

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCE

**INVESTIGATION OF HYDROGEN
PRODUCTION FROM THE CATALYTIC
DEHYDROGENATION OF SOLID HYDROGEN
STORAGE MATERIALS THROUGH
EXPERIMENTAL AND MODELING STUDIES**

by
Ceren ALPAYDIN

August, 2021
İZMİR

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**A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
In Partial Fulfillment of the Requirements for the Degree of Doctor of
Philosophy in Mechanical Engineering, Thermodynamics Program**

**by
Ceren ALPAYDIN**

**August, 2021
İZMİR**

Ph.D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “**INVESTIGATION OF HYDROGEN PRODUCTION FROM THE CATALYTIC DEHYDROGENATION OF SOLID HYDROGEN STORAGE MATERIALS THROUGH EXPERIMENTAL AND MODELING STUDIES**” completed by **CEREN ALPAYDIN** under supervision of **PROF. DR. CAN ÖZGÜR ÇOLPAN** and **ASSOC. PROF. DR. SENEM KARAHAN GÜLBAY** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

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INVESTIGATION OF HYDROGEN PRODUCTION FROM THE CATALYTIC DEHYDROGENATION OF SOLID HYDROGEN STORAGE MATERIALS THROUGH EXPERIMENTAL AND MODELING STUDIES

ABSTRACT

For the transition to hydrogen economy, the challenges of producing hydrogen in a clean and efficient manner, as well as storage, must be resolved. Since solid hydrogen storage materials are lightweight materials containing high amounts of hydrogen by weight, they can store hydrogen safely and can be an alternative way for clean hydrogen production.

This thesis focuses on the experimental and numerical investigation of hydrogen production from solid hydrogen storage materials and the economic and environmental evaluations for hydrogen-powered vehicles. In the experimental part of the thesis, firstly, PSSA stabilized PdAg catalyst was synthesized for hydrogen production from morpholine borane, and kinetic studies were carried out. Then, the initial TOF value was calculated, and the reusability of the catalyst was investigated.

In the numerical part of the thesis, three-dimensional modeling of batch and continuous reactors that can be used for hydrogen production from solid hydrogen storage materials in Comsol environment is given. In addition, a MATLAB Simulink model of a fuel cell vehicle with two different hydrogen storage, a sodium borohydride-based hydrogen storage system and a compressed gas hydrogen tank, was developed. Finally, fuel cell vehicles with sodium borohydride-based hydrogen storage system and compressed gas tank were examined economically and environmentally using the AFLEET tool and compared with a conventional internal combustion engine vehicle using gasoline as fuel in terms of total cost of ownership and environmental effects.

Keywords: Solid hydrogen storage materials, catalytic hydrolysis, fuel cell vehicles, mathematical modeling, economic evaluation, environmental analysis

KATI HİDROJEN DEPOLAMA MALZEMELERİNİN KATALİTİK DEHİDROJENLENMESİ YOLUYLA HİDROJEN ÜRETİMİNİN MODELLENMESİ VE DENEYSEL İNCELENMESİ

ÖZ

Hidrojen ekonomisine geçiş için, hidrojenin temiz ve verimli bir şekilde üretilmesinin yanı sıra depolama konusundaki zorluklar da çözülmelidir. Katı hidrojen depolama malzemeleri, ağırlıkça yüksek miktarda hidrojen içeren hafif malzemeler olduğu için hidrojeni güvenli bir şekilde depolayabilir ve temiz hidrojen üretimi için alternatif bir yol olabilir.

Bu tez, katı hidrojen depolama malzemelerinden hidrojen üretiminin deneysel ve sayısal olarak araştırılmasına ve hidrojen kullanan araçlar için ekonomik ve çevresel değerlendirme yapılmasına odaklanmaktadır. Tezin deneysel kısmında ilk olarak morfolin borandan hidrojen üretimi için PSSA ile stabilize edilmiş PdAg katalizörü sentezlenmiş, ve kinetik çalışmalar yapılmıştır. Daha sonra başlangıç TOF değeri hesaplanmış ve katalizörün yeniden kullanılabilirliği incelenmiştir.

Tezin sayısal kısmında ise Comsol ortamında katı hidrojen depolama malzemelerinden hidrojen üretimi için kullanılabilecek kesikli ve sürekli reaktörlerin üç boyutlu modellenmesine yer verilmiştir. Ek olarak sodyum borhidrür temelli bir hidrojen depolama sistemi ve sıkıştırılmış gaz hidrojen tankı olmak üzere iki farklı hidrojen deposu bulunduran yakıt pilli bir aracın MATLAB Simulink modeli geliştirilmiştir. Son olarak sodyum borhidrür temelli hidrojen depolama sistemi ve sıkıştırılmış gaz tankı bulunduran yakıt pilli araçlar AFLEET aracı kullanılarak ekonomik ve çevresel açıdan incelenmiş, yakıt olarak benzin kullanan geleneksel içten yanmalı motorlu araç ile toplam sahip olma maliyeti ve çevresel etkiler açısından karşılaştırılmıştır.

Anahtar kelimeler: Katı hidrojen depolama malzemeleri, katalitik hidroliz, yakıt pilli araçlar, matematiksel modelleme, ekonomik değerlendirme, çevresel analiz

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CHAPTER ONE

INTRODUCTION

1.1 Introduction

Fossil fuels are the most widely used resources to meet global energy needs today. Along with the increase in energy demand, fossil resources are gradually running out. In addition to the fact that fossil fuels have limited resources, fossil fuel utilization brings about many problems such as air pollution, water pollution, global warming, and detrimental effects on human and animal health (Veziroglu, 1987). These problems have reached serious dimensions today, and it is necessary to have permanent solutions to meet the energy demand sustainably. For this reason, efforts to use alternative energy resources (e.g., solar, wind, nuclear, hydrogen) have been accelerated in order to obtain clean energy. Unlike some intermittent energy resources such as solar and wind, hydrogen can be used to generate electricity continuously; and unlike nuclear, it has much fewer environmental issues if clean production methods are applied (Moury et al., 2012). Safe and environmentally friendly production of hydrogen is vital in the transition to hydrogen technologies. In addition to the efficient production of hydrogen, its proper storage is also important for the transition to hydrogen technologies. Since hydrogen is a low-density gas and much lighter than air, there are some difficulties in its storage. The physical methods used to store hydrogen are compressed gas, liquid and cryo-compressed storage. Hydrogen can be also chemically stored in metal hydrides and chemical hydrides (Rivard, Trudeau, & Zaghib, 2019).

In chemical hydrides, also called solid hydrogen storage materials, hydrogen can be safely stored at room temperature and ambient pressure. These materials undergo hydrolysis in the presence of a catalyst to release hydrogen. As a result of the hydrolysis hydrogen and by-products that are completely harmless to the environment are obtained. Borohydride salts, ammonia borane, and hydrazine borane

are frequently studied solid hydrogen storage materials, and new materials such as morpholine borane are also being investigated for clean hydrogen production.

Enabling the use of hydrogen in the transportation sector, which provides a substantial portion of greenhouse gas emissions, is an important step in preventing environmental damage. In this context, hydrogen-powered fuel cell vehicles (FCV) have become very attractive in the last decade. Several research studies have been done on the technical challenges of FCVs, modeling of FCV components and improving their performance, investigation hydrogen storages on FCVs and hydrogen supply infrastructure, modeling various powertrain configurations and energy management systems, and performing driving cycle simulations.

1.2 Motivation

Although there are many experimental studies in the literature for the production of hydrogen from solid hydrogen storage materials, most of these studies have focused on sodium borohydride, ammonia borane, or dimethylamine borane. One of the motivations of this thesis is that there is only one publication in the literature on hydrogen production from morpholine borane, which was examined experimentally within the scope of this thesis, and that more research is needed to disseminate this material as a hydrogen storage material.

Until now, mathematical studies on the use of hydrogen in fuel cell vehicles have been carried out, but the lack of a comparative study of a boron compound-based hydrogen storage system with a compressed gas tank in terms of vehicle range is another motivation of this thesis.

There are studies in the literature on the economic and environmental analysis of various hydrogen production processes, but the lack of a comparative evaluation of a vehicle using solid hydrogen storage material based hydrogen with a vehicle using compressed gas hydrogen tank or gasoline is another motivation.

1.3 Objectives

The objectives of this thesis were:

- To synthesize a unique catalyst for hydrogen production through dehydrogenation reaction of $C_4H_{12}BNO$.
- To determine the reaction order of $C_4H_{12}BNO$ hydrolysis reaction according to the catalyst and substrate by performing experiments with different substrate and catalyst concentrations.
- To calculate enthalpy and activation energy of the $C_4H_{12}BNO$ hydrolysis reaction.
- To determine catalytic activity and reusability of the synthesized catalyst during 10 cycles.
- To develop a numerical model of a batch reactor that can be used to produce hydrogen from solid hydrogen storage materials in Comsol Multiphysics environment.
- To compare a solid hydrogen storage material based hydrogen storage system and a compressed gas hydrogen storage system through fuel cell vehicle simulation in the Matlab Simulink environment.
- To perform economic and environmental analysis for a fuel cell vehicle with a solid hydrogen storage material based hydrogen storage system and to compare it with a fuel cell vehicle which having a compressed gas tank.

1.4 Thesis Outline

The content of this thesis is to investigate the production of hydrogen from solid hydrogen storage materials, both experimentally and numerically, and to investigate the availability of solid hydrogen storage materials-based hydrogen storage systems for

fuel cell vehicles. The following chapter provides a summary of the relevant background and literature review.

In the third chapter, the experimental method for hydrogen production from $C_4H_{12}BNO$ is described and the experimental results are shared. First, a comparison of hydrogen production performances of three different PSSA stabilized bimetallic Pd-based catalysts and monometallic Pd are presented. Secondly, optimization of PSSA amount and metal ratios for the PSSA stabilized PdAg, which is the most active among synthesized catalysts, is given. Finally, the results of the kinetic experiments with the optimized catalyst and the reusability of the catalyst are included.

The fourth chapter declares the Comsol Multiphysics model of a batch and continuous reactors that can be used to produce hydrogen from solid hydrogen storage materials. Firstly, the governing equations and boundary conditions are outlined, and then the results are given.

Chapter five includes the Matlab Simulink model of a fuel cell vehicle with a solid hydrogen storage material-based hydrogen storage system. A comparison of the performance of this storage system compared with a compressed gas tank is presented in terms of vehicle range in this chapter.

The sixth chapter was devoted to an economic and environmental analysis of a fuel cell vehicle with solid hydrogen storage materials-based hydrogen storage system.

The seventh chapter contains the conclusions derived from this thesis and potential future research targets.

CHAPTER TWO

BACKGROUND AND LITERATURE REVIEW

2.1 Hydrogen Production and Storage Methods

Today, the vast majority of hydrogen is produced by steam reforming, partial oxidation or gasification processes of fossil fuels (Conte et al., 2001). An overview of the conventional hydrogen production methods is given in Figure 2.1. In the steam reforming of natural gas, steam and natural gas react at high temperatures (700-1100°C), and hydrogen (H_2), carbon dioxide (CO_2) and carbon monoxide (CO) are obtained. Water-gas shift reaction, in which CO reacts with $H_2O_{(v)}$ to produce H_2 and CO_2 , occurs simultaneously with the reforming reaction. Hydrogen can also be produced by the gasification of coal or biomass. In the gasification process, the coal reacts with steam, air or oxygen. As a result of this reaction, various gases such as CO, CO_2 , H_2 , $H_2O_{(v)}$ and CH_4 are released, and a residue in the form of ash or molten slag is accumulated, depending on the gasifier system (Vamvuka, 2000). Electrolysis, in which water is separated into hydrogen and oxygen by using electricity, is another method for generating hydrogen. For this process, there has been an increasing interest in using electricity obtained from renewable energy technologies such as photovoltaic panels and wind turbines (Conte et al., 2001).

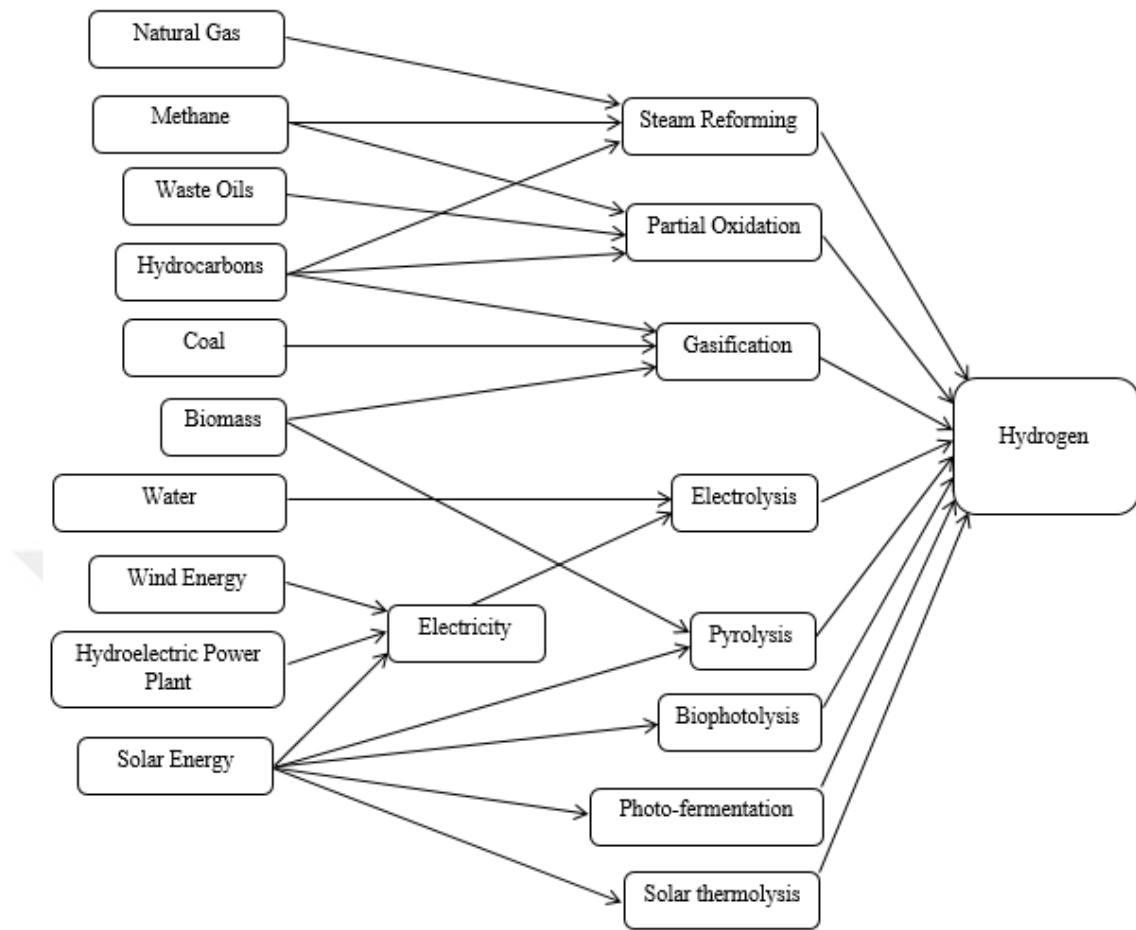


Figure 2.1 Different hydrogen production technologies

The most widely used method is to store hydrogen as compressed gas at high pressures in high-strength tanks (Manoharan et al., 2019). The efficiency of this method is relatively high and does not require a complex thermal management system, but the cost of storage tanks is high (Li et al., 2019). These storage tanks can generally be pressurized up to 250, 300 and 700 bar. The energy required to compress hydrogen to 700 bar varies between 5% and 20% of the lower heating value of hydrogen (Gardiner, 2009). In addition, considering that the gases heat up when compressed, the hydrogen needs to be cooled previously in order to prevent the tank from overheating (Gye et al., 2019). Therefore, since some energy is required for the pre-cooling of hydrogen, the overall efficiency decreases.

Hydrogen can be stored as a liquid at -259.2°C , when it stores as a liquid 1 liter of hydrogen is only 71.37×10^{-3} kg (Manoharan et al., 2019). Although this low weight is an advantage for reducing the size of the storage system, it is a disadvantage that about 35-40% of the energy content of the fuel is used to liquefy the hydrogen (Durbin & Malardier-Jugroot, 2013). The most important disadvantage of liquid hydrogen storage is the boiling problem (Durbin & Malardier-Jugroot, 2013). To keep the hydrogen liquid, heat transfer must be minimized, which requires a very thick layer of insulation, thus increasing the storage cost. However, since there will be no perfect insulation, there will be heat transfer from the environment to the liquid and therefore the pressure inside the tank will increase. Some hydrogen release must be allowed as the tank is not designed to hold a pressurized gas (Xu, Li, & Huang, 2015). The process of releasing hydrogen through a relief valve is called boiling. An unused reservoir of liquid hydrogen will eventually self-deplete due to boiling.

Compression of hydrogen by cooling is considered a hybrid method combining compressed gas and liquid hydrogen storage methods (Moreno-Blanco et al., 2019a). According to Gay Lussac's gas law, the volume of an ideal gas kept at constant pressure is proportional to the temperature, in other words, if the temperature drops by 1 K, the volume of an ideal gas will decrease by $1/273.15$. This relationship is also valid for real gases. Based on this principle, hydrogen is first cooled to temperatures close to the critical temperature, and the cooled hydrogen is then compressed. The storage tank must be designed to hold cryogenic hydrogen and withstand internal pressure. Compared to gas storage at 700 bar pressure, the need for high-strength material for cryo-compressed storage is less (Reed & Golda, 1994). Cryo-compressed hydrogen storage is a relatively new technology and is still in the R&D stage.

The storage of hydrogen in metal hydrides is based on chemical adsorption; the hydrogen molecule attaches to the metal surface, and elemental hydrogen is taken into the metal cage with heat release. To have a high amount of hydrogen flow rate, the appropriate amount of heat should be supplied to the metal hydride canister externally (Baetcke & Kaltschmitt, 2018). The advantages of metal hydride storage

systems are that they can operate at ambient pressure and allow storage at ambient temperature in the absence of hydrogen demand, very low probability of undesired hydrogen release, and relatively high volumetric energy density. The most important disadvantages are that the storage tanks are heavy due to the low gravimetric energy density, some metal hydrides require very high temperatures, and the absorption-release process of hydrogen is slow.

Apart from metal hydrides, hydrogen can be stored in solid form in metal organic frameworks, carbon nanotubes, and boron compounds. Metal organic frameworks are crystalline solids composed of metal ions connected by molecular bridges (Durbin & Malardier-Jugroot, 2013). They have attracted attention because they are very porous materials with large pore volume, but they are in the R&D stage due to difficulties such as requiring a low temperature of 77 K to store hydrogen, operating temperature in the range of 233-333 K, and low hydrogen storage capacity (Abdalla et al., 2018). Hydrogen storage in carbon nanotubes, which are known as good absorbers for gases, has also been investigated, but these materials are also in the R&D process because they do not allow storing high amounts of hydrogen without modification and are expensive (Rashidi et al., 2010). Hydrogen can be safely stored at room temperature and pressure in chemical hydrides. These materials undergo hydrolysis in the presence of a catalyst to release hydrogen. The advantages and disadvantages of hydrogen storage methods as well as ongoing R&D activities are given in Table 2.1.

