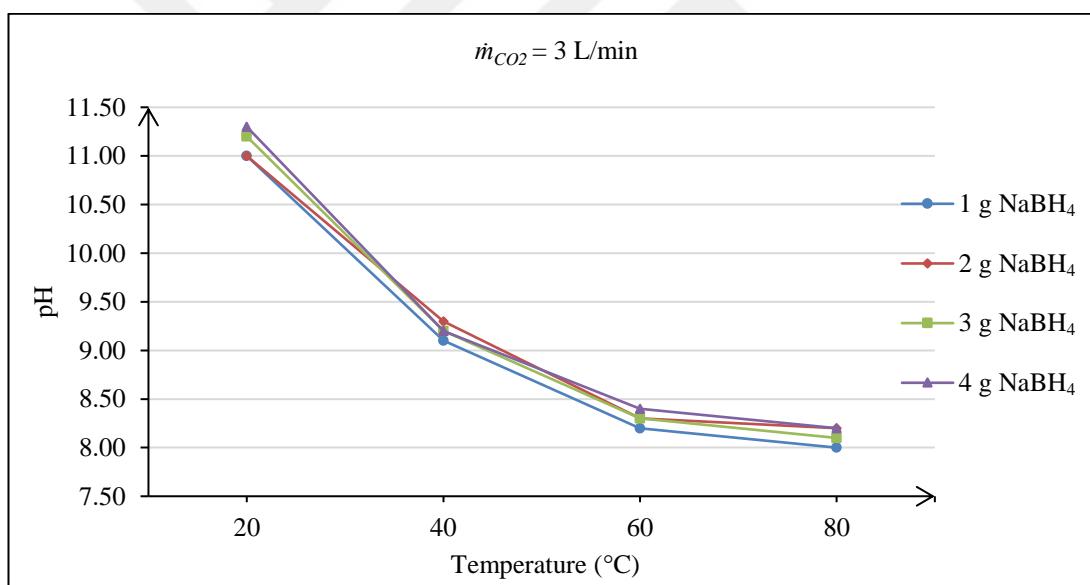**Figure 5.17** The pH value of solution – Temperature ($\dot{m}_{CO_2}$ = 3 L/min, 10% KOH solution).
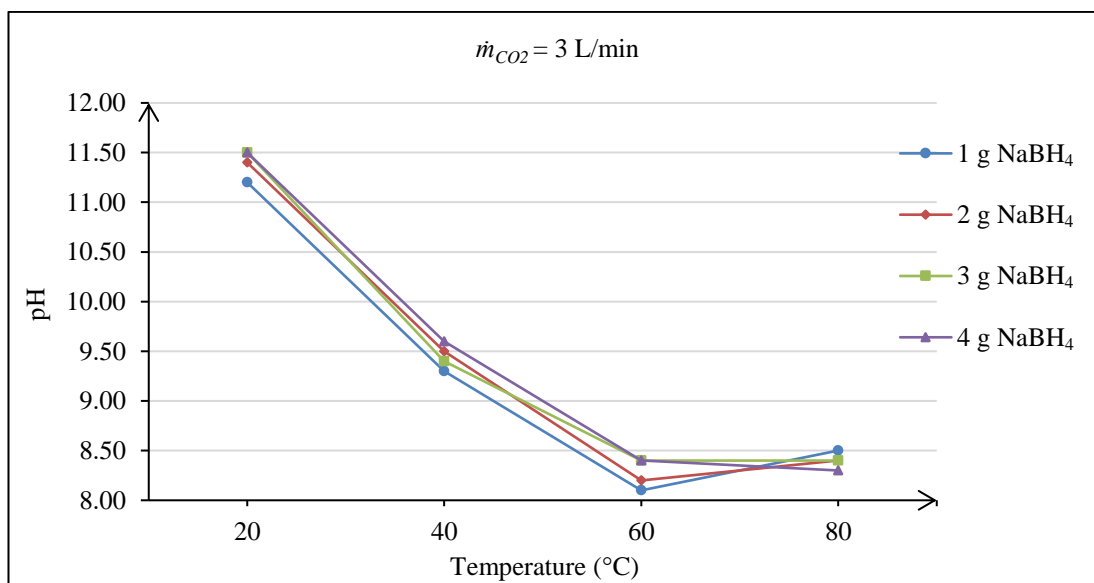
Figure 5.18 The pH value of solution – Temperature ($\dot{m}_{CO_2}$= 3 L/min, 15% KOH solution).

It can be seen from Figure 5.10 to Figure 5.18 that when temperature and flow rate of CO_2 gas increase, pH value of solution decreases. But, pH value of solution increases while the amount of KOH in solution increases.

5.2. Curve Fitting, Correlation Coefficients, and Coefficients of Determination Obtained from the Experimental Results

Linear equations are constructed for all test series, and correlation coefficients (R), and coefficients of determination (R^2) for these equations are given in Table 5.1 and Table 5.2.

Table 5.1 Correlation coefficients (R) and coefficients of determination (R^2) according to obtained H_2. [*]

$\dot{m}_{CO_2}$ = 1 L/min

5% KOH	Mass of NaBH₄ (g)				10% KOH	Mass of NaBH₄ (g)				15% KOH	Mass of NaBH₄ (g)			
T (°C)	1 g	2 g	3 g	4 g	T (°C)	1 g	2 g	3 g	4 g	T (°C)	1 g	2 g	3 g	4 g
20 °C	0.40	0.70	1.00	1.40	20 °C	0.35	0.65	0.90	1.30	20 °C	0.35	0.60	0.80	1.20
40 °C	0.45	0.75	1.15	1.50	40 °C	0.40	0.70	1.10	1.40	40 °C	0.40	0.65	1.10	1.25
60 °C	0.45	0.85	1.35	1.65	60 °C	0.45	0.85	1.25	1.50	60 °C	0.40	0.80	1.15	1.35
80 °C	0.55	1.00	1.50	1.95	80 °C	0.50	0.90	1.35	1.80	80 °C	0.45	0.90	1.25	1.60
R	0.9234	0.9759	0.9983	0.9691	R	1.0000	0.9762	0.9891	0.9562	R	0.9487	0.9845	0.9333	0.9431
R^2	**0.8526**	0.9524	0.9966	0.9391	R^2	1.0000	0.9529	0.9783	0.9143	R^2	0.9000	0.9692	0.8711	0.8895

$\dot{m}_{CO_2}$ = 2 L/min

5% KOH	1 g	2 g	3 g	4 g	10% KOH	1 g	2 g	3 g	4 g	15% KOH	1 g	2 g	3 g	4 g
20 °C	0.45	0.75	1.10	1.50	20 °C	0.40	0.75	1.00	1.40	20 °C	0.35	0.70	0.85	1.20
40 °C	0.45	0.80	1.25	1.65	40 °C	0.40	0.75	1.15	1.50	40 °C	0.40	0.70	1.10	1.40
60 °C	0.50	0.90	1.45	1.80	60 °C	0.45	0.85	1.35	1.65	60 °C	0.45	0.85	1.25	1.50
80 °C	0.60	1.10	1.65	2.10	80 °C	0.55	1.00	1.50	1.90	80 °C	0.50	0.95	1.40	1.70
R	0.9129	0.9592	0.9978	0.9827	R	0.9129	0.9288	0.9983	0.9795	R	1.0000	0.9487	0.9909	0.9923
R^2	0.8333	0.9200	0.9956	0.9657	R^2	0.8333	0.8627	0.9966	0.9595	R^2	1.0000	0.9000	0.9819	0.9846

$\dot{m}_{CO_2}$ = 3 L/min

5% KOH	1 g	2 g	3 g	4 g	10% KOH	1 g	2 g	3 g	4 g	15% KOH	1 g	2 g	3 g	4 g
20 °C	0.45	0.85	1.20	1.65	20 °C	0.45	0.80	1.10	1.50	20 °C	0.40	0.75	1.00	1.40
40 °C	0.50	0.90	1.30	1.85	40 °C	0.45	0.80	1.20	1.65	40 °C	0.40	0.75	1.15	1.50
60 °C	0.50	0.95	1.60	2.00	60 °C	0.45	0.85	1.45	1.80	60 °C	0.45	0.80	1.35	1.65
80 °C	0.65	1.15	1.90	2.20	80 °C	0.60	1.05	1.65	2.05	80 °C	0.55	1.00	1.50	1.95
R	0.8944	0.9327	0.9798	0.9985	R	0.7746	0.8677	0.9878	0.9909	R	0.9129	0.8677	0.9983	0.9691
R^2	0.8000	0.8699	0.9600	0.9969	R^2	0.6000	0.7529	0.9757	0.9818	R^2	0.8333	0.7529	0.9966	**0.9391**

[*] Correlation coefficients (R) and coefficients of determination (R^2) were calculated by MS Excel.

The graphs drawn according to the bold values at Table 5.1 are given in Figure 5.19 and 5.20.

Figure 5.19 The amount of obtained H_2 – Temperature (1 g of $NaBH_4$, 5% KOH, $\dot{m}_{CO_2}$= 1 L/min).
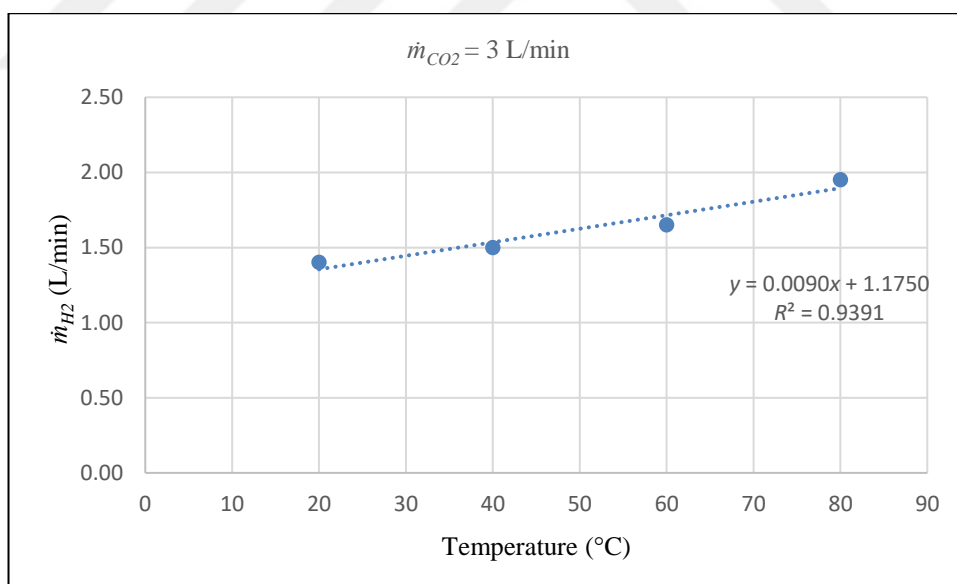
Figure 5.20 The amount of obtained H_2 – Temperature (4 g of $NaBH_4$, 15% KOH, $\dot{m}_{CO_2}$= 3 L/min).