Table 2.1 A comparison of the main hydrogen storage technologies

	Advantages	Disadvantages	Main ongoing R&D Activities
Compressed Gas	• Commercially available, mature technology • Favorable for long-term operations • Rapid refueling • Provides room temperature storage	• Low volumetric energy density • Requires energy for the compression process • Safety problems • Expensive storage vessels	• Developing low cost vessels (O'Malley et al., 2015) • Cost-effective development of multistage compressors required to compress hydrogen (Preuster, Alekseev, & Wasserscheid, 2017) • Minimizing the energy loss in the intercooling process required during the compression (Preuster, Alekseev, & Wasserscheid, 2017)

Table 2.1 continues

Liquid	• High volumetric capacity • Smaller and lighter vessel • Suitable for long range operation of a vehicle	• Hydrogen loss due to boiling • Requires energy for liquefaction process • Requires thermal management to reduce boiling • Safety problems in dormancy	• Development of insulation materials that can overcome boiling problems (Moradi & Groth, 2019) • Development of lighter and stronger composite tanks • Reducing the energy loss and cost of the process during the liquefaction (Niaz, Manzoor, & Pandith, 2015)
Cryo-compressed	• High volumetric capacity • Less hydrogen loss in dormancy according to compressed gas and liquid storage • Longer range	• Requires energy for compression and liquefaction process • Expensive storage vessels	• Developing low-cost vessels and determining vacuum quality (Aceves et al., 2011; Ahluwalia, Peng, & Hua, 2011) • Improving Well-to-Tank (WTT) efficiency (Ahluwalia, Peng, & Hua, 2011) • Increasing availability of infrastructure and reducing its cost (Moradi & Groth, 2019)
Metal Hydride	• Safe due to comparatively low operating pressure • Provides hydrogen production with high purity	• Heavy storage materials • Low gravimetric capacity • Requires thermal management • Needs high operating temperature to discharge high flow rate of hydrogen	• Improving hydrogen adsorption/desorption kinetics (Rusman & Dahari, 2016; Ren et al., 2017) • Developing new materials that allow hydrogen storage at low temperatures (Rusman & Dahari, 2016; Ren et al., 2017) • Preventing unwanted gas formation during the desorption process (Ren et al., 2017)
Chemical Hydride	• Provides hydrogen production at room temperature and ambient pressure • Safer as not containing high pressure equipment and no releasing toxic substances • Lighter storage materials • Ability to store more hydrogen per unit mass and volume compared to physical storage	• Expensive catalysts • Does not allow refueling on board	• Improving low-cost catalysts and hydrogen storage materials (Klebanoff et al., 2014; O'Malley et al., 2015) • Tackling challenges such as refilling and cycle life of the material and catalyst (O'Malley et al., 2015) • Performing life cycle cost analysis of the system (O'Malley et al., 2015) • System modeling, design, and performance studies (Klebanoff et al., 2014; O'Malley et al., 2015)

A summary of the recent studies on the modeling of hydrogen storage technologies found in the literature is given in Table 2.2. In these studies, mostly zero-dimensional modeling approach were used. The analyses were done using

simple engineering equations and establishing mass and energy balances. 1D, 2D and 3D models were mostly used in these studies to obtain more accurate results compared to 0D models and to examine the effects of design (e.g., insulation thickness), material type (e.g. Type III and IV hydrogen tanks) and operating conditions (e.g. constant or variable outflow temperature) on the temperature variations and hydrogen discharge behavior.

Table 2.2 Recent studies on the mathematical modeling of hydrogen storage technologies

	Authors	Modeling approach	Analyzed component(s)	Focus of the work	Results
Compressed Gas	Xiao, Bénard, & Chahine, 2016	0D	High pressure tank	To provide analytical solution for the temperature and pressure variations during cycle	The numerical solutions are very close to the analytical predictions with maximum errors in the order of 10^{-15} kg, 10^{-8} MPa and 10^{-6} K.
	Li et al., 2019	0D	Type III and Type IV storage tanks	To develop a single zone and dual zone thermodynamic models to examine the temperature variations	While the results for Case 1 (constant inflow and outflow temperature) and Case 3 (constant inflow, variable outflow temperature) were similar, higher temperature and pressure values were found for Case 2 (variable inflow and outflow temperature).
	Chen et al., 2019	0D	High pressure storage tank and a pressure regulator	To develop a pressure regulator model to examine the H₂ discharge behaviors	- H₂ temperature increases due to Joule-Thomson effect. - The strongest effect in increasing the H₂ outlet temperature is the regulator inlet temperature, the secondary effect is the regulator inlet pressure.
	Guo et al., 2014	1D	High pressure tank	- To simulate the thermal behavior of the tank - To examine the effect of various parameters on the temperature change	- Temperature increases linearly with the ambient temperature and the refueling gas temperature - Temperature remains constant after 10 cycles
	Yersak et al., 2017	1D	The polymer liner of the high-pressure tank	To model the plastic liner blistering during the discharging of type IV tanks	- Polyamide has a better blistering resistance than high-density polyethylene. 3 mm thick polyamide liner can resist blistering for 3 h of depressurization period.

Table 2.2 continues

	Authors	Modeling approach	Analyzed component(s)	Focus of the work	Results
Compressed Gas	Hua, Roh, & Ahluwalia, 2017	2D	Type IV storage tank	- To evaluate the impact of material and design changes for storage tanks - To provide a model for reducing the composite weight of conventional tanks	- Replacing the epoxy composite with a low-cost vinyl ester resin reduces the tank weight. - Replacing carbon fiber with glass fiber for the first helical layer could reduce the carbon fiber amount by 2–5%.
	Gangloff et al., 2017	3D	Type IV storage tank	- To model the H₂ storage system for a fuel cell electric truck analytically - To provide a basis for cost analyses for sizing the storage tank	The average fuel economy for FC electric trucks could vary between 5 and 25 miles/kg of hydrogen under real world driving conditions depending on the vehicle weight class and the mission.
Liquid Hydrogen	Winnefeld et al., 2018	0D	Liquid H ₂ storage tank	To perform mechanical and thermal analyses for a liquid H₂ storage tank in an aircraft	- The required H₂ mass for ventilation must be taken into account when calculating the fuel weight. - The required H₂ mass has a maximum share of the total system mass of nearly 70%.
	Stroman et al., 2014	1D	Liquid H ₂ storage system and an unmanned aerial vehicle	To examine a liquid H₂ storage system for unmanned aerial vehicles	- Liquid H₂ offers greater flight endurance than gas stored at pressures up to 34.5 MPa. - Low heat leak is achieved by the Dewar design and multilayer insulation. - Continuous fuel consumption eliminates conduction heat leak through fuel line.
Cryo-compressed Hydrogen	Moreno-Blanco et al., 2019	0D	Cryo-compressed storage tank and driving cycle	To determine cryo-compressed storage performance in terms of system storage density, system weight, and vent losses	250–350 bar is the most suitable storage pressure for cryo-compressed storage due to its low composite mass and high system density. - In storage tanks designed for pressures of 350 bar and above, H₂ is not lost when the vehicle is driven for 10 km/day or more.
	Yanxing et al., 2019	0D	Compression, refrigeration and storage unit	To examine the storage density and power consumption with thermodynamic analysis	- The recommended parameters for H₂ storage are at 35–110 K and 5–70 MPa regardless of ortho to para H₂ conversion. - The electrical energy consumption consists of compression and cooling down processes from 0.1 MPa at 300 K to the optimal states.

Table 2.2 continues

	Authors	Modeling approach	Analyzed component(s)	Focus of the work	Results
Cryo-compressed Hydrogen	Markert, Melideo, & Baraldi, 2014	3D	Cryo-compressed storage tank	To model the release of cryogenic compressed hydrogen at 200 K	- Excellent agreements are found with previous findings in the literature at ambient conditions using the ideal gas equation of state (EOS). - Real gas EOS, Peng–Robinson, and Beattie-Bridgeman gave good agreement with the former studies in the literature for the pressure drop and mass release rates. - The vessel pressure and the release rates decrease much faster with real gas EOS approximation compared to the ideal gas.
	Ahluwalia et al., 2018	3D	Cryo-compressed storage tank	- To examine the metal liner fatigue in Type 3 tanks at cryogenic temperatures - To investigate loss-free dormancy on the FC electric bus and light duty vehicle cycles	- Steel liners offer better performance than aluminum liners for Type 3 tanks. - A storage pressure of more than 500 bars is required for 7 days of dormancy. - Cryo-compressed H₂ storage saves over 20% in total cost.
Metal Hydride	Xiao et al., 2020	0D	Metal hydride H ₂ storage system	To develop a lumped parameter numerical model and obtain analytical solutions for hydriding, dormancy and dehydriding processes	- The pressure and the gaseous hydrogen mass in the metal hydride reactor are related to the source term. - The numerical model with variable source term shows better performance than that with constant source term.
	Chabane et al., 2019	0D	Metal hydride tank and PEMFC	To develop a numerical model for the heat and mass transfer in the PEMFC with a metal hydride tank	- Approximately 20% of the total heat produced by the FC should be transferred to metal hydride tank to maintain the temperature of the tank at 21°C. - The total mass of H₂ released from the hydride is about 145 g during the 31 h discharge period and the maximum H₂ production rate is 4 NL/min.
	Zhu et al., 2019	0D	Metal hydride tank and PEMFC	To integrate the thermal control of metal hydride tank into the energy management of the FC system	In the 1000 h steady-state operation, the output power of the FC was maintained by supplying excess hydrogen from metal hydride, and although the increased hydrogen consumption accelerated the capacity decline of the metal hydride tanks, the decline in fuel efficiency was reduced by 3% and fuel economy was saved by 10%.

Table 2.2 continues

	Authors	Modeling approach	Analyzed component(s)	Focus of the work	Results
Metal Hydride	Brooks et al., 2020	1D	Metal hydride H ₂ storage system	To develop a design tool for the estimation of the system parameters required to run the metal hydride storage system model	- The material physical properties such as bulk density and thermal conductivity can impact the overall system mass and volume. - It was estimated that the designed metal hydride tank could provide 5.4 kg of usable hydrogen for the US06 drive cycle.
	Baricco et al., 2017	2D	Metal hydride H ₂ storage system	To develop a mixed lithium amide/magnesium hydride system and integrate it with a FC stack installed in a light duty commercial vehicle	- The H₂ tank based on complex hydrides can be suitably used to feed a PEMFC, powering a 1 kW APU. - The storage system should be composed by twelve cylindrical vessels connected in parallel for the improvement of the heat transfer.
Chemical Hydride	Brooks et al., 2018	0-D	H ₂ generation system	- To develop a design tool to estimate the system parameters required to run the chemical hydride storage system model - To compare the performance of ammonia borane and alane, in terms of onboard efficiency and vehicle range	- Ammonia borane is more advantageous than alane for this system. - Some of the H₂ produced due to the endothermic alane reaction was used to maintain the reaction temperature, and therefore onboard efficiency and vehicle range decreased.
	Wang and Fang, 2017	0-D	PEMFC, battery set, solar cells, H ₂ generation module	To develop a hybrid PEMFC electric vehicle consisting of a 3 kW PEMFC, PV arrays, secondary battery sets, and a chemical hydrogen generation system	- The current power system can sustain vehicle travel around the National Taiwan University campus with H₂ generated from sodium borohydride. - The designed system has a drawback as the by-product (NaBO₂) needs to be collected and recycled.
	Li & Wang, 2016	0-D	PEMFC, H ₂ generation system, heat exchanger, and control module	To develop an on-demand H₂ generation system, which can produce H₂ from sodium borohydride solution, to operate PEMFC	- The system reaches its highest efficiency with 400 ml sodium borohydride solution of 15% by weight. - The H₂ generation system can hydrolyze sodium borohydride with a conversion rate of more than 90%.

Table 2.2 continues

	Authors	Modeling approach	Analyzed component(s)	Focus of the work	Results
Chemical Hydride	Xia et al., 2014	0-D	Portable H ₂ generator	• To develop a portable H₂ generator with a high H₂ storage capacity	• The H₂ generator can stably provide H₂ on demand to a 20 W fuel cell. • A gravimetric H₂ storage capacity of 3.88 wt.% was achieved. • The innovative design of H₂ generator has successfully prevented the clumping of a large quantity of the solid fuel.

The flow charts for the mathematical modeling of hydrogen storage methods are given in Figure 2.2. For compressed and cryogenic storage methods, mechanical analysis, energy balance, and mass balance should be applied consecutively (Xiao, Bénard, & Chahine, 2016; Gangloff et al., 2017; Ahluwalia et al., 2018). For metal hydrides, the equilibrium temperature at the maximum tank pressure must be determined first and then the equipment must be sized according to the method used for the thermal management of the metal hydride (Mohammadshahi, Gray, & Webb, 2016). Since endothermic and exothermic reactions take place during the absorption and desorption process in metal hydride hydrogen storage systems, the reaction rate is greatly affected by the temperature of the system and therefore it is important to establish a heat balance (Mohammadshahi, Gray, & Webb, 2016). In addition, the mass balance should be included in the model to examine the change in hydrogen concentration with time in the metal hydride bed (Mohammadshahi, Gray, & Webb, 2016). For chemical hydrides, reactor and fuel tank sizing should be done first. Then, since the hydrogen production rate is affected by the reaction kinetics, the reaction rate expression should be derived and the temperature-dependent reaction kinetics should be examined by considering the effect of exothermic reaction conditions. Finally, a mass balance must be established in order to obtain the amount of hydrogen produced and chemical hydride consumed (Pinto et al., 2013).

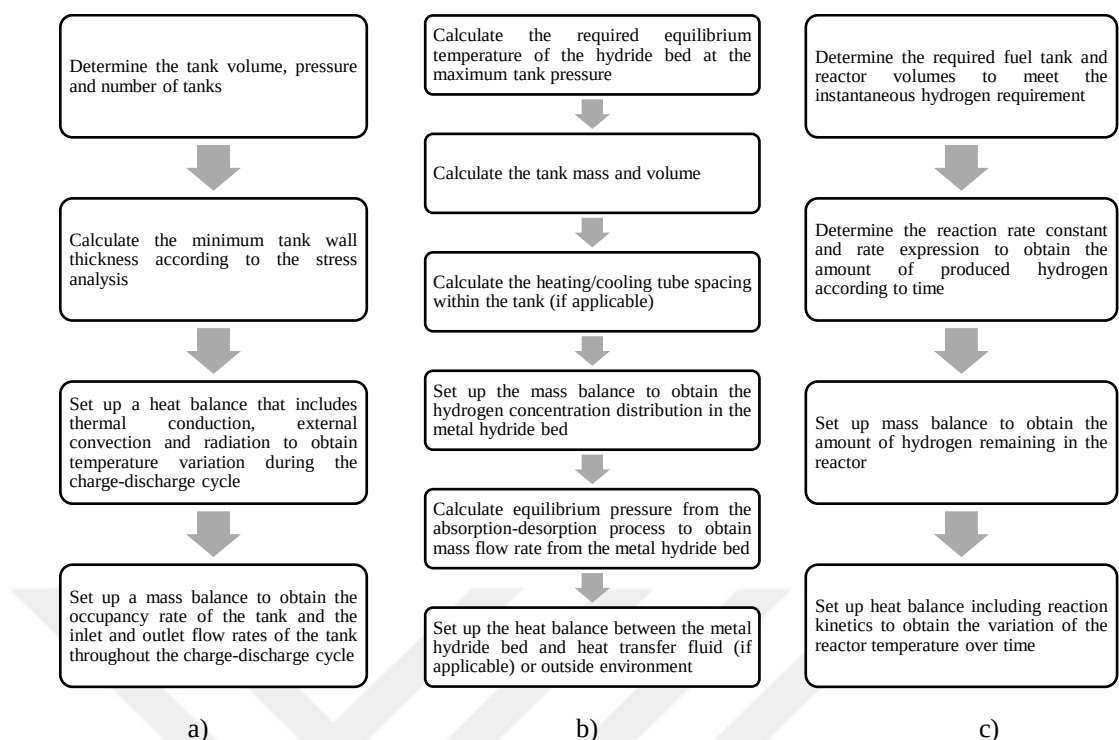


Figure 2.2 The flowcharts for mathematical modeling of different hydrogen storages a) compressed and cryogenic storage methods, b) metal hydrides, and c) chemical hydrides

2.2 Hydrogen Storage in Chemical Hydrides

Chemical hydrides, which are also known as solid hydrogen storage materials, contain a large number of hydrogen atoms and can be easily hydrolyzed at room temperature in the presence of a catalyst (Lai et al., 2015). As a result of the hydrolysis reaction, high amounts of hydrogen gas and by-products (e.g., H_3BO_3 , NaBO_2 , BO_2) which are entirely harmless to the environment are released (Chen et al., 2018). Due to these properties, it can be said that chemical hydrides are much more advantageous than other materials for storing solid hydrogen. Most tested chemical hydrides for hydrogen production are borohydride salts (e.g., LiBH_4 , KBH_4 , NaBH_4 , CaBH_4 , and AlBH_4), ammonia borane (NH_3BH_3), and hydrazine borane ($\text{N}_2\text{H}_4\text{BH}_3$) (Jepsen et al., 2014). Theoretically, using LiBH_4 yields better results than NaBH_4 in terms of H_2 production due to the lightness of Li (6.94 g mol^{-1}) and its high gravimetric H_2 concentration (18.5% by weight) (Demirci, 2018). However, Aiello et al. (Aiello, Sharp, & Matthews, 1999) reported that LiBH_4 is not suitable for the large-scale hydrogen production since less than 60% substrate conversion can

be achieved; and byproducts and unreacted LiBH_4 form a solid mass which is difficult to be removed from the inside of the reactor. KBH_4 is heavier than LiBH_4 and NaBH_4 , and has a low gravimetric hydrogen storage capacity (7.5% by weight). Because of these properties, it is more unfavorable than NaBH_4 for hydrogen production (Demirci, 2018). $\text{N}_2\text{H}_4\text{BH}_3$ contains 15.4 wt% H_2 , but there are disadvantages such as the release of large amounts of hydrazine and the creation of unwanted residues during hydrolysis of the $\text{N}_2\text{H}_4\text{BH}_3$ (Demirci, 2018). In addition, NH_3BH_3 is better than $\text{N}_2\text{H}_4\text{BH}_3$ due to a higher hydrogen density in weight basis. The more attractive materials in this category over the last two decades have been NaBH_4 and NH_3BH_3 and new materials such as morpholine borane ($\text{C}_4\text{H}_{12}\text{BNO}$) are also being investigated.

Hydrolysis is an attractive method for obtaining hydrogen from chemical hydrides because the reaction can start at room temperature, can proceed rapidly with various catalysts and can be controlled or stopped by means of removing catalyst from the solution (Yan et al., 2009). In the literature, many different methods are used for catalyst syntheses such as chemical reduction, redox replacement, sol-gel, electroless deposition, pyrolysis, galvanic replacement, and atomic layer deposition (ALD). The chemical reduction method is the most preferred among these methods because it is simple and economical. It can be simply defined as the reduction of metal precursors with the aid of different reducing agents in different solutions (Dang et al., 2011). Different sizes of nanoparticles can be synthesized by changing the molar ratio of the capping agents with the metal precursor salts. Characterization of the catalysts in the literature is mostly carried out by using methods such as XRD, SEM, TEM, EDS, XPS, ICP-OES, and BET. Investigation of the catalyst crystal structure and particle size calculations are performed by X-Ray Diffraction (XRD) analysis. The parameters such as pore size distribution and surface area are measured by the Brunauer-Emmett-Teller (BET) method. The elemental map of the catalyst is determined by inductively coupled plasma optical emission spectrometry (ICP/OES). The composition of the catalyst and atomic molar ratios are analyzed by energy dispersive spectroscopy (EDS). The surface electronic structure and electronic bonding structures are examined using X-ray photoelectron spectroscopy (XPS).

Detailed morphological information of the catalyst is obtained by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

In recent years, many studies have been carried out on obtaining hydrogen from boron compounds and catalysts of various compositions and structures have been synthesized. For example, Akbayrak, Özçifçi, & Tabak (2019), synthesized activated carbon-supported Rh, Ru and Pd nanoparticles by chemical reduction method. The synthesized catalysts were used in NH_3BH_3 hydrolysis, and it was stated that they were high performance catalysts with high reusability. TOF values for Rh/AC, Ru/AC and Pd/AC catalysts were calculated as 180 min^{-1} , 235 min^{-1} and 40 min^{-1} , respectively. The activation energy values of the hydrolysis reactions were found to be 39.9 kJ/mol, 68.3 kJ/mol and 67.5 kJ/mol, respectively. Dai et al., (2019), on the other hand, produced a very stable catalyst by attaching Al_2O_3 supported Pt catalysts to the cordierite honeycomb for use in the NaBH_4 hydrolysis reaction. The produced catalyst was transferred onto the support layer by wet impregnation and according to the SEM results, the catalyst was well dispersed. The TOF value for the dehydrogenation reaction was calculated as 53 min^{-1} . It has been stated that it would be advantageous to use the catalyst in hydrogen reactors because it is highly resistant to agglomeration. Pornea, Abebe, & Kim, (2019) synthesized Ni foam-supported NiCoP three-dimensional nanostructured catalyst by hydrothermal metal deposition method and used it for NaBH_4 hydrolysis. It was observed that the synthesized catalyst showed superior performance in terms of durability and catalytic activity. It was determined that $\text{Ni}_{0.8}\text{Co}_{1.2}\text{P/NF}$ catalyst had the highest performance among the synthesized catalysts in different compositions and this catalyst was able to maintain its catalytic activity until the fifth cycle. The hydrogen production rate was calculated as $3986 \text{ mL H}_2/\text{min}^{-1}$, and the activation energy was calculated as 38 kJ/mol. It is stated that the trimetallic catalyst system has advantages such as creating a synergistic effect between metals and preventing catalyst agglomeration. Uzundurukan & Devrim, (2019) produced multi-walled carbon nanotube supported Pt catalyst by microwave-polyol synthesis method and used it in NaBH_4 hydrolysis. It was found that the Pt/MWCNT catalyst was more effective than the Pt/C catalyst and the activation energies of the reaction for these catalysts were 27 kJ/mol and 36

kJ/mol, respectively. It was stated that the Pt/MWCNT catalyst provided a hydrogen production rate of 159 mmol/min, g for NaBH₄ hydrolysis at 67°C. Can and Metin, (2019) proposed C₄H₁₂BNO for the first time in the literature to produce hydrogen. Ag(0) and Pd(0) salts with PSMA stabilizing agent, which is a water-soluble polymer, were synthesized in situ and investigated as catalysts in the dehydrogenation of C₄H₁₂BNO. These catalysts showed remarkable performance with an initial TOF value of 16.1 min⁻¹ and 37.3 min⁻¹, respectively. The activation energy of the reaction was determined as 71.4 and 32.5 kJ mol⁻¹ for PSSA stabilized Ag(0) and Pd(0), respectively. It was concluded that C₄H₁₂BNO is at least three times more advantageous than NH₃BH₃ in terms of hydrogen content/cost ratio. Li et al., (2020) fixed very fine RuNi alloy particles on a porous graphitic carbon nitride support by reduction method. Catalysts in different molar ratios were synthesized and used in the NH₃BH₃ hydrolysis reaction and the optimum catalyst composition was determined. Ru_{0.5}Ni_{0.5}/G-C₃N₄ catalyst was the optimum catalyst and gave a TOF value of 803.3 min⁻¹ and the activation energy of the reaction was calculated as 14.1 kJ/mol when this catalyst was used. It has been stated that these values are quite good for NH₃BH₃ hydrolysis compared to similar bimetallic catalysts. Rakap, (2020) synthesized polyvinyl pyrrolidone supported bimetallic CoRh catalysts by alcohol reduction method and used them in the NH₃BH₃ dehydrogenation reaction. It was determined that the CoRh/PVP catalyst was a promising catalyst with a TOF value of 154 min⁻¹ at 25°C and the activation energy of the reaction was 42.7 kJ/mol when this catalyst was used.

2.3 Hydrogen Usage in Transportation Sector and Fuel Cell Vehicles

It is known that about a quarter of greenhouse gas emissions originates from the transportation sector with the excessive use of fossil fuels (Ghosh, 2020). In addition to being one of the fastest growing sectors in the world with increasing demand, the transportation sector consumes approximately 49% of the total oil production (Ghosh, 2020). To minimize the environmental impacts in the transportation sector and to reduce the dependence on oil, one of the most researched issues is the sustainability of the use of vehicles that operate with environmentally friendly fuels

and technologies (Manoharan et al., 2019). Today, battery-powered electric vehicles are the most researched issues to minimize environmental impact and reduce oil dependence in the transportation sector (Olabi, Wilberforce, & Abdelkareem, 2021). However, despite the developments in battery technology, the vehicle range provided by the batteries is limited (Baskar et al., 2020). Since the battery pack is the most expensive and degradable electric powertrain component of an electric vehicle, increasing the number of cells to extend the vehicle range causes higher costs and vehicle weights (Dinc & Otkur, 2020). For this reason, there has been increasing interest in hydrogen-powered fuel cell vehicles, which could offer a longer range at a lower price and have shorter refueling time than the battery electric vehicles (Trencher, 2020). Some specifications of commercialized FCVs are given in the Table 2.3.

Table 2.3 Specifications of some FCVs

Year	Vehicle	Fuel Cell Type and Size	Fuel Type	Max. Speed	Range	Ref.
2010-Present	Mercedes Benz GLC F-Cell	100 kW PEM	Compressed gas (4.4 kg H ₂ @700 bar)	160 km/h	478 km	Daimler, nd
2013-2018	Hyundai Tucson FCEV	100 kW PEM	Compressed gas (5.64 kg H ₂ @700 bar)	160 km/h	594 km	Hong & Kim, 2018
2015-Present	Toyota Mirai	114 kW PEM	Compressed gas (5.6 kg H ₂ @700 bar)	180 km/h	650 km	Toyota, 2020
2016-Present	Honda Clarity FCV	103 kW PEM	Compressed gas (4.1 kg H ₂ @350 bar)	180 km/h	589 km	Franck & Franck, 2019
2017-Present	Roewe 950	56 kW PEM	Compressed gas (4.18 kg H ₂ @700 bar)	215 km/h	430 km	Deloitte, 2019
2018-Present	Hyundai Nexo	95 kW PEM	Compressed gas (6.33 kg H ₂ @700 bar)	180 km/h	756 km	Hong & Kim, 2018
To be launched in 2022	BMW i Hydrogen Next	125 kW PEM	Compressed gas (6 kg H ₂ @700 bar)	n/a	Between 500-600 km	BMW Group, 2020

The transition to FCVs in the automotive industry has become an important research topic, especially in the last decade (Das, Tan, & Yatim, 2017; Wang et al.,

2018; Ajanovic & Haas, 2019). Figure 2.3 shows a bar graph of the distribution of studies on FCV modeling and simulation over the years, obtained by searching the words "fuel cell vehicle modeling" using the Web of Science search engine. The topics of these studies are generally on the technical challenges of the FCVs (e.g. Cai et al., 2012; Mohammadi et al., 2013; Chen, Laghrouche, & Djerdir, 2019), the examination of the performance of power sources such as PEMFC stack and battery (e.g. Boettner et al., 2002; Rajabzadeh, Bathaee, & Aliakbar, 2016), investigation of hydrogen storage methods and hydrogen supply infrastructure (e.g. Ogumerem & Pistikopoulos, 2019; Ba et al., 2020; Whiston et al., 2021), modeling various powertrain configurations and energy management systems (e.g. Song et al., 2018; Yao et al., 2019; Nassif & Almeida, 2020), and performing drive cycle simulations (e.g. Kang & Min, 2016; Koteswara & Srinivasulu, 2019; Changizian et al., 2020).

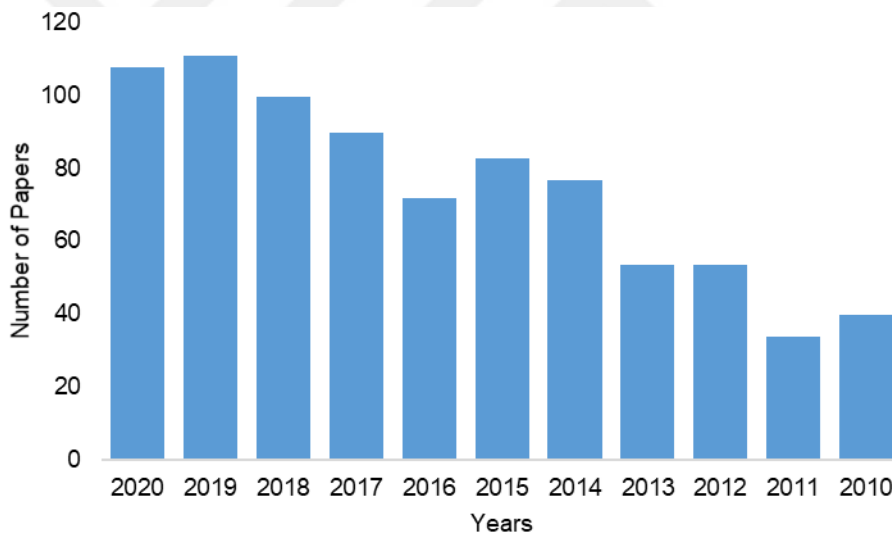


Figure 2.3 Distribution of the number of publications made in the last ten years on fuel cell vehicle modeling by years

Modeling and simulation serve as a tool in the selection of the design and operating parameters of FCVs to achieve high performance from these vehicles. These studies are crucial to assess the vehicle range (Hong & Kim, 2018; Deloitte, 2019), storage performance (Brooks et al., 2020), hydrogen consumption (Fernández, Cilleruelo, & Martínez, 2016), cost (Casolari et al., 2014; Li et al., 2016), and system efficiency (Samsun et al., 2016) of an FCV. In addition to these parameters, the

climate and road conditions of a region that a vehicle is operated greatly affect the fuel consumption of the vehicle and the average life of the equipment. For this reason, dynamic simulation studies are needed to evaluate various scenarios and enable the comparison of various technologies (e.g. converters, batteries, storage systems, electric motors, fuel cell stacks) (Kumar, Nema, & Gupta, 2020). The accuracy of these simulations depends on the establishment of reliable mathematical models for the vehicle dynamics and components. The behavior and performance of the components as well as the vehicle should be examined under various operating conditions when the vehicle power requirements change such as starting, acceleration, and braking periods (Sulaiman et al., 2015). Models with high accuracy should be developed to minimize the costs associated with the experimental procedures (Lekshmi & Lal, 2019). The powertrain components and energy management system could be properly designed through these modeling and simulation studies to achieve high performance and low cost of the overall system (Tran et al., 2020). To have widespread use of FCEVs, the first condition is that the driving range provided by a full fuel tank should be similar to or better than that of an internal combustion engine vehicle (ICEV) (Wang et al., 2018). In addition, the vehicle should perform well during acceleration (e.g. acceleration from 0 km/h to 100 km/h should be less than 10 s) and under cold ambient conditions (start-up is less than 30 s when the ambient temperature is at -30°C) (Wang et al., 2018). Furthermore, to test the durability of the fuel cell, which is one of the obstacles towards the commercialization of FCVs, the fuel cell stack should be able to offer a lifetime of 8000 hours with $<10\%$ drop in rated power after durability test, according to US DOE testing protocol (US Department of Energy, 2020). Other features determined by DOE as the ultimate target for fuel cell power systems are 70% peak energy efficiency, 850 W/L power density, 650 W/kg specific power, and 30 \$/kW cost (US Department of Energy, 2020). There are several studies in the literature on the modeling and simulation of FCVs. For example, Feroldi & Carignano, (2016) used a polynomial approximation for the fuel cell efficiency and hydrogen consumption in their fuel cell hybrid vehicle model based on driving cycles. Huang, Kuo, & Han, (2017) developed a simulation model in Matlab Simulink for a fuel cell scooter to determine the hydrogen consumption according to the vehicle speed and slope angle.

Gao et al., (2016) carried out a drive cycle simulation for two different configurations of fuel cell hybrid buses to calculate the system efficiency of the components from the energy flow distributions. Karaoğlu et al., (2019) developed a Matlab Simulink model for a small-sized fuel cell hybrid vehicle equipped with a direct methanol fuel cell unit to determine methanol consumption, state of charge (SOC), and vehicle range as a result of drive cycle simulation. Shusheng et al., (2020) used ADVISOR simulation tool to calculate the efficiency diagrams and hydrogen consumptions of a fuel cell stack in various powertrain modes according to the drive cycle simulation. In Table 2.4, the topics of the review studies conducted on fuel cell vehicles in the last decade and the results that can be derived from these studies are summarized.

Table 2.4 The key review papers on FCVs published in the last ten years

Authors	Topic	Conclusions
Chan, Bouscayrol, & Chen, 2010	• The architectures and energy management models of BEVs, HEVs and FCVs	• Even if a good architecture is chosen, a good energy management and efficient system control are needed for satisfactory performance. • A commercialization roadmap aimed at lowering costs and improving performance is required.
Sulaiman et al., 2015	• Besides EMS, batteries and supercapacitors have also been investigated for FCVs.	• EMS should have an optimum control strategy or a strategy to minimize fuel consumption without affecting power load distribution. • EMS should be tested in a specific speed range, on hardware or in a real-time application.
Gröger, Gasteiger, & Suchsland, 2015	• Technological barriers for BEVs and FCVs have been investigated. • For BEV applications, the limits of Li-ion batteries and their energy densities at the cell and system levels have been studied.	• The volumetric energy densities of the innovative Li-ion batteries are lower. • Advanced catalysts are successful in meeting long-term DOE efficiency and durability aims.

Table 2.4 continues

Authors	Topic	Conclusions
Wilberforce et al., 2017	• The challenges preventing the spread of fuel cell technology in the automotive industry have been studied. • The progress made by automobile manufacturers of EVs and FCVs was examined.	• FCV costs should be reduced by lowering the platinum content of catalysts or by producing Pt-free catalysts without reducing FC performance. • The necessary infrastructure for service and maintenance should be improved. • Hydrogen produced from renewable sources is essential for completely zero-emission vehicles.
Das, Tan, & Yatim, 2017	• The challenges and futures of FCV technology are discussed. • Different types of energy sources and different power topologies of FCV are examined.	• FCVs have great growth potential in the transportation sector • In order to compete with ICEV, FCVs need to reduce their power train costs through technological research.
Lü et al., 2018	• Examination of batteries and supercapacitors • Determining the advantages and disadvantages of hybrid power system combinations	• Hydrogen transportation, energy consumption optimization, dynamic response, fault diagnosis, energy management, heat balance, safety, emergency plan in the FCV operation process issues should be developed.
Tanç et al., 2019	• The status of FCVs in the next quarter century is examined	• For FCVs to become widespread between 2030 and 2050, it is necessary to achieve advanced energy optimization, expand their range and increase hydrogen refueling stations. • Research should be conducted on cell life and density improved cold-start performance, and improvement of fuel storage devices and membrane materials.

Table 2.4 continues

Authors	Topic	Conclusions
Ajanovic & Haas, 2019	• Different types of EVs and their development are discussed. • Cost analysis of BEVs and FCVs has been made, and environmental assessment of BEVs and FCVs compared to traditional ICEV has been given.	• The future of BEVs and FCVs is directly related to the pace of technological advances, especially in terms of batteries and fuel cells. • The lifetime and annual use of automobiles have a significant impact on total emissions per km driven.
Bairabathina & Balamurugan, 2020	• The effect of transport electrification on the current power system was examined. • FCVs and BEVs have been compared.	• The cost, performance and efficiency of the fuel cell system and the economical hydrogen production and storage should be improved. • Non-isolated multi-input high cascade DC-DC converters should be designed with fewer switches, high voltage gain, low voltage/current stress, and high efficiency.
Ghosh, 2020	• Different socio-technical challenges for EV acquisition and the global situation of EVs were examined.	• The main challenges with EVs are the lack of a suitable energy storage system, a high-performance fast charging facility, and an efficient battery management system. • The increase in EV purchasing is directly linked to government incentives policies and the fact that manufacturers are creating models that will attract consumers.
Ma et al., 2021	• System configurations, energy management strategies, various fuel cell and battery power systems have been studied.	• To improve overall efficiency and performance, system design and control strategy should be optimized, and the cost of basic materials and system should be reduced. • To expand the market, the hydrogen supply infrastructure must be expanded, the public must be informed, and the government must adopt a policy of incentives.

Table 2.4 continues

Authors	Topic	Conclusions
Asghar et al., 2021	• The challenges and opportunities for EVs in Pakistan have been explored.	• It is important for the widespread use of EVs that the government promotes economic advantages, the effects of production and product innovation. • Technical difficulties, lack of expertise and lack of market knowledge stand out in assessing the economic benefits between EV and ICEV for developing countries.
Balali & Stegen, 2021	• Different EV technologies consisting of BEVs, HEVs and FCVs have been studied. • Environmental impacts and costs of FCVs have been studied.	• The main limitations of developing an optimum EV using FC and SC are i) finding the best algorithm for the vehicle's energy management system ii) to reduce the cost of vehicles and energy resources iii) increasing the number of hydrogen stations to refuel the hydrogen tank and power the FC stack.

Although significant progress has been done towards the widespread commercial use of fuel cell vehicles [115], there are still challenges with manufacturing cost (Trencher, Taeihagh, & Yarime, 2020), establishing a hydrogen refueling network and sustainable hydrogen supply (Trencher, 2020), and transportation and storage of hydrogen (Ren et al., 2020). Among these challenges, hydrogen storage technology has critical importance for the performance and cost of FCVs and should enable high security, fast refueling, and low weight and size (Rivard, Trudeau, & Zaghib, 2019). The most common method for storing hydrogen on vehicles is to store it as compressed gas at high pressures (e.g. 250, 300, and 700 bar) (Li et al., 2019). Storing hydrogen at 700 bar is generally preferable as it decreases storage space in the vehicles and extends the driving range (Kim, Lee, & Yoon, 2010). Most of the prototypes, demonstration cars, and commercially produced fuel cell vehicles up to now have compressed hydrogen tanks as the hydrogen storage unit (see Table 2.3). Compared to other methods, storing hydrogen as compressed gas is relatively efficient, does not

require a complex thermal management system, and refueling is easy; but this method has problems such as high energy consumption for the compression process and the manufacturing cost of the high-safety composite tank (Li et al., 2019). Liquid hydrogen is suitable for extending the vehicle range and offers the possibility of storing more hydrogen for the same volume in the vehicle (Mori & Hirose, 2009). However, despite this advantage, the use of liquid hydrogen in the vehicle has some disadvantages such as liquefaction costs (Yanxing et al., 2019), difficulties in insulating cryogenic containers (Mori & Hirose, 2009), and boiling problem (Durbin & Malardier-Jugroot, 2013). Compared to compressed gas storage, metal hydride storage systems have the advantage of operating at low pressure (Davids et al., 2019); and compared to liquid storage, they have the advantage of allowing storage at ambient temperature when there is no hydrogen demand. There is also a very low probability of undesired hydrogen leakage, and it has relatively a high volumetric energy density. The most important disadvantages are that the gravimetric energy density is low, storage tanks are heavy, some metal hydrides require very high dehydrogenation temperatures, and the absorption-release process of hydrogen is slow (Yanxing et al., 2019). While chemical hydride based hydrogen storage has advantages such as using non-toxic high-safety materials and low storage pressure, it also has some disadvantages such as inability to recharge onboard and slow kinetics (Lim et al., 2010).