Table 5.2 Correlation coefficients (R) and coefficients of determination (R^2) according to pH values of aqueous alkaline $NaBH_4$ solution. [*]

$\dot{m}_{CO_2}$ = 1 L/min	5% KOH	Mass of NaBH₄ (g)				10% KOH	Mass of NaBH₄ (g)				15% KOH	Mass of NaBH₄ (g)			
	T (°C)	1 g	2 g	3 g	4 g	T (°C)	1 g	2 g	3 g	4 g	T (°C)	1 g	2 g	3 g	4 g
	20 °C	13.10	13.20	13.40	13.10	20 °C	13.20	13.40	13.70	13.50	20 °C	13.30	13.60	13.80	13.60
	40 °C	12.10	12.70	12.30	12.00	40 °C	12.40	13.10	12.60	12.30	40 °C	12.50	13.20	12.70	12.50
	60 °C	10.50	10.30	10.50	10.70	60 °C	10.80	10.50	10.70	11.00	60 °C	11.00	10.60	10.80	11.20
	80 °C	9.60	9.80	9.30	9.50	80 °C	10.10	10.00	9.80	9.90	80 °C	10.30	10.20	10.00	10.10
	R	-0.9941	-0.9574	-0.9957	-0.9995	R	-0.9879	-0.9452	-0.9908	-0.9995	R	-0.9897	-0.9457	-0.9887	-0.9994
	R^2	**0.9883**	0.9166	0.9913	0.9990	R^2	0.9759	0.8933	0.9817	0.9990	R^2	0.9796	0.8943	0.9776	0.9989

$\dot{m}_{CO_2}$ = 2 L/min	5% KOH	1 g	2 g	3 g	4 g	10% KOH	1 g	2 g	3 g	4 g	15% KOH	1 g	2 g	3 g	4 g
	20 °C	12.70	12.50	12.60	12.70	20 °C	12.90	13.00	12.80	13.00	20 °C	13.30	13.40	13.40	13.50
	40 °C	11.30	11.20	11.10	11.20	40 °C	11.50	11.30	11.40	11.40	40 °C	12.20	12.00	12.40	12.30
	60 °C	9.10	9.10	9.20	9.10	60 °C	9.20	9.40	9.40	9.50	60 °C	9.70	9.70	9.60	9.60
	80 °C	8.90	8.80	8.90	8.70	80 °C	9.20	9.00	9.10	9.00	80 °C	9.40	9.30	9.40	9.30
	R	-0.9617	-0.9679	-0.9684	-0.9726	R	-0.9485	-0.9719	-0.9685	-0.9776	R	-0.9622	-0.9712	-0.9522	-0.9612
	R^2	0.9248	0.9368	0.9378	0.9460	R^2	0.8996	0.9446	0.9380	0.9558	R^2	**0.9258**	0.9432	0.9066	0.9240

$\dot{m}_{CO_2}$ = 3 L/min	5% KOH	1 g	2 g	3 g	4 g	10% KOH	1 g	2 g	3 g	4 g	15% KOH	1 g	2 g	3 g	4 g
	20 °C	9.90	9.80	9.70	9.90	20 °C	11.00	11.00	11.20	11.30	20 °C	11.20	11.40	11.50	11.50
	40 °C	8.90	9.00	9.20	9.10	40 °C	9.10	9.30	9.20	9.20	40 °C	9.30	9.50	9.40	9.60
	60 °C	8.00	8.10	8.10	8.20	60 °C	8.20	8.30	8.30	8.40	60 °C	8.10	8.20	8.40	8.40
	80 °C	8.20	8.10	8.30	8.10	80 °C	8.00	8.20	8.10	8.20	80 °C	8.50	8.40	8.40	8.30
	R	-0.9025	-0.9463	-0.9069	-0.9613	R	-0.9332	-0.9344	-0.9296	-0.9199	R	-0.8720	-0.9070	-0.9099	-0.9365
	R^2	0.8145	0.8955	0.8225	0.9241	R^2	0.8708	0.8731	0.8641	0.8462	R^2	0.7604	0.8227	0.8279	0.8770

[*] Correlation coefficients (R) and coefficients of determination (R^2) were calculated by MS Excel.

The graphs drawn according to the bold values at Table 5.2 are given in Figure 5.21 and 5.22.
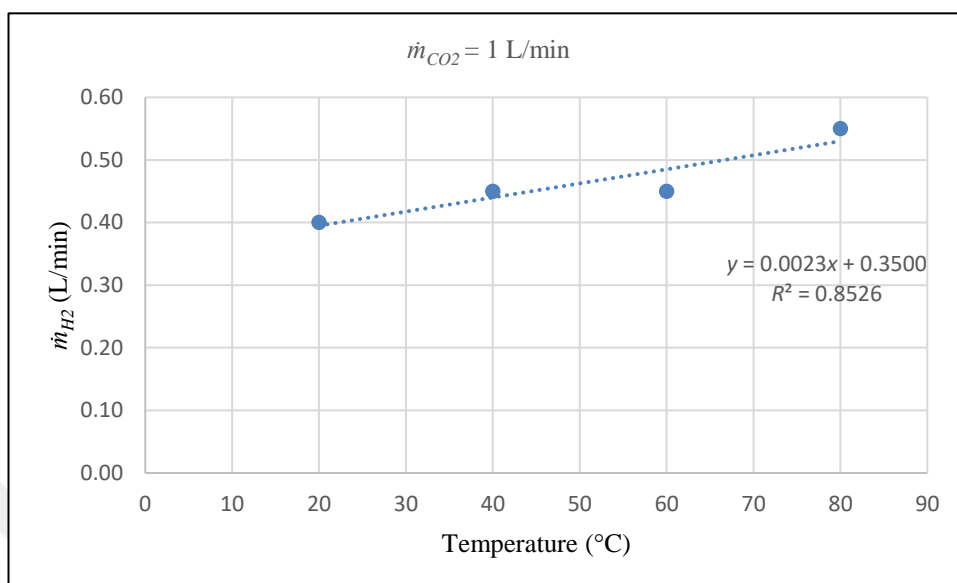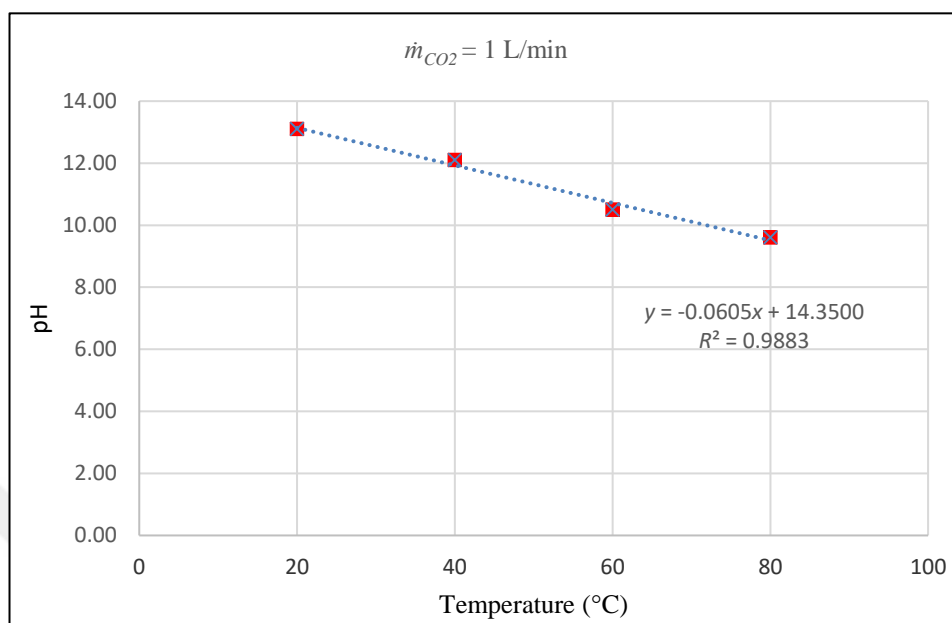

Figure 5.21 The pH value of solution – Temperature (1 g of $NaBH_4$, 5% KOH, $\dot{m}_{CO_2}$ = 1 L/min).
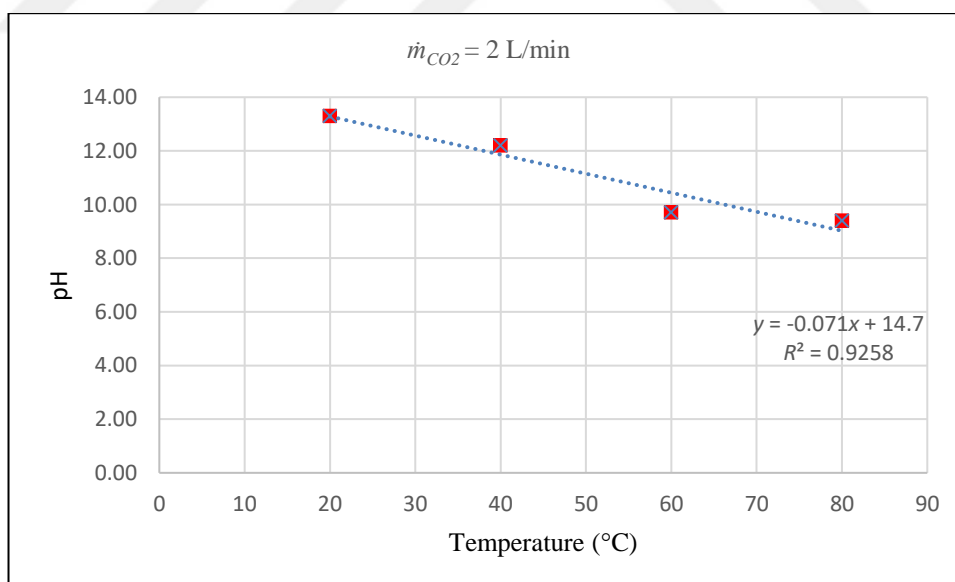
Figure 5.22 The pH value of solution – Temperature (1 g of $NaBH_4$, 15% KOH, $\dot{m}_{CO_2}$ = 2 L/min).