2.4 Chemical Hydride Based Hydrogen Storage Systems Usage in Fuel Cell Vehicles

Among the solid hydrogen storage materials, chemical hydrides have come to the fore due to their high hydrogen content (Yao, Ding, & Lu, 2020). These compounds undergo hydrolysis in the presence of a catalyst at room temperature, releasing hydrogen without creating dangerous by-products (Fakioğlu, Yürüm, & Veziroğlu, 2004). There are various studies in the literature on the use of chemical hydrides in fuel cell vehicles. Tomoda et al., (2015) designed and simulated an H_2 production system that can produce H_2 by hydrolysis of sodium borohydride ($NaBH_4$) powder in Matlab Simulink environment, and the performance of the system was examined for a 5 kW polymer electrolyte fuel cell. Nickel catalyst was used in the system and the reaction

followed a first-order kinetic. The H_2 production system operated with an average H_2 production rate of 50 L/min. To control the production rate, the H_2 pressure supplied to the fuel cell was regulated to be approximately 50 kPa by controlling the amount of dissolved $NaBH_4$ fed to the reactor. It is stated that the difference between experimental and simulation results for hydrogen production rate is less than 2 L/min and the error is 1%. Li & Wang, (2016) developed an H_2 generation system based on $NaBH_4$ hydrolysis, which can generate H_2 on-demand to operate a 3 kW PEMFC. The system was designed to feed the solution to the fuel cell at an average speed of 30 SLPM. $NaBH_4$ solution concentration and batch volume were examined parametrically. In addition, a mathematical model was developed to examine H_2 production, system temperature, and batch intervals of $NaBH_4$ solution. It is stated that $NaBH_4$ solution can meet the hydrogen requirement of the fuel cell with a conversion rate of around 90%, the system reaches the highest efficiency with 15% $NaBH_4$ by weight and a batch of 400 mL, and the model can successfully predict the temperature response. Wang & Fang, (2017) developed a model that includes power management and control strategies for a hybrid vehicle with a chemical H_2 generation system using the Matlab Sim-Power System. The vehicle has a 3 kW PEMFC stack, PV panels, and batteries as a secondary energy source. In the chemical H_2 production system, 400 mL of 15% $NaBH_4$ solution by weight was used and 150 L H_2 was produced in 335 seconds in each batch. The vehicle was tested on a 2.5 km route at the National Taiwan University campus. Later, a simulation model was created, and it was stated that the model could effectively predict experimental responses and be applied for performance analysis. Sanli et al., (2018) examined the direct borohydride-peroxide fuel cell and battery hybrid system for the first time in the literature. They designed a hybrid motorcycle powered by a 120 W fuel cell system with a 10-cell stack and 12 LiPo batteries of 6300 mAh as an auxiliary energy source. Performance tests were carried out under a 60 W constant load. During the tests, the temperature was not controlled, and the flow rate was kept constant at 950 mL/min. According to the performance tests, the hybrid system exhibited an efficiency of 67%. However, it was concluded that the main control unit should be improved for a more stable power output. Brooks et al., (2018) developed a system design tool in the Matlab Simulink environment to guide material manufacturers in determining the design parameters of the storage

system in fuel cell vehicles. The developed design tool provides estimates to determine the dimensions of the H_2 storage system components and the control parameters required for this storage system, once the total system mass and volume are known. A tank that allows 5.6 kg of usable H_2 mass was modeled to provide a range of 300 miles to a light-duty vehicle with an 80 kW fuel cell stack. They investigated alane (AlH_3) decomposition as an endothermic reaction and ammonia borane (NH_3BH_3) hydrolysis as an exothermic reaction. As a result of the analyses, it was found that NH_3BH_3 is a more suitable material in terms of mass and volume of the storage system compared to AlH_3 . The literature survey shows chemical hydride-based hydrogen storage is a promising technique to be used in FCVs; however, its competitiveness with compressed H_2 storage should be further investigated. In this context, it is also shown that mathematical modeling and simulation is an effective tool that can predict changes in the system requirements and can be used to examine the effect of chemical hydride-based hydrogen storage system performance on the range of an FCV.

CHAPTER THREE

HYDROGEN PRODUCTION FROM MORPHOLINE BORANE IN THE PRESENCE OF PSSA STABILIZED PDAG

3.1 Materials and Synthesis of PSSA Stabilized Pd-Based Catalyst

In this thesis, four different catalysts, PSSA stabilized Pd, PdNi, PdCo, and PdAg, were investigated for hydrogen production from morpholine borane. Poly(4-styrenesulfonic acid-co-maleic acid) sodium salt (PSSA, MW 20000), palladium (II) nitrate dihydride 40% Pd basis, silver nitrate ($\geq 99\%$), nickel (II) chloride hexahydride (99.99%), cobalt (II) chloride hexahydrate (98%), borane morpholine complex (95%) were purchased from Sigma-Aldrich. Distilled water was used in all experiments. Synthesis of catalysts and hydrolysis experiments of $C_4H_{12}BNO$ were carried out in a jacketed schlenk flask as can be seen in Figure 3.1.

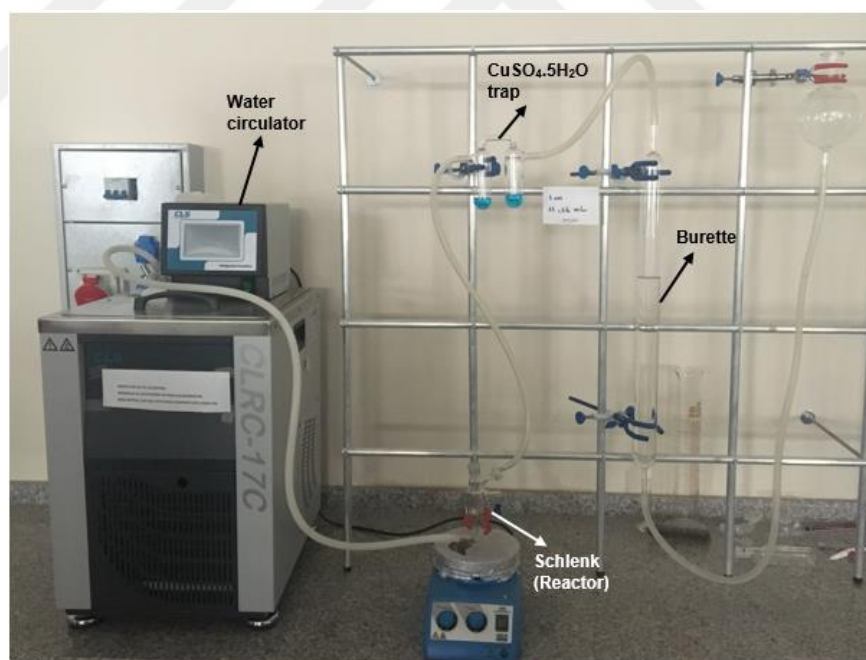


Figure 3.1 Experimental set-up

First, 2 mM PSSA was added to the reactor as a solid for in situ synthesis of catalysts. Then, depending on the catalyst to be synthesized, 2 mM Pd, 2 mM PdAg (1 mM Pd and 1 mM Ag), 2 mM PdCo (1 mM Pd and 1 mM Co), or 2 mM PdNi (1

mM Pd and 1 mM Ni) was dissolved in 7 mL water and added to the reactor. The temperature of the reactor was controlled with the help of a temperature-controlled water circulator. PSSA and metal precursors were mixed with a magnetic stirrer at the desired temperature for 15 minutes. Finally, 100 mM morpholine borane was dissolved in 3 mL water and added to the reactor with a syringe to initiate the catalytic hydrolysis reaction. The connection of Schlenk to the water-filled column was provided with a plastic hose and the change of the water level in the water-filled column and the hydrogen gas output was observed volumetrically. The reaction was carried out at 25°C with 10 mL solution volume. Hydrogen production performances of synthesized Pd-based catalysts are given in Figure 3.2.

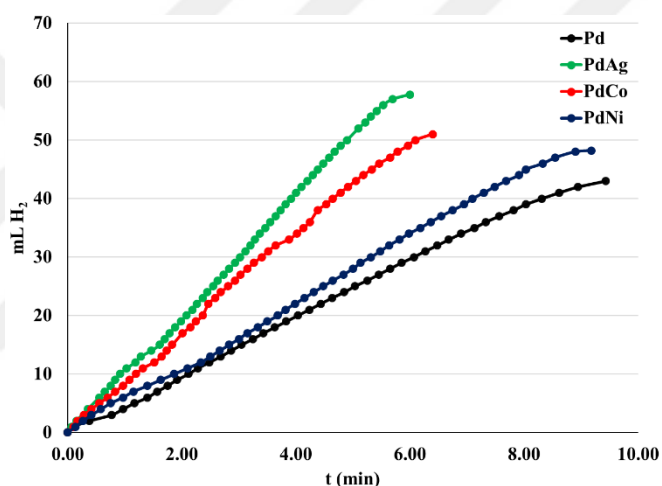


Figure 3.2 Hydrogen production performances of PSSA stabilized Pd-based catalysts ([metal]=2 mM, [PSSA]=2 mM, [MB]=100 mM, T=25°C, V=10 mL)

As can be seen in Figure 3.2, all bimetallic catalysts had higher performance than monometallic Pd catalysts. The catalytic activity order of the synthesized catalysts is determined as Pd<PdNi<PdCo<PdAg and 43, 48.2, 51 and 58 mL hydrogen output were observed, respectively. Since PSSA stabilized PdAg was determined as the most active catalyst, subsequent experiments were continued with this catalyst.

3.2 Characterization Studies

TEM image of PSSA stabilized PdAg catalyst is given in Figure 3.3. From Figure 3.3, it can be concluded that the particles are properly dispersed, and no

agglomeration occurs. The average particle size was determined as 7.09 nm. It has been observed that the largest sized particles have a size between 12-15 nm and they constitute 13% of the total number of particles. In addition, almost half of the particles (48%) have a size between 7 and 9 nm. The smallest sized particles, with sizes between 3 and 5 nm, are 29% of all particles.

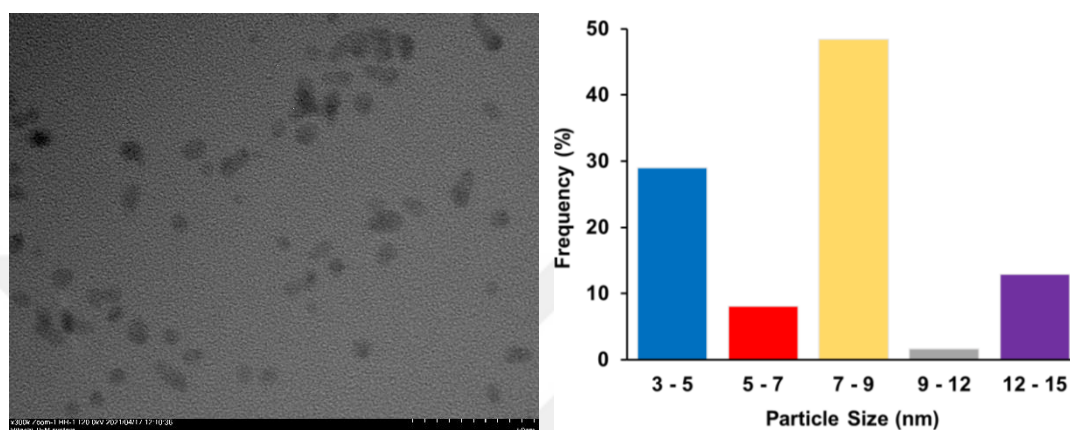


Figure 3.3 TEM image and particle size histogram of PSSA stabilized PdAg nanoparticles

Figure 3.4 shows the B-NMR spectra taken before and after the hydrolysis reaction of morpholine borane. In Figure 3.4a, a quartet at $\delta=-17.134$ ppm was observed in the B-NMR spectrum of unreacted morpholine borane. This result is consistent with the B-NMR spectrum given at $\delta=-16.2$ ppm for pristine morpholine borane in the reference article (Can & Metin, 2019). As can be seen in Figure 3.4b, this quartet disappeared after hydrolysis of morpholine borane to form a large singlet at $\delta=10.108$. In the reference article (Can & Metin, 2019), the singlet value for hydrolyzed morpholine borane is observed at $\delta=13.6$ ppm.

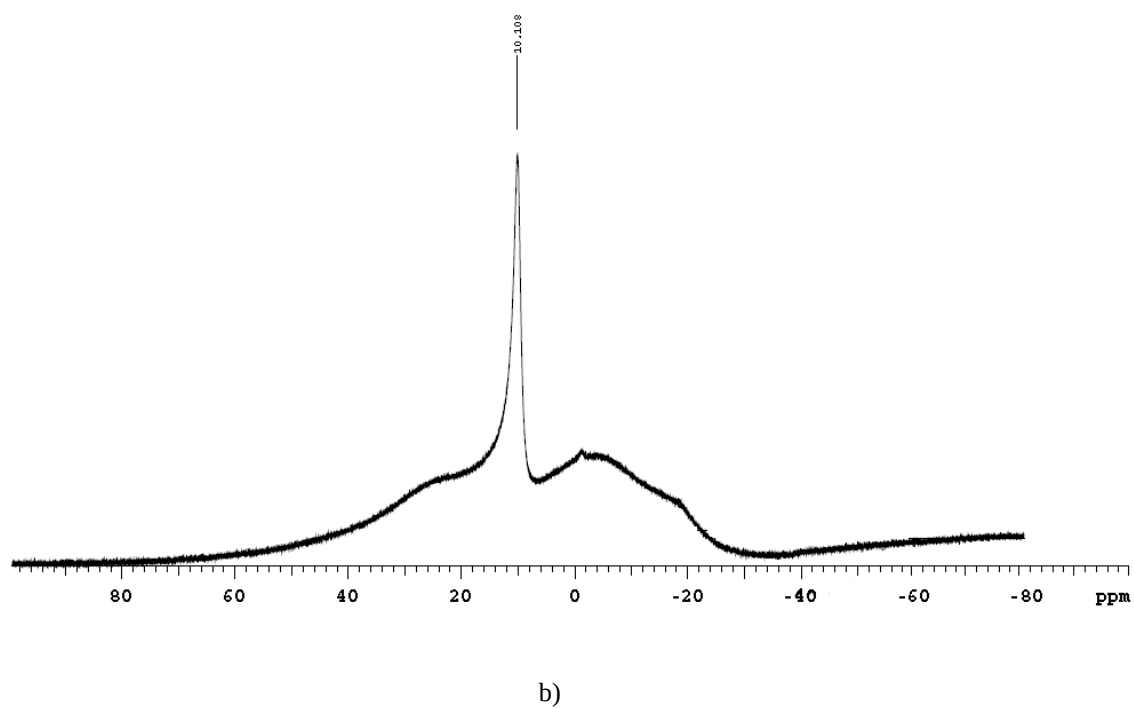
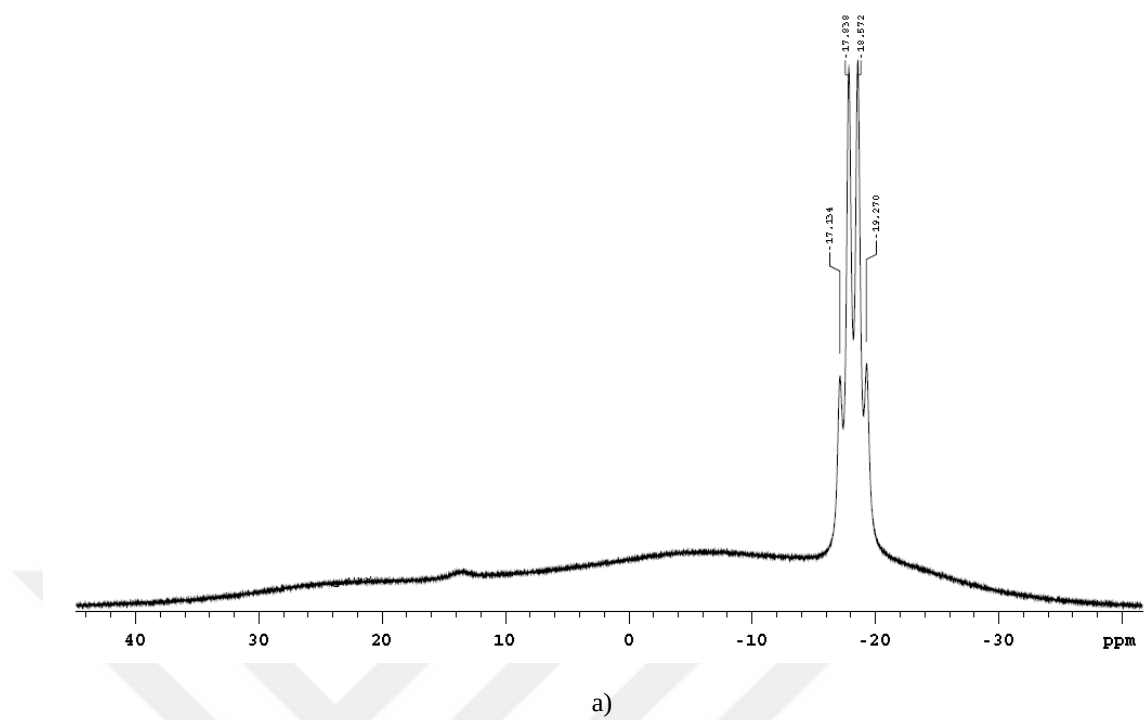


Figure 3.4 B-NMR spectrum of morpholine borane taken in D₂O a) before hydrolysis b) after hydrolysis

3.3 Optimization of PSSA and Metal Amounts

In the optimization studies of the amount of PSSA for the 2 mM PdAg catalyst, 8 different [metal]/[PSSA] ratios as 1/0, 1/0.25, 1/0.50, 1/1, 1/2, 1/4, 1/8 and 1/16 were studied and the results are presented in Figure 3.5.

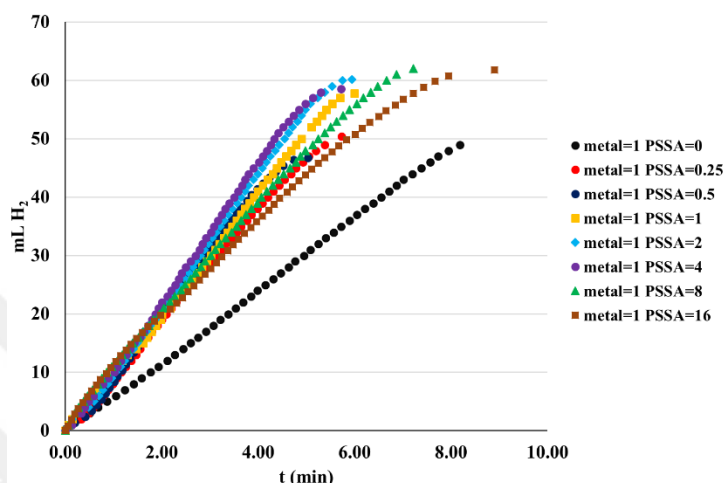


Figure 3.5 Hydrogen production performance of PdAg catalyst for different [metal]/[PSSA] ratios ([PdAg]=2 mM, [MB]=100 mM, T=25°C, V=10 mL)

In Figure 3.5, it can be seen that the hydrogen production rate and the amount of produced hydrogen decrease significantly in the case where the stabilizer is not used ([metal]/[PSSA]=1/0). When PSSA was added at a ratio of 1/0.25, the amount of produced hydrogen did not change, but the reaction accelerated. When the PSSA ratio was increased to 1/1, both the reaction rate and the amount of produced hydrogen increased. After this point, the amount of PSSA was continuously increased by 2 times the previous one, and an increase was observed up to 1/4. The reaction rate decreased when the PSSA amount was increased to 1/8, and the decrease in the reaction rate continued when it was increased to 1/16. The reason for this situation is that when the amount of PSSA is increased, the large PSSA molecules in the reaction medium reduce the catalyst-substrate interaction and accordingly the catalyst performance decreases. Based on Figure 3.5, the optimum [metal]/[PSSA] ratio was determined as 1/4.