The comparison of some catalysts used to obtain hydrogen from the alkaline solutions of $NaBH_4$ and the hydrogen amounts obtained with CO_2 gas used as catalyst in the experiments at 60 °C are given in Table 5.3.

Table 5.3 Comparison of some catalysts used for hydrogen production at 60 °C.

Catalyst	Flow rate (L/min)	$NaBH_4$ (mass fraction %)	NaOH (mass fraction %)
Ni_3B (1 g)	1.30	10	5
Co_3B (1 g)	6.00	5	5
Ru (1 g)	18.60	5	5
CO_2 (1 L/min)	1.65	1.6	5 (KOH)
CO_2 (2 L/min)	1.80	1.6	5 (KOH)
CO_2 (3 L/min)	2.00	1.6	5 (KOH)

CHAPTER 6

CONCLUSION AND DISCUSSION

The main purpose of this study is; to obtain hydrogen from the aqueous alkaline solution of $NaBH_4$ without the use of expensive metal catalysts such as Ru, Pt, and Co, by changing the pH of the solution by supplying only CO_2 gas. In this study; the concentration of KOH in the solution, the temperature, the amount of $NaBH_4$, and volumetric flow rate of CO_2 gas were taken as variable.

CO_2 gas, known to have weak acidic character, could not very quickly lower the pH of the aqueous basic $NaBH_4$ solution, resulting in a controlled hydrogen production. If strong acids such as HCl were added directly to the solution, there was an uncontrollable violent outgassing.

The studies, in the literature, have been shown that when it is added by about 5-10% of H_2 to combustion engines using gasoline, diesel, LPG and CNG, fuel consumption and emissions reduce by about 7-15%.

In systems where internal combustion engines are used, it is assessed that the pH value of the solution can be changed by designing a system using $NaBH_4$ solution and CO_2 gas generated at the end of combustion. So that hydrogen can be produced without using expensive catalysts. CO_2 gas produced as a result of combustion can be sent to the solution at the time of need and a controlled hydrogen production can be achieved and the obtained hydrogen gas can be sent to the motor by this system. Thus, an increase in combustion efficiency and a reduction in fuel consumption and waste gas amount may be possible.

The use of such a system in the automotive industry is not yet economical because the price of the $NaBH_4$ compound is high. However, it is thought that this system can be applied to critical defense vehicles such as the Unmanned Aerial Vehicle (UAV) where the economy is the second plan, but flight time is very critical.

REFERENCES

[1]   International Energy Agency. *World Energy Outlook 2010*. Paris: IEA Publications. 2010

[2]   Lackner, K. S. *Comparative Impacts of Fossil Fuels and Alternative Energy Sources.* Cambridge: RSC Publishing. 2010

[3]   Enerji ve Tabii Kaynaklar Bakanlığı. İklim Değişikliği: Azaltım. Retrieved April 15, 2017, from http://www.eie.gov.tr/iklim_deg/azaltim.aspx. 2012

[4]   Shasby, B. M. Alternative Fuels: Incompletely Addressing the Problems of the Automobile. Unpublished master's thesis, Virginia Polytechnic Institute and State University. 2004

[5]   Roussière, T.L. Catalytic Reforming of Methane in the Presence of CO_2 and H_2O at High Pressure. Unpublished Ph.D. thesis, Karlsruher Institut für Technologie (KIT). 2013

[6]   Yaying J., Wenzhao L., Yanxin C., Chunying Y., Fengyun Y., & Hengyong X. Partial Oxidation of Methane with Air or O_2 and Steam to Synthesis Gas over a Ni-Based Catalyst. Journal of Natural Gas Chemistry, *Vol.9*, No.4, 291-303. 2000

[7]   Higman C., & Burgt, M. *Gasification.* United States of America: Gulf Professional Publishing. 2003

[8]   Federal Ministry for the Environment, Nature Conservation and Nuclear Safety. *Ecological, Economic and Structural Comparison of Renewable Energy Technologies* (*RE*) *with Carbon Capture and Storage* (*CCS*) *An Integrated Approach.* Wuppertal: Offset Company. 2008

[9] Dopp R. B. High Rate and High Efficiency Hydrogen Generation via Water Electrolysis Catalyzed by Nano Powders. Retrieved April 15, 2017, from http://www.grid-shift.com/white_papers/docs/3D_Water_Electrolysis_Abstract% 202.htm. May 2, 2010

[10] Agrafiotis C., Roeb M., Konstandopoulos A. G., Nalbandian L., Zaspalis V. T., Sattler C., et al. Solar Water Splitting for Hydrogen Production with Monolithic Reactors. Solar Energy, 79, 409-421. 2005

[11] Klebanoff L. *Hydrogen Storage Technology Materials and Applications*. Florida: CRC Press. 2013

[12] Hirscher M. *Handbook of Hydrogen Storage: New Materials for Future Energy Store*. Weinheim: Wiley-VCH. 2010

[13] Shelby J. E. Glass Microspheres for Hydrogen Storage. Retrieved April 17, 2017, from https://hydrogendoedev.nrel.gov/pdfs/review08/stp_27_shelby. pdf. April 18, 2008

[14] Züttel A., Nützenadel Ch., Sudan P., Mauron Ph., Emmenegger Ch., Rentsch S., et al. Hydrogen sorption by carbon nanotubes and other carbon nanostructures. Journal of Alloys and Compounds, 330-332, 676-682. 2002

[15] Sherif S. A., Barbir F., & Veziroğlu T. N. Principles of Hydrogen Energy Production, Storage and Utilization. Journal of Scientific & Industrial Research, 62, 46-63., 2003

[16] Sim J., & Kim T. Accelerated hydrolysis of solid-state $NaBH_4$ by injecting $NaHCO_3$ solution for hydrogen generation. Applied Energy, 160, 999-1006. 2015

[17] Aiello R., Sharp J. H., & Matthews M. A. Production of hydrogen from chemical hydrides via hydrolysis with steam. International Journal of Hydrogen Energy, 24, 1123-1130. 1999

[18] Marrero-Alfonso E. Y., Gray J. R., Davis T. A., & Matthews M. A. Hydrolysis of sodium borohydride with steam. International Journal of Hydrogen Energy, 32, 4717–4722. 2007

[19] Marrero-Alfonso E. Y., Gray J. R., Davis T. A., & Matthews M. A. Minimizing water utilization in hydrolysis of sodium borohydride: The role of sodium metaborate hydrates., International Journal of Hydrogen Energy, 32, 4723–4730. 2007

[20] Beiard, A. M., Davis, T. A., & Matthews M. A. Deliquescence in the hydrolysis of sodium borohydride by water vapor. Industrial & Engineering Chemistry Research, 49, 9596–9599. 2010

[21] Minkina V. G., Shabunya S. I., Kalinin V. I., Martynenko V. V., & Smirnova A. L. Stability of alkaline aqueous solutions of sodium borohydride. International Journal of Hydrogen Energy, 37, 3313–3318. 2012

[22] Akdim, O., Demirci, U. B., & Miele, P. Acetic acid, a relatively green single-use catalyst for hydrogen generation from sodium borohydride. International Journal of Hydrogen Energy, 36, 13669–13675. 2011

[23] Javed, U., & Subramanian, V. Hydrogen generation using a borohydride-based semi-continuous milli-scale rector: effects of physicochemical parameters on hydrogen yield. Energy & Fuels, 23, 408–413. 2008

[24] Prosini, P. P., & Gislon, P. A hydrogen refill for cellular phone. Journal of Power Sources, 161, 290–293., 2006

[25] Murugesan, S., & Subramanian, V. R. Effects of acid accelerators on hydrogen generation from solid sodium borohydride using small scale devices. Journal of Power Sources, 187, 216–223. 2009

[26] Liu, H., Boyd, C. M., Beaird, A. M., & Matthews, M. A. Vapor phase batch hydrolysis of $NaBH_4$ at elevated temperature and pressure. International Journal of Hydrogen Energy, 36, 6472–6477. 2011

[27] Amendola, S. C., Sharp-Goldman S. L., Janjua, M. S., Spencer, N. C., Kelly, M. T., Petillo, P. J. et al. A safe, portable, hydrogen gas generator using aqueous borohydride solution and Ru catalyst. International Journal of Hydrogen Energy, 25, 969–975. 2000

[28] Hua, D., Hanxi, Y., Xinping, A., & Chuansin, C. Hydrogen production from catalytic hydrolysis of sodium borohydride solution using nickel boride catalyst. International Journal of Hydrogen Energy, 28, 1095–100. 2003

[29] Ye, W., Zhang, H., Xu, D., Ma, L., & Yi, B. Hydrogen generation utilizing alkaline sodium borohydride solution and supported cobalt catalyst. Journal of Power Sources, 164, 544–548. 2007

[30] Ingersoll, J. C., Mani, N., Thenmozhiyal, J. C., & Muthaiah, A. Catalytic hydrolysis of sodium borohydride by a novel nickel-cobalt-boride catalyst. Journal of Power Sources, 173, 450–457. 2007

[31] Walter, J. C., Zurawski, A., Montgomery, D., Thornburg, M., & Revankar, S. Sodium borohydride hydrolysis kinetics comparison for nickel, cobalt, and ruthenium boride catalyst. Journal of Power Sources, 179, 335–339. 2008

[32] US Department of Energy. *Hydrogen & Our Energy Future.* United States: DOE/EE. 2015

[33] Ganesh H. R., Subramanian V., Balasubramanian V., Mallikarjuna J. M., Ramesh A., & Sharma R. P. Hydrogen fueled spark ignition engine with electronically controlled manifold injection: An experimental study. Journal of Renewable Energy, 33, 1324–1333. 2008

[34] Escalante Soberanis M. A., & Fernandez A. M. A review on the technical adaptations for internal combustion engines to operate with gas/hydrogen mixtures. International Journal of Hydrogen Energy, 28, 569–577. 2003

[35] Akansu S. O., Dulger Z., Kahraman N., & Veziroğlu T. N. Internal combustion engines fueled by natural gas-hydrogen mixtures. International Journal of Hydrogen Energy, 29, 1527–1539. 2004