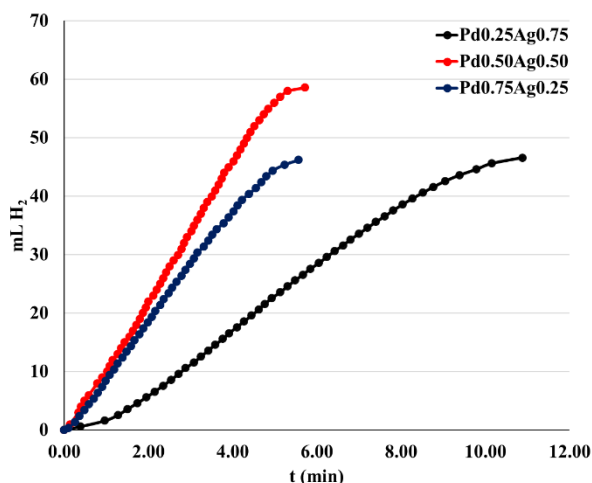


Figure 3.6 Investigation of the effect of Pd and Ag metal amounts on hydrogen production performance ([PdAg]=2 mM, [PSSA]=8 mM, [MB]=100 mM, T=25°C, V=10 mL)

Pd_{0.25}Ag_{0.75} (2 mM PdAg, 0.5 mM Pd, 1.5 mM Ag), Pd_{0.50}Ag_{0.50} (2 mM PdAg, 1 mM Pd, 1 mM Ag) and Pd_{0.75}Ag_{0.25} (2 mM PdAg, 1.5 mM Pd, 0.5 mM Ag) catalysts were synthesized to examine the effect of Pd and Ag amounts on hydrogen production performance. In Figure 3.6, hydrogen production results for the synthesized catalysts at three different metal ratios are given. Accordingly, the best performance was obtained with Pd_{0.50}Ag_{0.50} catalyst. If the curve of the Pd_{0.25}Ag_{0.75} catalyst is examined, it can be seen that the reaction proceeds very slowly at the beginning. The reason for this may be that as the amount of Ag increases, the reduction of nanoparticles slows down, and an induction period is required for the formation of the bimetallic catalyst.

3.4 Kinetic Studies

In order to determine the reaction order according to the catalyst, five different catalyst concentrations, 1, 1.5, 2, 2.5 and 3 mM, were examined. The results of different catalyst concentrations are given in Figure 3.7. It was observed that the reaction rate increased when the catalyst concentration was increased. The rate constants were calculated from the slope of each curve in the graph, and it was determined that the reaction was first order according to the catalyst from the slope of the graph drawn as $\ln [\text{cat}]$ on the x-axis and $\ln (k)$ on the y-axis.

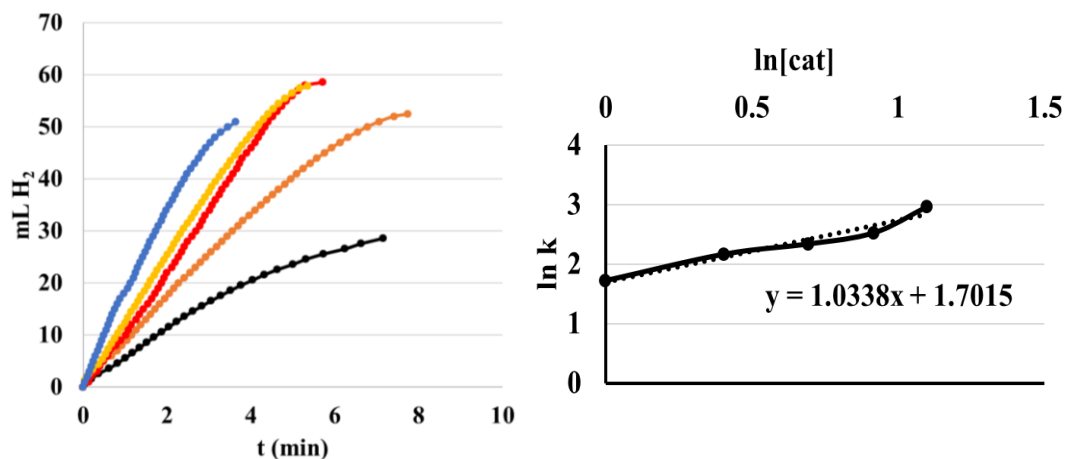


Figure 3.7 Determination of the reaction order according to the catalyst concentration ([PdAg]=1, 1.5, 2, 2.5, 3 mM, [PSSA]=4, 6, 8, 10, 12 mM, [MB]=100 mM, T=25°C, V=10 mL)

In order to determine the reaction order according to the substrate, four different substrate concentrations, 50, 100, 150 and 200 mM, were examined. The results of different substrate concentrations are given in Figure 3.8. It was observed that the reaction rate was not affected when the substrate concentration was increased. The rate constants were calculated from the slope of each curve in the graph, and it was determined that the reaction was zero order according to the substrate, from the slope of the graph drawn as $\ln [\text{subs}]$ on the x-axis and $\ln (k)$ on the y-axis.

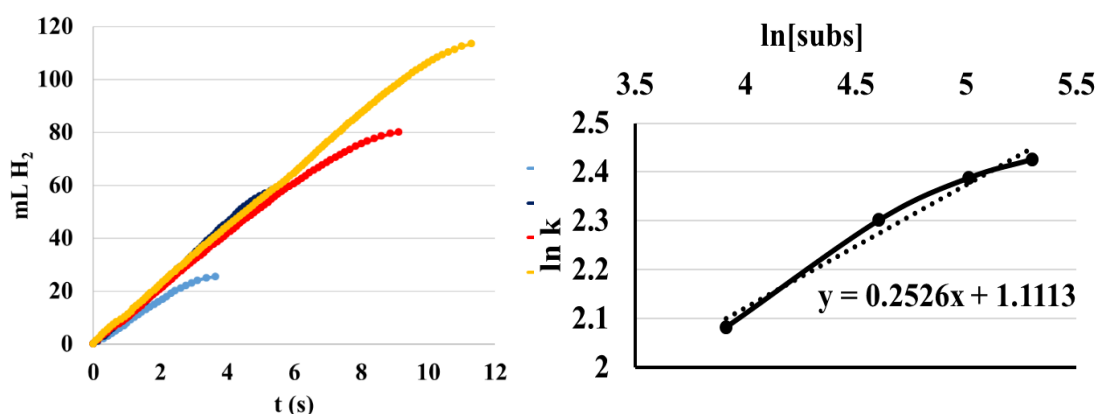


Figure 3.8 Determination of the reaction order according to the substrate concentration ([PdAg]=2 mM, [PSSA]=8 mM, [MB]=50, 100, 150, 200 mM, T=25°C, V=10 mL)

The performance of PSSA stabilized Pd_{0.50}Ag_{0.50} catalyst for four different temperatures, 15°C, 20°C, 25°C and 30°C is presented in Figure 3.9. As expected, hydrogen production performance increases with temperature. Rate constants for

different temperatures were determined from the slope of the curves in Figure 3.9 as 4.88, 7.77, 11.48 and 15.35 mL H₂/min for 15°C, 20°C, 25°C and 30°C, respectively.

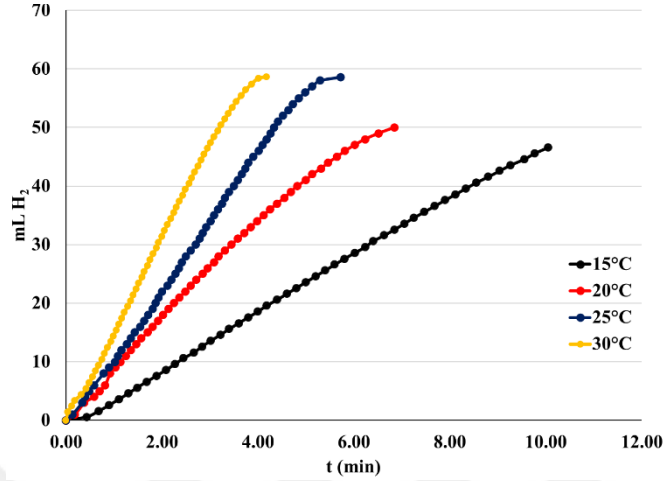


Figure 3.9 Hydrogen production performance of Pd_{0.50}Ag_{0.50} catalyst for four different temperatures ([PdAg]=2 mM, [PSSA]=8 mM, [MB]=100 mM, V=10 mL)

Arrhenius and Eyring plots are given in Figure 3.10. The activation energy of the reaction can be calculated from the slope of the Arrhenius plot (Equation 3.1), and the enthalpy of the reaction can be calculated from the slope of the Eyring plot (Equation 3.2).

$$m_{Arrhenius} = \frac{-E_a}{R} \quad (3.1)$$

$$m_{Eyring} = \frac{\Delta H}{R} \quad (3.2)$$

Accordingly, with R=8.314 J/mol K, the activation energy of the reaction and the enthalpy were calculated as 55.681 kJ/mol and -53.225 kJ/mol, respectively.

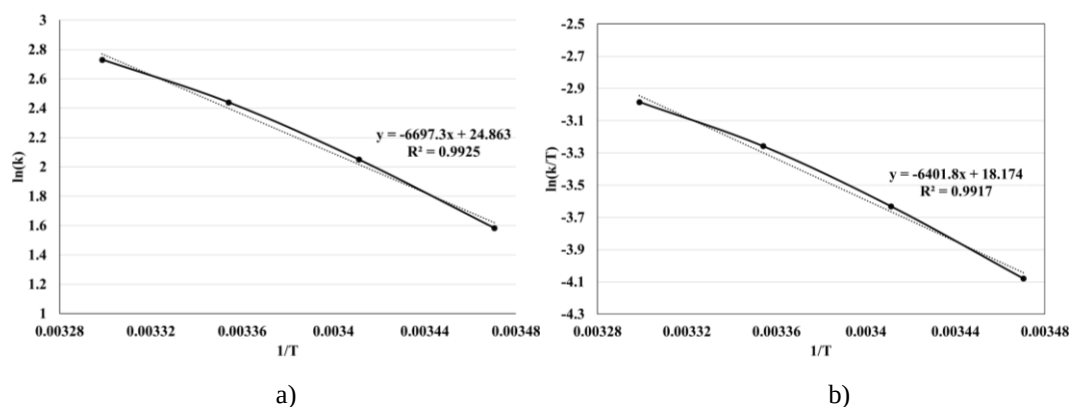


Figure 3.10 a) Arrhenius plot, b) Eyring plot

3.5 Determination of Catalyst Reusability

Experiments were performed by halving the volume to calculate the initial TOF value of the reaction. First, 8 mM PSSA was added to the reactor as a solid. Then, 2 mM PdAg was dissolved in 3.5 mL of water and added to the reactor. The catalyst and stabilizing agent were mixed with a magnetic stirrer for 15 minutes, and the reaction was initiated by dissolving 100 mM MB in 1.5 mL water and adding it to the reactor. When the hydrogen production ceased, 100 mM MB was added to the reactor as a solid and this process was continued for 20 cycles. During the 10th cycle, the catalyst was bulked up in the reaction medium (56 minutes in Figure 3.11), and the reaction rate decreased. The amount of produced hydrogen (mL) during the experiment was converted to mole hydrogen with the help of the ideal gas equation, and the graph of mol H₂/mol catalyst versus time is presented in Figure 3.11. The initial TOF value was calculated as 10.27 min⁻¹ from the slope of this graph.

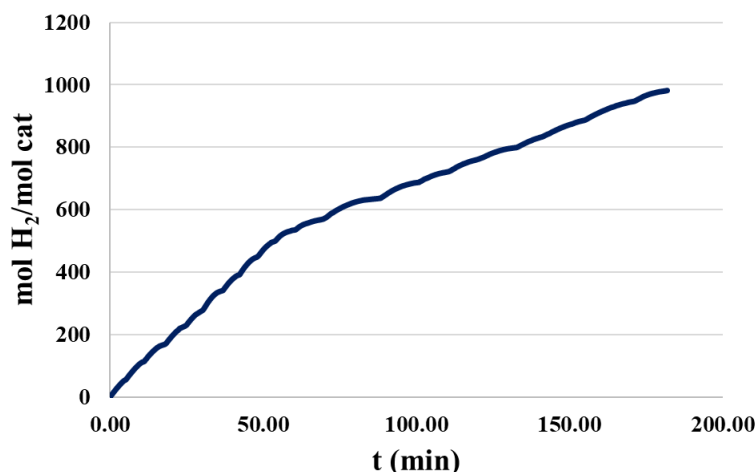


Figure 3.11 Determination of the initial TOF value ([PdAg]=2 mM, [PSSA]=8 mM, [MB]=100 mM, T=25°C, V=5 mL, 20 cycles)

The reusability of the PSSA stabilized PdAg catalyst was investigated over 10 cycles and the amount of produced hydrogen against time is given in Figure 3.12. During the first two cycles, 28.6 mL of hydrogen production was observed in each cycle. At the end of the third cycle, the amount of produced hydrogen decreased to 28.4 mL, and then it gradually decreased, and 24.4 mL of hydrogen production was observed at the end of the ninth cycle. During the tenth cycle, the catalyst was bulked in the reaction medium, and 17.8 mL of hydrogen output was observed. A comparison of the reaction rate between the first and last cycles is given in Figure 3.12b.

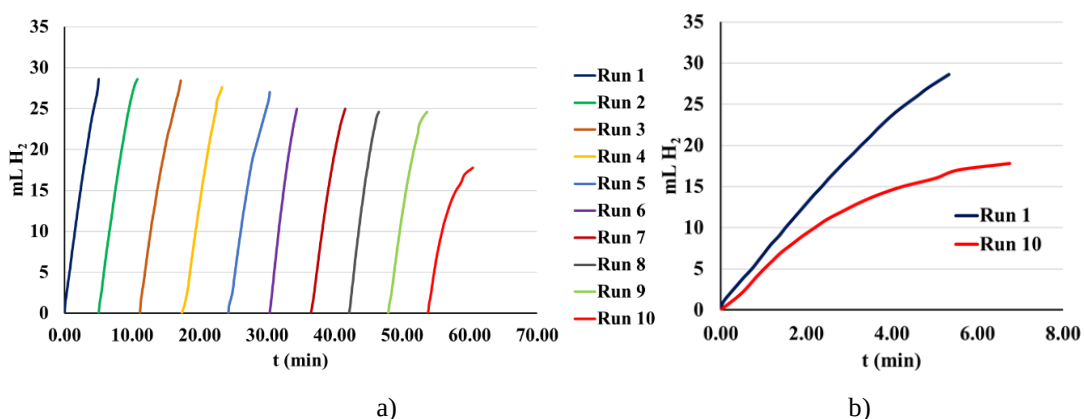


Figure 3.12 Investigation of reusability of the catalyst ([PdAg]=2 mM, [PSSA]=8 mM, [MB]=100 mM, T=25°C, V=5 mL) a) during ten cycle b) at the end of first and last cycle

The decrease in the catalytic activity of the PSSA stabilized PdAg catalyst and conversion ratio of the substrate over ten cycles is given in Figure 3.13. The catalytic activity is 100% during the first two cycles, and then gradually decreases to 72.35% in the last cycle. At the end of five cycles, the PSSA stabilized PdAg catalyst retained 91.02% of its catalytic activity. When the mol H₂/mol substrate ratios were examined for ten cycles, it was observed that the catalyst was able to transform the substrate at a rate of 77.46% in the first cycle. The conversion rate gradually decreases as the cycles progress, and 66.08% conversion is observed at the end of the ninth cycle. The bulk catalyst, on the other hand, is capable of converting less than half (48.21%) of the substrate during the tenth cycle.

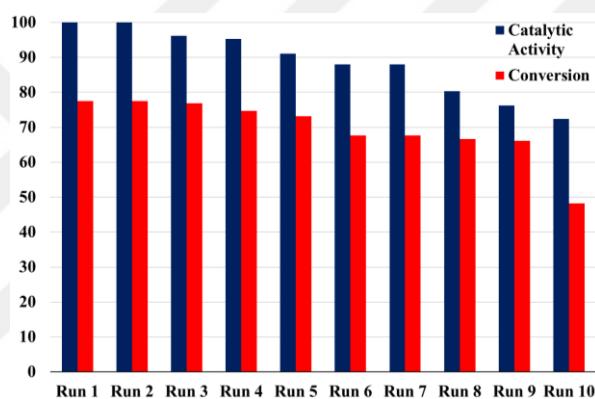


Figure 3.13 Conversion rate and catalytic activity of the catalyst during ten cycles ([PdAg]=2 mM, [PSSA]=8 mM, [MB]=100 mM, T=25°C, V=5 mL)

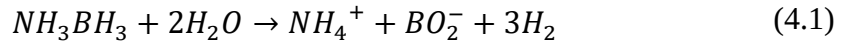
CHAPTER FOUR

NUMERICAL INVESTIGATION OF HYDROGEN PRODUCTION FROM SOLID HYDROGEN STORAGE MATERIALS

4.1 Batch Reactor Model

For the numerical model in the Comsol Multiphysics environment, the schlenk flask was considered as a constant volume batch catalytic reactor. The total volume of the laboratory scale catalytic reactor was designed to be 25 mL and the solution volume to be 10 mL. This reactor was handled in three different sections as (i) NH_3BH_3 solution zone, (ii) hydrogen storage zone, and (iii) reactor walls, drawn in Solidworks program and transferred to Comsol Multiphysics environment. In the mathematical model, reaction engineering (domain i), transport of diluted species (domain i and ii), heat transfer in fluids (domain i and ii) and heat transfer in solids (domain iii) modules are used.

The overall equation of the hydrolysis reaction of NH_3BH_3 (Basu et al., 2010);



The species balance equation was used to observe the change in concentration of species in solution.

$$\frac{dc_i}{dt} + \nabla(-D_i \nabla c_i) = R_i = r_i V_r \quad (4.2)$$

where c_i is the initial concentration of the species, D_i is the diffusion coefficient of species, R_i is the reaction rate, and V_r is the reactor volume.

Initial NH_3BH_3 concentration and diffusion coefficient of NH_3BH_3 were defined as boundary conditions at 200 mol m^{-3} and $2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (Basu et al., 2010), respectively.

In all regions of the computational area, the conservation of energy equation was applied to determine the temperature distribution.

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p u \nabla T + \nabla q = Q \quad (4.3)$$

$$q = -k \nabla T \quad (4.4)$$

where ρ is the density, C_p is the heat capacity, u is the velocity field, k is the thermal conductivity and Q is the heat source of the reaction. The hydrolysis reaction of NH_3BH_3 is exothermic; therefore, when hydrogen is produced, heat is released. The relation with the reaction rate and the generated heat can be given by the following equation.

$$Q = -V_r \sum_i H_i r_i \quad (4.5)$$

where H is the reaction enthalpy.