[36] Bysveen M. Engine characteristics of emissions and performance using mixtures of natural gas and hydrogen. Journal of Energy, 32, 482–489. 2007

[37] Saravanan N. An experimental investigation on DI diesel engine with hydrogen fuel. Journal of Renewable Energy, 33, 415–421. 2008

[38] Greenwood J. B., Erickson P. A., Hwang J., & Jordan E. A. Experimental results of hydrogen enrichment of ethanol in an ultra-lean internal combustion engine. International Journal of Hydrogen Energy, 39, 12980–12990. 2014

[39] Worldwatch Institute. Making Better Energy Choices. Retrieved April 22, 2017, from http://www.worldwatch.org/node/808. 2016

[40] Çevre ve Orman Bakanlığı DSİ Genel Müdürlüğü. *Çevre ve Temiz Enerji: Hidroelektrik.* Ankara: MRK Matbaacılık. 2011

[41] British Petrolium. *BP Statistical World Review of Energy*. United Kingdom: Pureprint Group. 2014

[42] Dunlap R. A. *Sustainable Energy, SI Edition.*, Stamford: Cengage Learning. 2015

[43] Beşergil B. *Yakıtlar Yağlar*. Ankara: Gazi Kitabevi. 2014

[44] 123RF. Stock Photo–Hydrogen atom on white background. Retrieved April 22, 2017, from https://www.123rf.com/photo_24659997_hydrogen-atom-on-white-background.html. 2005

[45] Şahin M. *Hidrojen Enerjisi Teknolojileri*. Ankara: Anıl Matbaacılık. 2006

[46] Elemental Matter. Hydrogen Properties. Retrieved April 22, 2017, from http://www.elementalmatter.info/hydrogen-properties.htm. 2017

[47] Hofstra University. Energy Content of some Combustibles (in MJ/kg). Retrieved April 22, 2017, from https://people.hofstra.edu/geotrans/eng/ch8en/conc8en/energycontent.html. 2017

[48] National Academy of Sciences. *The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs*. Washington: The National Academies Press. 2004

[49] Şenaktaş B. Hidrojen Enerjisi, Üretimi ve Uygulamaları. Yayınlanmamış yüksek lisans tezi, Pamukkale Üniversitesi. 2005

[50] Kumar S. *Clean Hydrogen Production Methods.* Switzerland: Springer International Publishing. 2015

[51] Iaquaniello G., Antonetti E., Cucchiella B., Palo E., Salladini A., Guarinoni A., et al. *Natural Gas – Extraction to End Use*. Rijeka-Crotia: Intech. 2012

[52] Kıncay O., Ağustos H., & Akbulut U. Producing Hydrogen from Natural Gas by Thermal Methods. Journal of Engineering and Natural Sciences, *Vol: 26* Issue: 1, s. 1-17. 2008

[53] Air Liquide, "Gas POX – Natural Gas Partial Oxidation". Retrieved April 22, 2017, from https://www.engineering-airliquide.com/gas-pox-natural-gas-partial -oxidation. 2017

[54] Gasification & Syngas Technologies Council. The Gasification Process. Retrieved April 22, 2017, from http://gasification-syngas.org/technology/the-gasification-process/. 2017

[55] Mançuhan C. Yakma Yerine Neden Gazlaştırma. Su ve Çevre Teknolojileri Dergisi, Sayı: 6, s. 1-2. Ocak-Şubat 2006

[56] U.S. Department of Energy. How Coal Gasification Power Plants Work. Retrieved April 22, 2017, from https://energy.gov/fe/how-coal-gasification-power-plants-work. 2017

[57] Gaudernack B., & Lynum S. Hydrogen from Natural Gas without Release of CO_2 to the Atmosphere. International Journal of Hydrogen Energy, 23, 1087-1093. 1998

[58] Penn State University. Covalent Bonds. Retrieved April 22, 2017, from https://online.science.psu.edu/biol011_sandbox_7239/node/7333. 2017

[59] Arlı E. Suyun Hidrojen Bağı ve Özellikleri. Yayınlanmamış yüksek lisans tezi, Çukurova Üniversitesi. 2007

[60] Elektrik Rehberiniz. Suyun Elektrolizi. Retrieved April 22, 2017, from www.elektrikrehberiniz.com/elektrik/suyun-elektrolizi-5764. January 11, 2014

[61] Saylor Academy. General Chemistry: Principles, Patterns, and Applications. Retrieved April 23, 2017, from https://saylordotorg.github.io/text_general-chemistry-principles-patterns-and-applications-v1.0/s23-07-electrolysis.html. 2012

[62] Yıldızbilir F. Yakıt Pili ile Elektrik Enerjisi Üretimi. Yayınlanmamış yüksek lisans tezi, Fırat Üniversitesi. 2006

[63] Öztürk M., Elbir A., Özek N., & Yakut A. K. Güneş Hidrojen Üretim Metotlarının İncelenmesi. International Advanced Technologies Symposium (IATS'11), 16-18 May 2011, 231–237. 2011

[64] Dan H. Sulfur-Iodine Thermochemical Cycle for Hydrogen Production. Unpublished master's thesis, Central Ostrobothnia University of Applied Sciences. 2009

[65] Baş Ş. *Hidrojen Enerjisinin Yükselişi*. Ankara: T.C. Kalkınma Bakanlığı. 2013

[66] Krishna R., Titus E., Salimian M., Okhay O., Rajendran S., Rajkumar A., et al. *Hydrogen Storage for Energy Application.* Rijeka-Crotia: Intech. 2012

[67] Sanghai Y. S. Techno-Economic Analysis of Hydrogen Fuel Cell System Used as an Electricity Storage Technology in A Wind Farm with High Amounts of Intermittent Energy. Unpublished master's thesis, University of Massachusetts. 2013

[68] Kantürk A. Borakstan Sodyum Borhidrür Üretimi ve Üretimi Etkileyen Parametrelerin İncelenmesi. Yayınlanmamış yüksek lisans tezi, Yıldız Teknik Üniversitesi. 2006

[69] Türkmen Ü. Değişik Elektrotların (Fe, Fe/Ni, Fe/Ni-Zn, Fe/Ni-Al) Hidrojen Gazı Eldesine Etkilerinin Araştırılması. Yayınlanmamış yüksek lisans tezi, Çukurova Üniversitesi. 2006

[70] Çimen T. Sıvı Hidrojen Tanklarının Isıl Analizi ve Optimal Tasarımı. Yayınlanmamış yüksek lisans tezi, İstanbul Teknik Üniversitesi. 2006

[71] Gül K. E. Hidrojenin İçten Yanmalı Motorlarda Yakıt Olarak Kullanılması ve Performansa Etkileri. Yayınlanmamış yüksek lisans tezi, Yıldız Teknik Üniversitesi. 2006

[72] Karatepe N., Özyuğuran A., & Yavuz R. Karbon Yapılı Malzemelerin Hidrojen Depolanmasında Kullanımı. Dünya Enerji Konseyi Türk Milli Komitesi–Türkiye 10.Enerji Kongresi, 407–416. 2006

[73] Ajayan P. M., Charlier J. C., & Rinzler A. G. Carbon nanotubes: From macromolecules to nanotechnology. The Fifth Annual German-American Frontiers of Science Symposium, 14199–14200. 1999

[74] Atkinson K., Roth S., Hirscher M., & Grünwald W. Carbon nanostructures: An efficient hydrogen storage medium for fuel cells. Fuel Cells Bulletin, 38, 9–13. 2001

[75] Darkrim F. L., Malbrunot P., & and Tartaglia G. P. Review of hydrogen storage by adsorption in carbon nanotubes. International Journal of Hydrogen Energy, 27, 193-202. 2002

[76] Demirci Ü. B., & Miele P. *Boron Hydrides High Potential Hydrogen Storage Material*. Lyon: Nova Science Publishers. 2011

[77] Schlapbach L., & Züttel A., Hydrogen-storage materials for mobile applications. Nature (International Weekly Journal of Science), 414, 353-358. 2001

[78] Çakanyıldırım Ç., & Gürü M. Production of $NaBH_4$ and Hydrogen Release with Catalyst. Renewable Energy, 34, 2362-2365. 2009

[79] Yenialaca Ç. *Bor ve Kullanım Alanları*, Ankara: Gazi Üniversitesi. 2009

[80] Enerji ve Tabii Kaynaklar Bakanlığı. Hidrojen Üretimi. Retrieved April 24, 2017, from http://www.eie.gov.tr/teknoloji/h_uretimi.aspx. 2012

[81] Aslan Ö. Hidrojen Ekonomisine Doğru. İstanbul Ticaret Üniversitesi Sosyal Bilimler Dergisi, Yıl: 6 Sayı: 11, s. 283-298. Bahar 2007/2

[82] Demirci A. Elektroliz Yöntemi İle Elde Edilen Hidrojenin Dizel Motor Dolgusuna İlavesinin Performans ve Emisyonlara Etkisi. Yayınlanmamış yüksek lisans tezi, Marmara Üniversitesi. 2010

[83] Kahraman N., Akansu S. O., & Albayrak B. İçten Yanmalı Motorlarda Alternatif Yakıt Olarak Hidrojen Kullanılması. Mühendis ve Makina Dergisi, *Cilt: 48,* Sayı: 569, s. 9-15. 2007

[84] Karakış E. *Türkiye 2013 Yıllık Enerji İstatistikleri Raporu*. Ankara: Enerji İstatistikleri Daire Başkanlığı. 2014

[85] Demir M. The Relationship between Energy Import and Current Account Deficit: The Case of Turkey with Var Analysis. Journal of Academic Researches and Studies, 5, 9, s. 2-27. 2013

[86] Veziroğlu, T. N. *Karadeniz Dip Sularının Hidrojen Enerjisi Potansiyeli*. 5. Ulusal Temiz Enerji Sempozyumu. 2004

[87] Elektrik Mühendisleri Odası. Hidrojen Enerjisi ve Türkiye'deki Hidrojen Potansiyeli. Retrieved April 25, 2017, from http://www.emo.org.tr/ekler/ 51c5ffd6b62cc21 _ek.pdf. 2005

[88] Ulusal Bor Araştırma Enstitüsü. Bor-Rezervler. Retrieved April 26, 2017, from http://www.boren.gov.tr/tr/bor/bor-rezervleri. 2016

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