To solve the conservation of energy equation, various boundary conditions are applied in different regions of the computational domain. In the reactor walls, natural convection occurs between the external walls of the reactor and the environment.

$$q_{conv} = h(T_{ext} - T) \quad (4.6)$$

where h is the convective heat transfer coefficient and calculated for vertical cylinder by Comsol multiphysics. T_{ext} is the external surface temperature.

The initial temperature of the NH_3BH_3 solution is defined as 25, 30, 35, and 40°C, respectively. The hydrogen storage area and the external walls of the reactor are defined at $T_{\text{amb}}=20^\circ\text{C}$.

Finally, the general energy equation for a constant volume batch reactor can be written as follows.

$$V_r \sum_i c_i C_{p_i} \frac{dT}{dt} = Q + V_r \frac{dP}{dt} \quad (4.7)$$

P is the reactor pressure and is calculated from the ideal gas equation.

$$P = RT \sum c_i \quad (4.8)$$

where R is the ideal gas constant ($R=8.314 \text{ J/molK}$).

Experimental studies were carried out for 200 mM initial NH_3BH_3 concentration and 1 mM carbon supported Pt catalyst (Pt/C) concentration for four different temperatures to validate the mathematical model. The amount of produced hydrogen against time is presented in Figure 4.1. For temperatures of 25, 30, 35 and 40°C, the reaction was completed in 3.32, 2.5, 1.92 and 1.38 minutes, respectively.

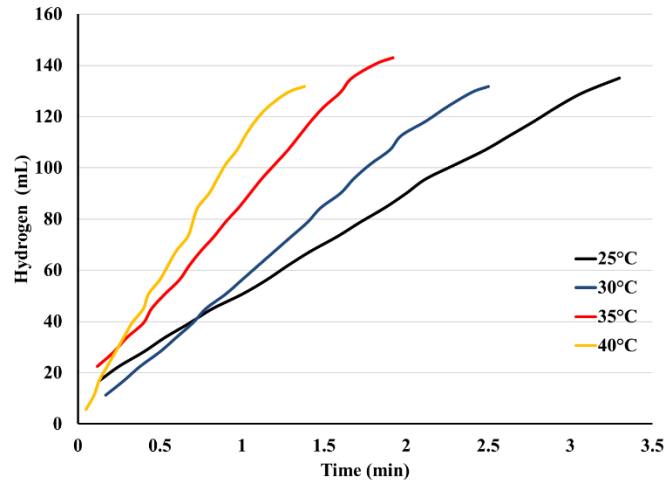


Figure 4.1 Time dependent hydrogen production at four different temperatures

It can be seen that the time-dependent hydrogen production amounts increase linearly from Figure 4.1. Accordingly, it was concluded that the zero-order kinetic model can be used to describe the behavior of the hydrolysis reaction. According to the zero-order kinetic behavior, the rate of consumption of NH_3BH_3 should be equal to the reaction rate constant and the reaction rate should be independent of the reactant concentration. The volumetric hydrogen production amounts were converted to the produced hydrogen gas concentration and the consumed NH_3BH_3 concentration was calculated for each time step.

$$\frac{d[\text{NH}_3\text{BH}_3]}{dt} = k \quad (4.9)$$

$$c_{\text{NH}_3\text{BH}_3_0} - c_{\text{NH}_3\text{BH}_3} = kt \quad (4.10)$$

Figure 4.2 shows $[\text{NH}_3\text{BH}_3]_0 - [\text{NH}_3\text{BH}_3]$ values versus time for four different temperatures. The slope of this graph is equal to the reaction rate constant.

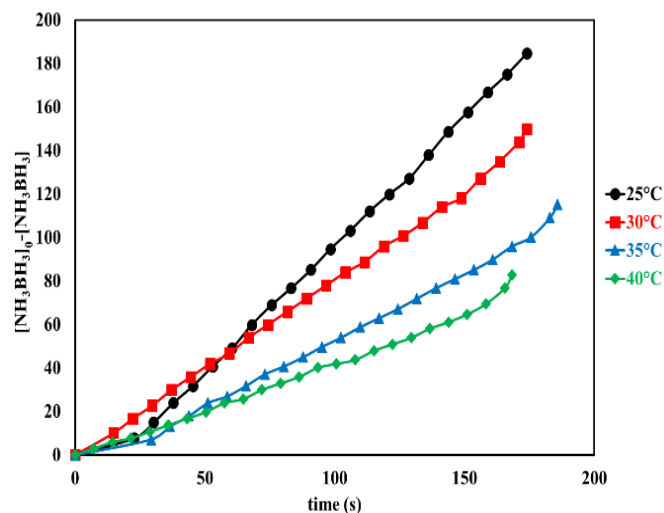


Figure 4.2 Data analysis for zero order kinetic model

The rate constant for the NH_3BH_3 hydrolysis reaction examined at an initial concentration of 200 mol/m^3 in the presence of Pt/C catalyst was calculated as 0.96, 1.25, 1.82 and $2.40 \text{ mol m}^{-3}\text{s}^{-1}$ for four different temperatures, respectively.

The reaction rate constants were used to generate the Arrhenius (Figure 4.3a) and Eyring (Figure 4.3b) plots. The activation energy of the reaction was calculated from the slope of the Arrhenius plot as $E_a = 48.493 \text{ kJ mol}^{-1}$. The reaction enthalpy was calculated as $\Delta H = -45.954 \text{ kJ mol}^{-1}$ from the slope of the Eyring plot.

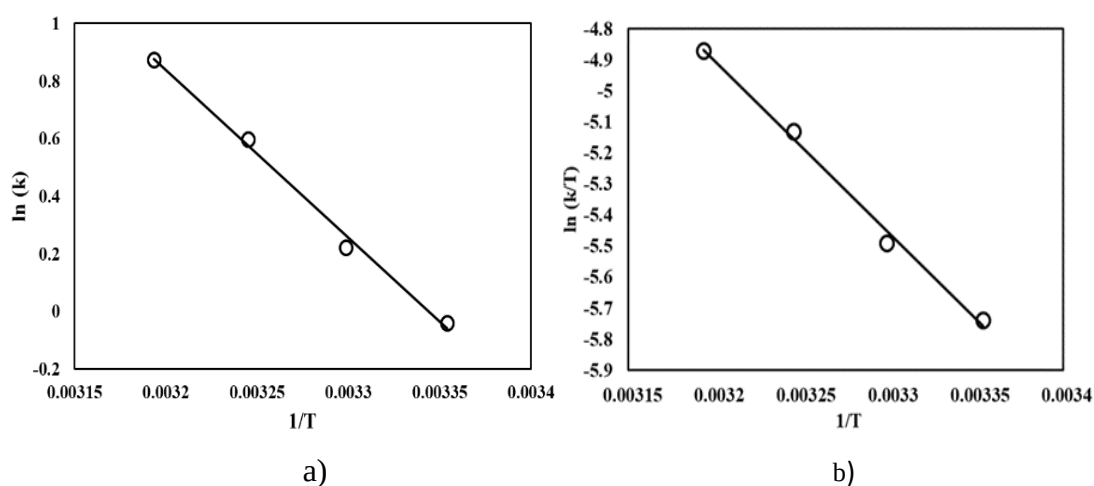


Figure 4.3 a) Arrhenius plot, b) Eyring plot

The mathematical model results developed in the Comsol Multiphysics environment were compared with the experimental findings and the results are shown in Figure 4.4. Accordingly, it can be concluded that the numerical model can predict the experimental results with sufficient precision.

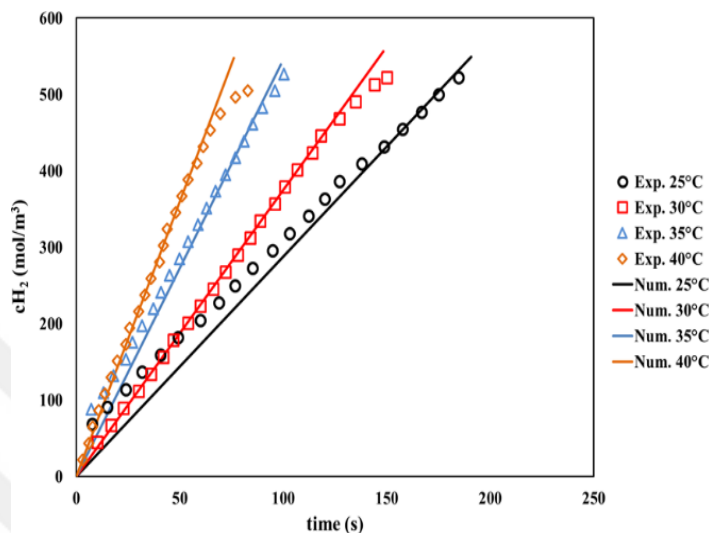


Figure 4.4 Comparison of experimental and numerical results for hydrolysis reaction of NH_3BH_3 in the presence of Pt/C catalyst

In Figure 4.5, reactor surface temperatures are given for 35°C and 40°C. Since the hydrolysis reaction of NH_3BH_3 is an exothermic reaction, the temperature increases with time throughout the reaction. However, because a very small solution volume (10 mL) was investigated, it was observed that the reactor temperature did not change significantly as a result of the reaction.

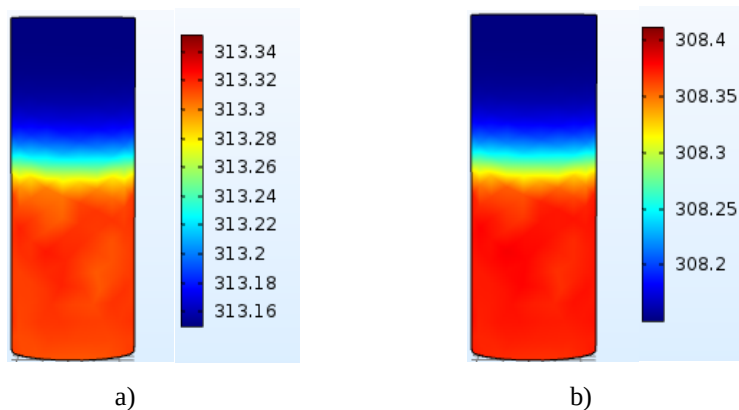


Figure 4.5 Temperature distribution on the reactor surface a) 40°C b) 35°C

4.2 Continuous Porous Reactor Model

The modeled reactor for hydrogen production from NH_3BH_3 is a tubular porous reactor and has a fixed catalyst bed in the middle where the reaction takes place. The substrate solution is fed continuously from the reactor inlet, the fed solution is hydrolyzed in the catalyst bed and the products are taken from the reactor outlet. To model this phenomenon, reacting flow in the porous media module of Comsol was used. This module interface supports both free flow domains (laminar flow region at the reactor inlet) and flow domains in porous media (solution flow in the catalyst bed). The modeled reactor is given in Figure 4.6. Only half of the reactor was modeled using the symmetry condition.

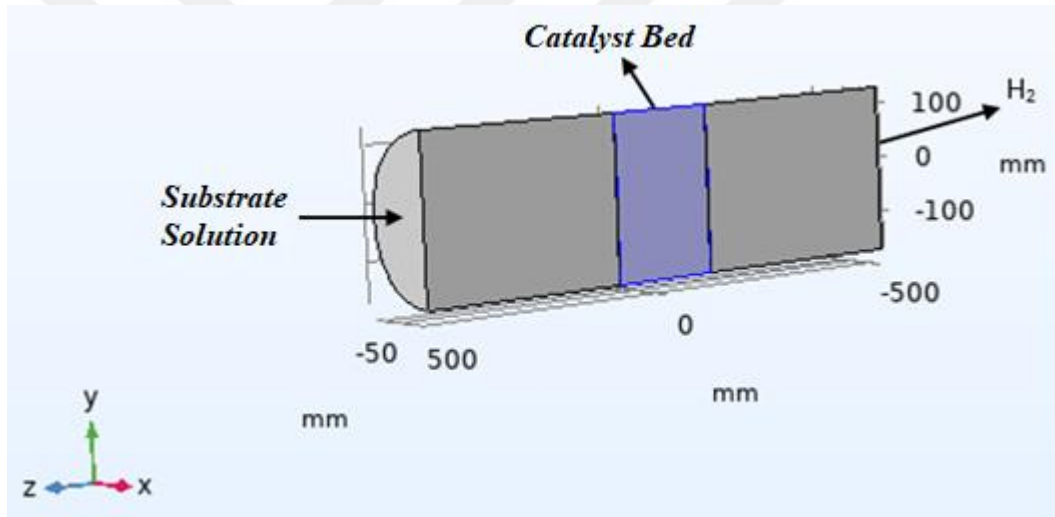


Figure 4.6 Continuous porous reactor

Navier-Stokes equations were used to describe the fluid flow in the free flow regions, and the Brinkman approach, which is a combination of Darcy and Navier Stokes equations, was used to describe the flow in the porous catalyst bed.

For mass transfer, Fick's diffusion approach can be used.

$$u\nabla c_i = \nabla(D_i\nabla c_i) + R_i \quad (4.11)$$

In this equation, c_i is the concentration (mol/m^3), D_i is the diffusivity (m^2/s), and R_i is the reaction rate ($\text{mol/m}^3\text{s}$). Since the reaction takes place only in the catalyst bed, the reaction rate term in the free flow regions is zero. The reaction for NH_3BH_3 hydrolysis in the presence of Ni foam supported Ru catalyst (Basu et al., 2010) is a first-order irreversible reaction and the reaction rates can be written as;

$$R_{\text{NH}_3\text{BH}_3} = -k_r c_{\text{NH}_3\text{BH}_3} \quad (4.12)$$

$$R_{\text{H}_2} = -3k_r c_{\text{NH}_3\text{BH}_3} \quad (4.13)$$

where k_r is the reaction rate constant and is calculated experimentally.

As the boundary condition, a constant velocity profile is assumed at the reactor inlet and constant pressure at the outlet. Similarly, the assumption of constant concentration at the inlet and mass transfer by convection at the outlet is made. The parameters used in the model and their values are given in Table 4.1.

Table 4.1 Parameters for the porous reactor

Parameter		Value	Reference
T_{reaction}	Reaction temperature	296.15 K	(Basu et al, 2009)
ρ_{solution}	Density of NH_3BH_3 solution	978 kg/m^3	(Basu et al, 2009)
μ_{solution}	Kinematic viscosity of NH_3BH_3 solution	8.90×10^{-4} Pa.s	Assumed as water
ε_{Ru}	Porosity of Ruthenium catalyst bed	0.4	(Basu et al, 2009)
κ_{Ru}	Permeability of Ruthenium catalyst bed	1.5×10^{-15}	(Basu et al, 2009)
P_{in}	Inlet pressure	112 kPa	(Basu et al, 2009)
P_{out}	Outlet pressure	101 kPa	(Basu et al, 2009)
u_{in}	Inlet velocity	2.87×10^{-4} m/s	(Basu et al, 2009)
D_{AB}	Diffusivity of NH_3BH_3	1.67×10^{-10} m^2/s	(Basu et al, 2009)
D_{H}	Diffusivity of hydrogen	5.11×10^{-5} m^2/s	(Basu et al, 2009)
$C_{\text{AB,in}}$	Initial concentration of NH_3BH_3	1710 mol/m^3	(Basu et al, 2009)
$C_{\text{H,in}}$	Initial concentration of hydrogen	0.1 mol/m^3	(Basu et al, 2009)
r	Reaction rate	0.35 $\text{mol/m}^3\text{min}$	(Basu et al, 2009)

For the steady-state case, the problem is solved, and the results are presented below.

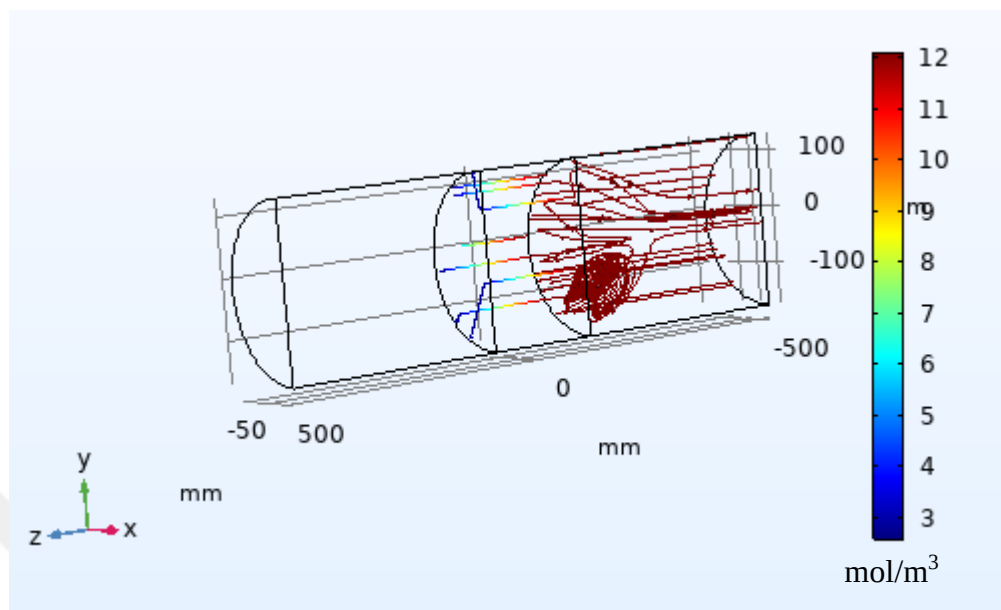


Figure 4.7 Distribution of hydrogen concentration in the reactor, streamline (total flux)

While the hydrogen concentration at the inlet of the reactor is close to zero, when hydrogen is produced in the catalyst bed, the hydrogen concentration at the outlet increases.

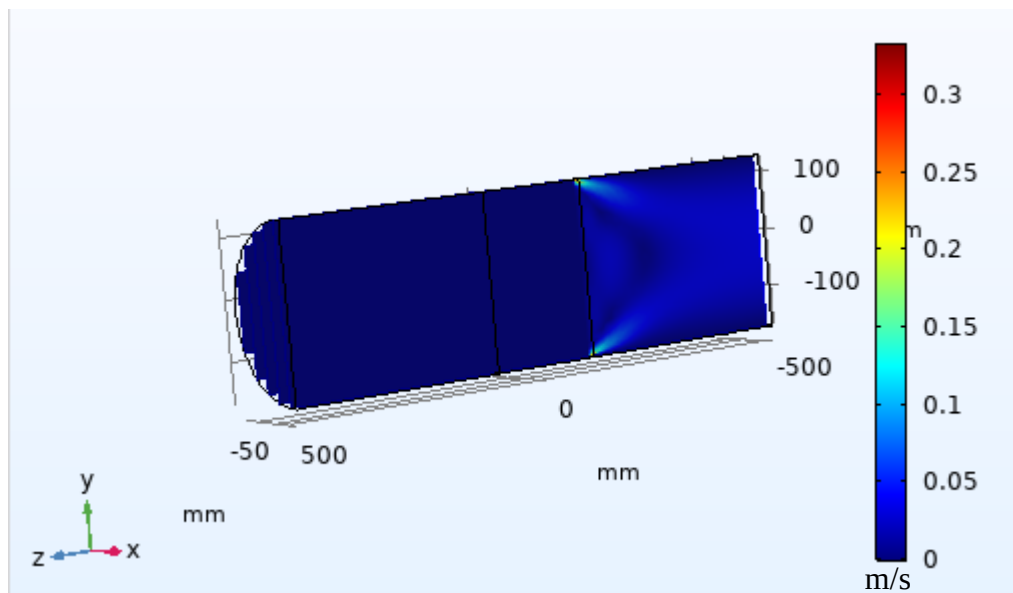


Figure 4.8 Velocity magnitude for free flow and porous flow

The flow is homogeneous at the inlet of the reactor and through the catalyst bed, and the velocity profile changes as hydrogen is produced.

The pressure drop across the porous catalyst bed can be seen in Figure 4.9.

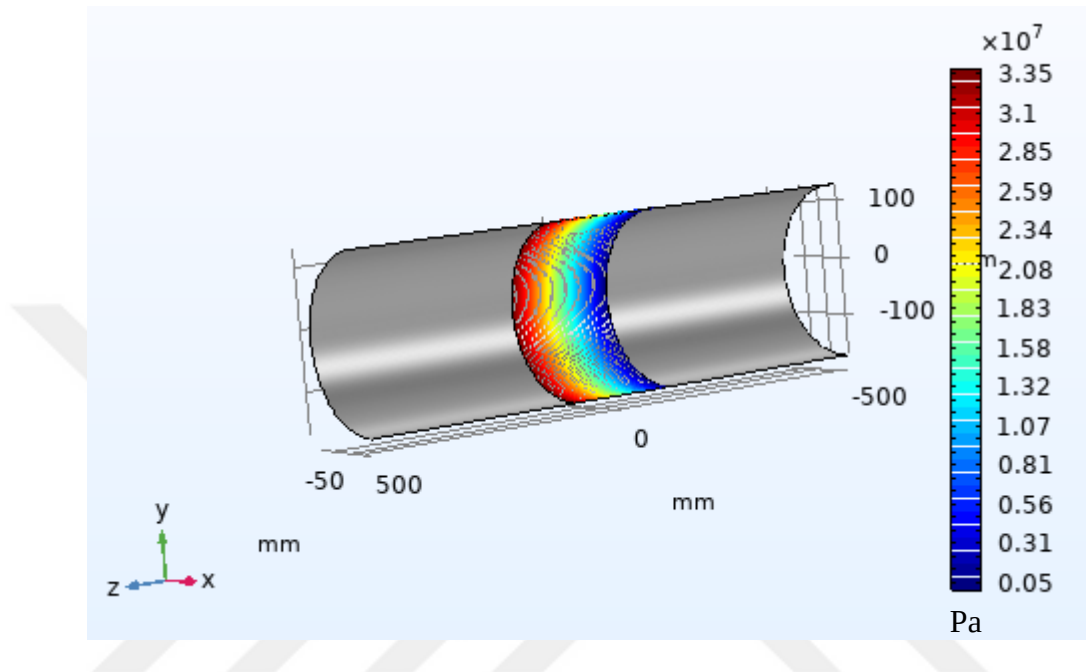


Figure 4.9 Pressure drop in the reactor

CHAPTER FIVE

MATLAB SIMULINK MODEL OF A FUEL CELL VEHICLE WITH SBH HYDROGEN STORAGE SYSTEM

5.1 Component Modeling

Two different configurations of a PEMFC-based FCV, in which the main difference originates from the hydrogen storage unit, are investigated. This unit is either a compressed hydrogen tank (Configuration-1, see Figure 5.1a) or a hydrogen storage system including an on-board hydrogen production unit based on the catalytic hydrolysis of NaBH_4 solution (Configuration-2, see Figure 5.1b). As a case study, for Configuration-1, an internal volume of 80 L and refilling pressure of 700 bar was considered. For Configuration-2, it was considered that the system includes a 50 L fuel storage tank (NaBH_4), a 20 L batch reactor (HR) with 10 L solution and 10 L gas storage volumes, and a 20 L hydrogen storage tank (LPHS) at 150 bars.

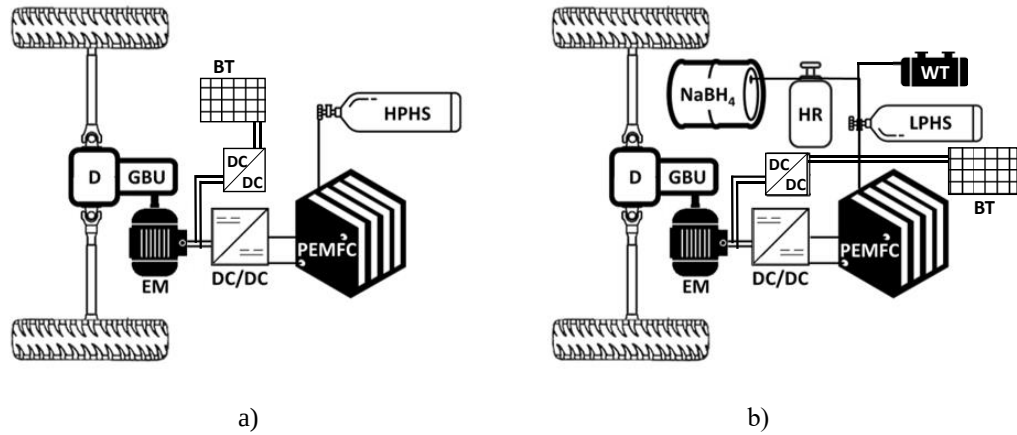


Figure 5.1 Configuration of the fuel cell electric vehicle powertrain based on a) (Configuration-1) compressed hydrogen storage and b) (Configuration-2) sodium borohydride hydrogen storage system (HPHS: High Pressure Hydrogen Storage, LPHS: Low Pressure Hydrogen Storage, WT: Waste Tank, NaBH_4 : sodium borohydride solution, HR: Hydrogen Reactor, PEMFC: Proton Exchange Membrane Fuel Cell, DC/DC: DC/DC converter, EM: Electric Motor, BT: Battery, GBU: Gearbox Unit, D: Differential)

In Configuration-1, the instantaneous hydrogen flow (mol/sec) required for the operation of the PEMFC stack is drawn from the high-pressure hydrogen storage

(HPHS) tank through a pressure regulator and fed into the system. In Configuration-2, it is considered that the hydrogen reactor is filled with the catalyst (e.g., nickel foam supported ruthenium) and the hydrogen production initiates when fuel from the fuel tank is fed to the reactor. As the NaBH_4 fuel inside the reactor is used up, fresh NaBH_4 solution is fed to the reactor from the fuel tank. The produced hydrogen is stored in the 10 L storage section located in the upper part of the reactor, while the excess hydrogen is transferred to the low-pressure storage (LPHS) tank. By-products (NaBO_2 and unreacted NaBH_4) are transferred to the waste tank for disposal during refueling. A required amount of hydrogen is supplied from the LPHS tank to the PEMFC stack with the help of a pressure regulator. The fuel cell system converts the chemical energy of the fuel into electrical energy and the generated electrical energy is fed to the electric motor through a DC/DC converter. The generated power in the electric motor is sent to the gearbox unit. The Gearbox unit adjusts the rotation speed and torque received from the electric motor according to the gear and transmits it to the differential. The differential transmits the movement to the wheels by adjusting the rotation speed and torque.

5.1.1 Fuel Cell System Model

In a PEMFC stack, the power output of the stack (P_{FC}), depends on the operating cell voltage (V_{cell}), current density corresponding to this voltage (i_{cell}), the active area of the cell (A_{cell}), and the number of cells in the stack (n_{cell}) (Mench, 2008).

$$P_{FC} = n_{cell} \cdot i_{cell} \cdot V_{cell} \cdot A_{cell} \quad (5.1)$$

Cell voltage can be found from a zero-dimensional electrochemical model by subtracting the voltage losses (activation, ohmic, concentration, and other losses due to species crossover, short-circuiting, etc.) from the maximum open circuit voltage (Nernst voltage) as shown in Equation 5.2 (Mench, 2008).

$$V_{cell} = V_{Nernst} - V_{activation} - V_{ohmic} - V_{concentration} - V_{other} \quad (5.2)$$

The Nernst voltage can be expressed as a function of temperature and activity of species as follows (Mench, 2008);

$$V_{Nernst} = \frac{\Delta G}{n_{eq} \cdot F} + \frac{R_u \cdot T_{cell}}{n_{eq} \cdot F} \cdot \ln \left(\frac{(a_{H_2})^{y_{H_2}} \cdot (a_{O_2})^{y_{O_2}}}{(a_{H_2O})^{y_{H_2O}}} \right) \quad (5.3)$$

In this equation, the first term on the right side is the temperature dependent term, whereas the second term depends both on temperature and thermodynamic activity. Here ΔG is the Gibbs free energy change of the overall reaction, R_u is the universal gas constant, T_{cell} is the temperature of the cell, n_{eq} is the number of electrons transferred per mole of oxidized hydrogen, F is the Faraday constant, y is the stoichiometric ratio, and a is the thermodynamic activity coefficient of reacting species. For an ideal gas, a is the ratio of the partial pressure of the species concerned to the reference pressure (1 atm). For water vapor, the reference pressure is equal to P_{sat} , since the partial pressure of the vapor cannot exceed the saturation pressure. In this case, the activity is $a_{H_2O} = P_v / P_{H_2O}^{sat}$, which is the relative humidity, RH . The saturation pressure (P_{sat}) is the maximum vapor pressure that can be achieved at equilibrium and is only a function of temperature. Since water formation always occurs on the catalyst surface, after a while an equilibrium between the liquid and gas phase is established here. Therefore, assuming sufficient time, an equilibrium gas-phase mixture of fully saturated ($RH=1$, $P_v=P_{sat}$) air and vapor is formed here, hence the activity of water here is considered to be equal to 1 (Mench, 2008).

To calculate the Nernst voltage, the partial pressures of oxygen and hydrogen must be calculated first. Following equations can be used to calculate the partial pressure of oxygen, hydrogen, and saturation pressure of water respectively (Kandidayeni et al., 2019);

$$P_{O_2} = P_C - (RH_c \cdot P_{H_2O}^{sat}) - \frac{0.79}{0.21} P_{O_2} \exp \left(\frac{0.291 \left(\frac{i_{cell}}{A_{cell}} \right)}{T_{cell}^{0.832}} \right) \quad (5.4)$$

$$P_{H_2} = 0.5RH_a \cdot P_{H_2O}^{sat} \left(\exp \left(\frac{1.635 \left(\frac{i_{cell}}{A_{cell}} \right)}{T_{cell}^{1.334}} \cdot \frac{RH_c \cdot P_{H_2O}^{sat}}{P_a} \right) \right)^{-1} - 1 \quad (5.5)$$

$$P_{H_2O}^{sat} = -2.95 \cdot 10^2 \cdot (T_{cell} - 273.15) - 9.18 \cdot 10^{-5} \cdot (T_{cell} - 273.15)^2 + 1.44 \cdot 10^{-7} \cdot (T_{cell} - 273.15)^3 - 2.18 \quad (5.6)$$

where P_c and P_a are the initial partial pressures of cathode and anode; RH_c and RH_a are the relative humidity of water vapor in the cathode and anode, respectively.

After calculating the Nernst voltage, the voltage losses must be calculated. Activation losses can be calculated using the Tafel equation (Mench, 2008);

$$V_{activation,anode} = \left(\frac{R \cdot T_{cell}}{\alpha_a \cdot F} \right) \cdot \ln \left(\frac{i_{cell}}{i_{o,a}} \right) \quad (5.7)$$

$$V_{activation,cathode} = \left(\frac{R \cdot T_{cell}}{\alpha_c \cdot F} \right) \cdot \ln \left(\frac{i_{cell} + i_x}{i_{o,c}} \right) \quad (5.8)$$

where α is the transfer coefficient, i_x is the crossover current density, and i_0 is the exchange current density referring to the magnitude of current density when the forward and backward reaction rates are equal to each other. Ohmic losses, which are the losses caused by the resistances to transport of ions and electrons along the cell components and contact resistances mainly caused by an imperfect match between cell connections are calculated as follows (Chang, 2011);

$$V_{ohmic} = i_{cell} \cdot \left(\sum_k \frac{l_k}{\sigma_k} + R_{contact}'' \right) \quad (5.9)$$

where l is the thickness, σ is the effective ionic conductivity, and $R_{contact}''$ is the area specific contact resistance. The Ohmic losses due to the transport of electrons through the components are generally negligible (Mench, 2008).

Concentration loss occurs due to the change in the concentration of reacting species during its transport from the gas channel to the catalyst layer and can be calculated by Equation 5.10 (Spiegel, 2008). Concentration losses also occur due to the blockage of diffusion paths and the accumulation of reaction products on the electrode surface (Mench, 2008).

$$V_{concentration} = \alpha' \cdot i_{cell}^{k_m} \cdot \ln \left(1 - \frac{i_{cell}}{i_l} \right) \quad (5.10)$$

where α' is the amplification constant, k_m is the mass transport constant, and i_l is the limiting current density.

Other losses, V_{other} , shown in Equation 5.2, may occur due to electrical short circuits in the fuel cell and crossover of the reactants.

After modeling the fuel cell stack, the required molar flow rate of hydrogen per active area fed to the stack can be determined by the following equation (Mench, 2008). Here it is assumed that the fuel cell stack operates in dead-end mode (i.e., the stoichiometric ratio of the anode is equal to 1).

$$\dot{n}_{H_2,FC}'' = \frac{n_{cell} \cdot i_{cell}}{n_{eq} \cdot F} \quad (5.11)$$

5.1.2 Compressed Hydrogen Storage Model

In the literature, many equations of state such as van der Waals, Redlich-Kwong and Peng-Robinson are used in estimating the pressure, temperature and volume relations of gases. In addition to these methods, the ideal gas equation is also used frequently in the modeling of compressed gas tanks (Xiao, Bénard, & Chahine, 2016; Li et al., 2019). In this part of the study, the ideal gas approach is used in modeling of HPHS and LPHS tanks, since it is easy to apply and can predict the pressure change with 2.86% margin of error compared to the Peng-Robinson equation of state for this

problem. Hence, to determine the initial hydrogen amount in the HPHS tank, the equation can be modified as follows.

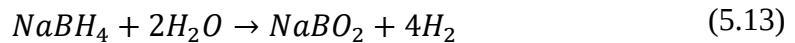
$$n_{H_2} = \frac{P_{HPHS} \cdot V_{HPHS}}{R_u \cdot T_{Tank}} \quad (5.12)$$

where P_{Tank} is the pressure of the tank, V_{Tank} is the volume of the tank, R_u is the universal gas constant (0.08206 L atm mol⁻¹K⁻¹), and T_{Tank} is the tank temperature considered equal to the ambient temperature.

Two-stage pressure reduction process is required in general to feed hydrogen into the fuel cell from the compressed tanks (Chen et al., 2017). The high pressure hydrogen regulator reduces the high pressure hydrogen gas to a certain level, which depends on the design of the pressure regulator (Hua, Roh, & Ahluwalia, 2017); and then the low pressure hydrogen regulator reduces the hydrogen gas pressure from this level to the fuel cell feed pressure. These pressure levels are given in Table 5.1 for the HPHS tank and the LPHS tank.

5.1.3 Sodium Borohydride-Based Storage System Model

The kinetics of the catalytic hydrolysis reaction must be known in order to model the NaBH₄ based hydrogen storage system. The general hydrolysis equation of 10% by weight NaBH₄ solution in the presence of Ni foam/Ru catalyst is as follows (Pinto et al., 2013);



In order to write the rate expression of the reaction, the Langmuir-Hinselwood approach, which is frequently used in determining the kinetic behavior of catalytic reactions, was used. Accordingly, the rate expression of the reaction is written as (Pinto et al., 2013);

$$\frac{dc_{NaBH_4}}{dt} = -r_{NaBH_4} = A \cdot \exp\left(-\frac{E_a}{R_u \cdot T_{reaction}}\right) \cdot \frac{K_a \cdot c_{NaBH_4}}{1 + K_a \cdot c_{NaBH_4}} \quad (5.14)$$

where A is the pre-exponential coefficient, E_a is the activation energy of the reaction, R_u is the universal gas constant, $T_{reaction}$ is the reaction temperature, K_a is the Langmuir-Hinselwood adsorption constant, and c_{NaBH_4} is the concentration of $NaBH_4$ (Pinto et al., 2013).

In order to obtain the amount of hydrogen released over time during the reaction, the experimental data published by Pinto et al. (Pinto et al., 2013) were used. According to Equation 5.14, a zero-dimensional reaction model was established in the Comsol Multiphysics environment and the amount of $NaBH_4$ spent for each time step was determined in moles. Considering the reaction stoichiometry, the time-dependent expression of the amount of hydrogen released in each time step for the given conditions is derived in the Comsol environment as follows.

$$\frac{dc_{H_2}}{dt} = 3 \cdot 10^{-14}t^5 - 2 \cdot 10^{-10}t^4 + 5 \cdot 10^{-7}t^3 - 6 \cdot 10^{-4}t^2 + 0.4014t - 0.0226 \quad (5.15)$$

Equation 5.15 was transferred to the system level code developed in Matlab Simulink as an input parameter. Considering the stoichiometric ratios in Equation 5.13, the volume of the required $NaBH_4$ solution to produce the initial hydrogen amount in the HPHS tank can be calculated as follows (Pinto et al., 2013);

$$V_{solution} = \frac{n_{NaBH_4} \cdot M_{NaBH_4}}{\rho_{NaBH_4}} + \frac{n_{H_2O} \cdot M_{H_2O}}{\rho_{H_2O}} \quad (5.16)$$

where n_{NaBH_4} and n_{H_2O} are the numbers of moles of $NaBH_4$ and H_2O , M_{NaBH_4} and M_{H_2O} are the molecular weight of $NaBH_4$ and H_2O , and ρ_{NaBH_4} and ρ_{H_2O} are the density of $NaBH_4$ and H_2O , respectively.

Values of all input parameters used in the hydrogen storage system and PEMFC system model are given in Table 5.1.

Table 5.1 Input parameters for the hydrogen storage and PEMFC system

	Parameter	Symbol	Value	Unit	Ref.
NaBH ₄ based H ₂ storage	Pre-exponential coefficient	A	1.33×10^{-7}	mol/min	(Pinto et al., 2013)
	Activation energy of the reaction	E _a	67267	J/mol	(Pinto et al., 2013)
	Reaction temperature	T _{reaction}	298.15	K	(Pinto et al., 2013)
	Adsorption coefficient	K _a	22.2	L/mol	(Pinto et al., 2013)
	Low pressure tank pressure	P _{LPHS}	150	bar	-
	Low pressure tank volume	V _{LPHS}	20	L	-
	Minimum pressure level for LPHS	P _{LPHS,min}	10	bar	-
HPHS Tank	High pressure tank pressure	P _{HPHS}	700	bar	-
	High pressure tank volume	V _{HPHS}	80	L	-
	Tank temperature	T _{Tank}	298.15	K	-
	Minimum pressure level for HPHS	P _{HPHS,min}	30	bar	-
PEMFC System	Fuel cell temperature	T _{cell}	80	°C	(Spiegel, 2008)
	Active area of the fuel cell	A _{cell}	300	cm ²	(Spiegel, 2008)
	Number of cells	n	370	-	-
	Hydrogen pressure in the fuel cell	P _a	303.98	kPa	(Spiegel, 2008)
	Air pressure in the fuel cell	P _c	303.98	kPa	(Spiegel, 2008)
	Relative humidity of the anode	RH _a	%100	-	-
	Relative humidity of the cathode	RH _c	%100	-	-
	Transfer coefficient of the anode	α _a	0.84	-	(Shimpalee, Beuscher, & Zee, 2006)
	Transfer coefficient of the cathode	α _c	2	-	(Shimpalee, Beuscher, & Zee, 2006)
	Exchange current density of the anode	i _{o,a}	0.6	A/cm ²	(Shimpalee, Beuscher, & Zee, 2006)
	Exchange current density of the cathode	i _{o,c}	0.0006	A/cm ²	(Shimpalee, Beuscher, & Zee, 2006)
	Anode thickness	l _{anode}	10×10^{-5}	cm	(Mench, 2008)
	Cathode thickness	l _{cathode}	5×10^{-5}	cm	(Mench, 2008)
	Electrode thickness	l _{electrode}	51×10^{-5}	cm	(Mench, 2008)
	Conductivity of anode	σ _{anode}	0.332	S/cm	(Mench, 2008)
	Conductivity of cathode	σ _{cathode}	0.332	S/cm	(Mench, 2008)
	Conductivity of electrode	σ _{electrode}	0.83	S/cm	(Mench, 2008)
	Contact resistance	R _{contact}	0.03	Ohm/cm ²	(Mench, 2008)
	Crossover current density	i _x	0.32	mA/cm ²	(Francia et al., 2011)
	Amplification constant	α'	0.085	-	(Spiegel, 2008)
	Mass transport constant	k	1.1	-	(Spiegel, 2008)
	Limiting current density	i _l	1.4	A/cm ²	(Spiegel, 2008)

5.1.4 Vehicle Model

Evaluation of the performance of a fuel cell vehicle (FCV) is generally done through a vehicle simulation according to a proper vehicle speed profile by assessing the effects of vehicle components and their parameters. The power requirements of the electric motor of the passenger car are found by calculating the resistive forces of the vehicle motion under a given speed profile. These resistive forces including rolling resistance (F_R), grading resistance (F_{St}), air resistance (F_L), and acceleration resistance (F_a) cause torque demand in vehicle tires that electric motor must overcome. The equations used to calculate these resistive forces are given below.

$$F_R = m \cdot g \cdot f_R \quad (5.17)$$

$$F_{St} = m \cdot g \cdot \sin \delta \quad (5.18)$$

$$F_L = \frac{1}{2} \cdot \rho_a \cdot A \cdot C_W \cdot V^2 \quad (5.19)$$

$$F_a = m \cdot a \quad (5.20)$$

where m is the vehicle mass, g is the acceleration of gravity, f_R is the coefficient of rolling resistance, δ is the slope angle, ρ_a is the density of air, C_W is the aerodynamic coefficient of the vehicle, V is the vehicle speed, and a is the acceleration of the vehicle in the positive (traction) or negative (braking) direction.

According to the motion equation of the vehicle and the model characteristics of the FCV components, the main assumptions of the vehicle powertrain model are as follows (Huang, Kuo, & Han, 2017):

- Longitudinal movement of the vehicle is considered for the motion equations,
- Tire radius is assumed constant and tire slip is ignored,

- Vibrations and the effect of dampers are neglected in the vehicle,
- The vehicle moves in a straight road without slope angle ($\delta=0^\circ$) and steering angle,
- The effect of wind on air resistance is ignored,
- Electric motor efficiency, DC/DC converter efficiency, mechanical efficiency, and electric motor voltage are assumed constant,
- Enough power capacity exists on the electric motor and fuel cell stack during the operation of the vehicle.

The power requirement in the electric motor of the vehicle (P_{EM}) can be shown as a function of the total resistive forces, the vehicle speed, the mechanical efficiency (η_M), and the electric motor efficiency (η_{EM}), as shown in Equation 5.21. According to the electric motor power, the current output of the electric motor (I_{EM}) can be found using constant motor voltage (V_{EM}), as shown in Equation 5.22. The current demand from the fuel cell stack (I_{FC}) can be calculated by Equation 5.23 and Equation 5.24 according to the positive and negative signs of the electric motor current. The effect of the efficiency of the DC/DC converter is included in this equation to find the stack current for the positive electric motor current requirements. Additionally, if the electric motor current is equal to zero, which means the vehicle is stopping, there is no current output from the fuel cell stack and battery. On the other hand, I_{FC} is limited to a maximum value of 250 A and the battery current (I_{Bat}) is produced when the current demand is above 250 A, which can be shown in Equation 5.25. The battery also operates when the electric motor current is negative, for recharging with regenerative energy.

$$P_{EM} = \frac{(F_R + F_{St} + F_L + F_a) \cdot V}{\eta_M \cdot \eta_{EM}} \quad (5.21)$$

$$I_{EM} = \frac{P_{EM}}{V_{EM}} \quad (5.22)$$

$$I_{FC} = \frac{P_{EM}}{V_{EM} \cdot \eta_{DC/DC}} \Rightarrow I_{EM} > 0 \quad (5.23)$$

$$I_{FC} = 0 \Rightarrow I_{EM} \leq 0 \quad (5.24)$$

$$I_{Bat} = \frac{I_{EM} - I_{FC}}{\eta_{Bat}} \Rightarrow I_{EM} > 250 \text{ A} \quad (5.25)$$

$$I_{Bat} = 0 \Rightarrow 250 \text{ A} < I_{EM} \leq 0 \quad (5.26)$$

$$I_{Bat} = 0 \Rightarrow I_{EM} \leq 0 \quad (5.27)$$

$$P_{Bat} = I_{Bat} \times V_{Bat} \quad (5.28)$$

Fuel cell stack current, which is the main parameter to determine the hydrogen consumption, is an output parameter of the vehicle model.

5.1.5 Battery Model

The battery block is designed to determine the state of charge (SOC) of the vehicle battery for 1.6 kWh battery capacity (Q_{Bat}) using an equivalent circuit model. The battery is defined as a constant voltage source of 245 V for charging and discharging. The SOC history is calculated using Equation 5.29 according to the battery capacity and instantaneous battery power starting from the initial SOC value (SOC_i). On the other hand, the vehicle range (R) is represented in Equation 5.18 as a function of the driving cycle distance and the total energy consumption during the cycle time (from 0 to t_{last}).

$$SOC(t) = SOC_i - \frac{1}{Q_{Bat}} \int_0^t P_{Bat} \cdot dt \quad (5.29)$$

$$R = \left(\int_0^{t_{last}} V \cdot dt \right) \cdot \frac{Q_{Bat}}{\int_0^{t_{last}} P_{Bat} \cdot dt} \quad (5.30)$$

where V is the vehicle speed according to the drive cycle and P_{Bat} is battery power output.

5.2 Vehicle Simulation

A fuel cell hybrid powertrain system model is developed in Matlab/Simulink environment to compare the vehicle range of an FCV for two different powertrain configurations as shown in Figure 5.2. The main input parameters for the vehicle and powertrain components are listed in Table 5.2. The vehicle resistance forces (Equations 5.17-5.20) are calculated to find the electric motor power requirement (Equation 5.21) in the Electric Motor block based on the input parameters of the simulation such as the vehicle speed and the accelerations from the vehicle speed profile. A DC/DC converter block is integrated into the outlet of the electric motor block. The current output of the DC/DC converter is demanded by the fuel cell and battery. The battery management block is designed to determine the battery current. The battery operates as a secondary energy source when the current request from the fuel cell is over 250 A. On the other hand, regenerative energy is stored in the battery if the electric motor current has negative values. The battery block is used for the SOC estimation according to the battery current. The fuel cell stack current requirements are the input parameters of the “H₂ balance for FC current” subsystem and two subsystems called “Partial Pressures and Voltage Losses” and “Output Voltage of FC”, as shown in Figure 5.2, to find the stack voltage. Hydrogen consumption of the fuel cell vehicle is calculated by the “Fuel Cell” block in the simulation model (Figure 5.2) during the operation time of the vehicle based on the drive cycle. Additionally, the amount of hydrogen production is determined for Configuration-1 that NaBH₄ compounds are used as the hydrogen source as discussed in Section 5.1.3 (Equation 5.15). On the other hand, the “Fuel Cell” block of the simulation model includes the calculation of pressure loss of the hydrogen tank according to Section 5.1.2 (Equation 5.12) for Configuration-2. Fuel cell stack voltage, which is the other main output of the

simulation, is calculated according to the voltage losses and Nernst voltage (Section 5.1.1).

Table 5.2 The main input parameters of the vehicle simulation

Parameter	Symbol	Value	Unit
Vehicle mass	m	1850	kg
Coefficient of rolling resistant	f_R	0.015	-
Aerodynamic drag coefficient	C_W	0.29	-
Projection area of the vehicle	A	2.37	m ²
Density of air	ρ	1.22	kg/m ³
Dynamic tire radius	r_{dyn}	0.33	m
Battery capacity	Q_{Bat}	1.6	kWh
Battery voltage	V_{Bat}	245	V
Battery efficiency	η_B	0.9	-
Mechanical efficiency	η_M	0.9	-
Electric motor efficiency	η_{EM}	0.9	-
Electric motor voltage	V_{EM}	650	V
Converter efficiency	$\eta_{DC/DC}$	0.9	-

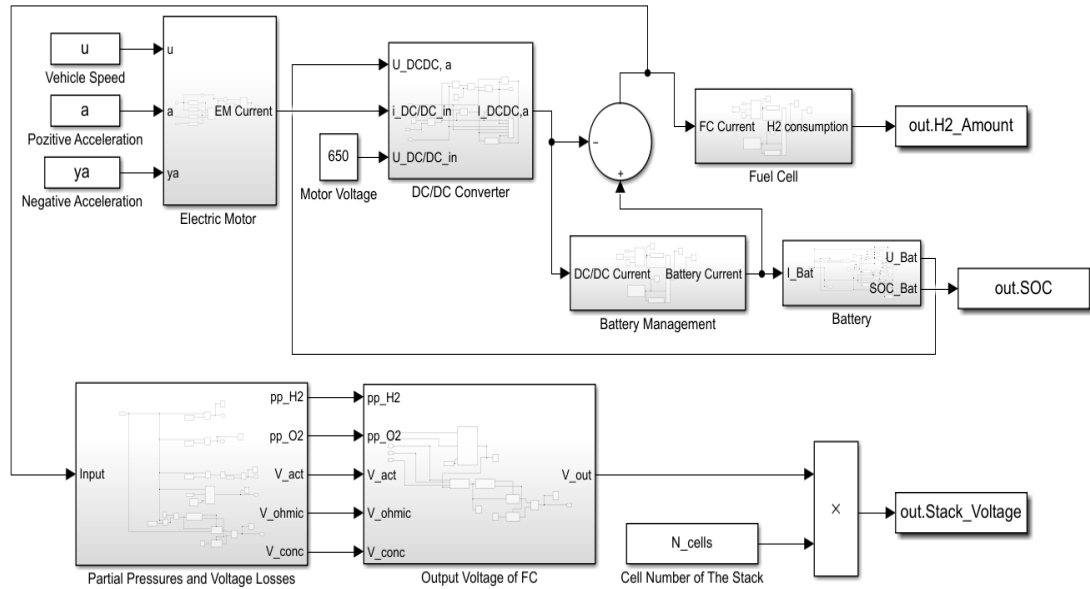


Figure 5.2 Simulink model of the fuel cell electric vehicle powertrain

The drive cycle profile of the New European Drive Cycle (NEDC) is used as the input parameters of the simulation model to define the operating characteristics of the

vehicle. NEDC is the standard test cycle in Europe for the calculations of emission regulations and vehicle performance of passenger cars and light-duty vehicles. NEDC drive cycle is a combination of Urban Drive Cycle (UDC or called ECE-15) and Extra Urban Driving Cycle (EUDC), which has 50 km/h maximum speed in the first part of the cycle (from beginning to 780 seconds) for urban and 120 km/h maximum speed in the last part of the cycle (after 780 seconds) as extra-urban driving conditions. NEDC drive cycle contains 1.042 m/s^2 maximum acceleration, 0.506 m/s^2 average acceleration during the cycle time, and 10.9314 km distance can be achieved at the end of the cycle. For the simulation of the FCV, vehicle speed variations in NEDC are shown in Figure 5.3a. FC stack current requirement is calculated during the simulation time presented in Figure 5.3b to determine the stack voltage of the fuel cell.

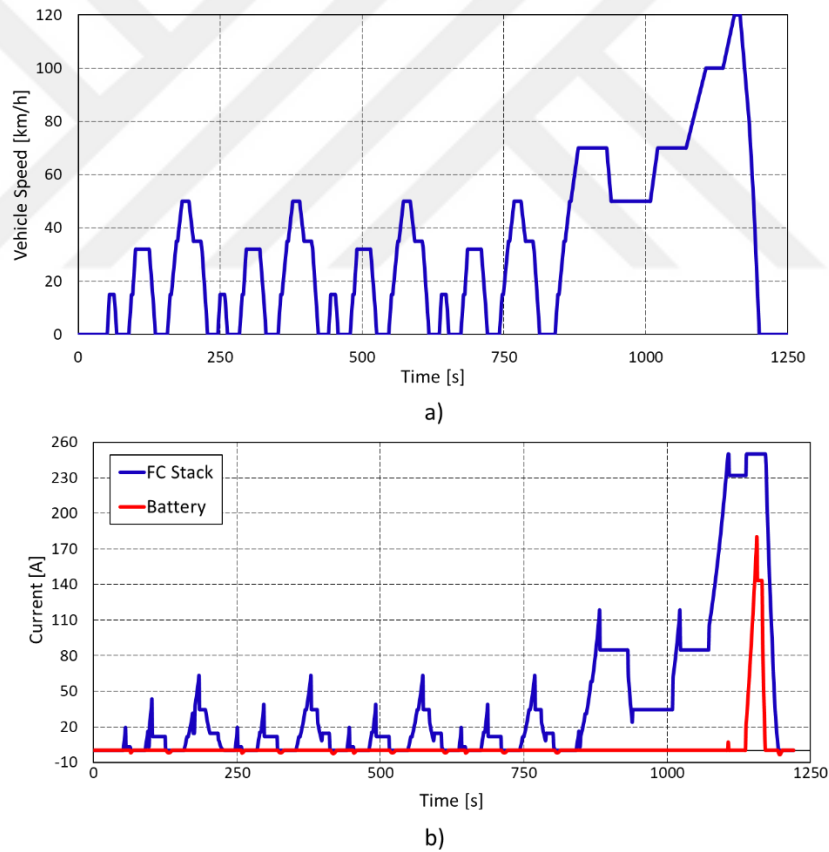


Figure 5.3 a) Speed input of the vehicle for drive cycle simulation and b) fuel cell stack current requirements

5.3 Results and Discussion

Current requirements of the fuel cell stack, which are determined by the vehicle model mentioned in Section 5.2, are the main parameters to calculate the stack voltage and operating cell voltage during the simulation time of the NEDC drive cycle. The cell voltage of the fuel cell is calculated according to Equation 5.2 for the required current of the fuel cell. To determine the stack voltage, it is assumed that each cell produces the same voltage for the current input. The stack voltage is shown in Figure 5.4a for the operation of the FCV during the simulation period. Stack voltage output changes between 360 V and 300 V until the current requirements of the fuel cell are above 110 A. Higher current demands (>100 A) from the fuel cell cause lower stack voltage outputs (min 200 A) of the fuel cell. Additionally, operating points for the fuel cell voltage are given in Figure 5.4b according to the current density of the fuel cell stack.

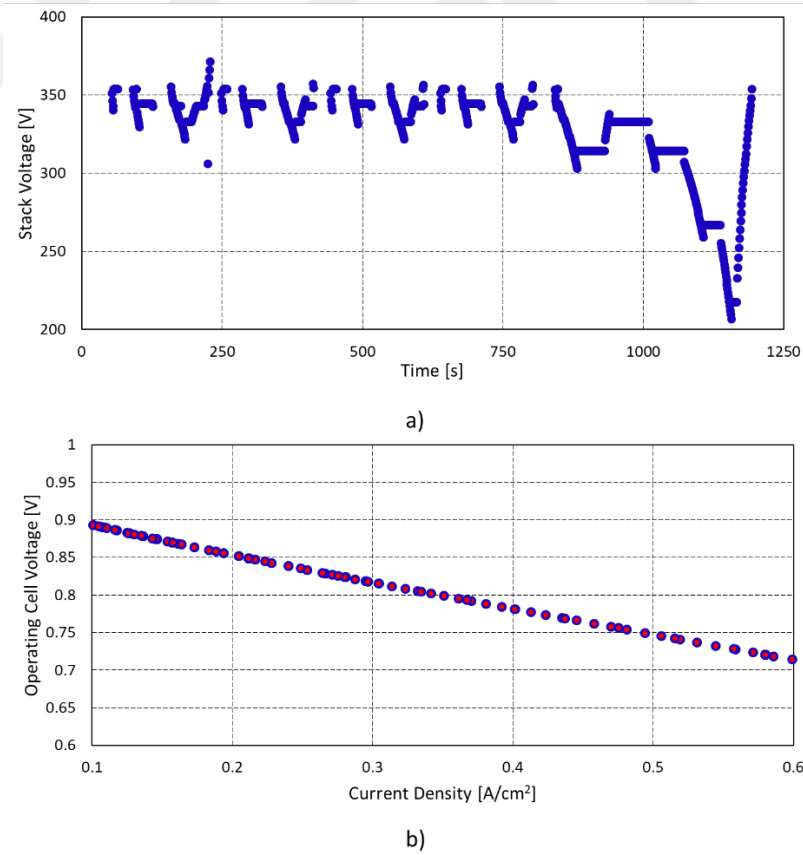


Figure 5.4 a) Stack voltage and b) operating points of the fuel cell during the drive cycle simulation

The battery starts to operate at the end of the drive cycle when the current requirement of the electric motor is higher than 250 A. Before the operation of the battery, regenerative energy is stored in the battery. SOC condition of the battery is shown in Figure 5.5 for the drive cycle simulation period. Regions for the SOC increase for the stored regenerative energy and the SOC decrease for starting the operation of the battery are clearly shown in Figure 5.5. The final SOC value is found as about 68% at the end of the drive cycle.

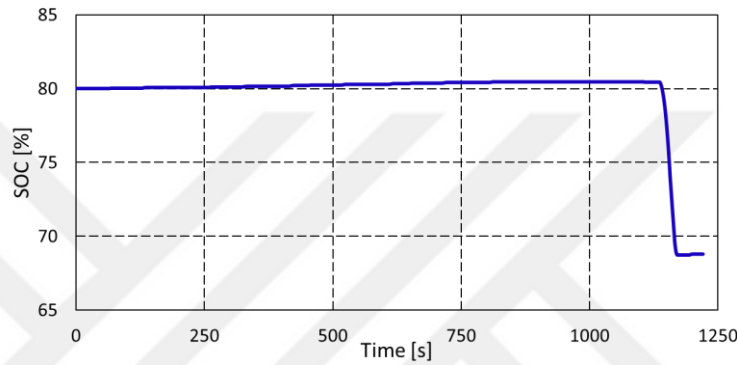


Figure 5.5 SOC history of the battery during the drive cycle simulation period

Figure 5.6 shows the total and instantaneous hydrogen production and consumption values over time. As seen in Figure 5.6a, after feeding NaBH_4 fuel to the reactor, hydrogen production starts at a rate of 0.4 mol/s. Instantaneous hydrogen production is above the consumption until the 567th second, but after this second, the instantaneous hydrogen production decreases with the decrease of fuel in the reactor. However, more than the consumed hydrogen until the 567th second is produced, and since the excess hydrogen is stored in the LPHS, there is no need to feed fresh fuel to the reactor until the end of the cycle. In addition, the maximum hydrogen consumption rate of the vehicle occurs at the 1105th second of the cycle and its value is 0.48 mol/s.

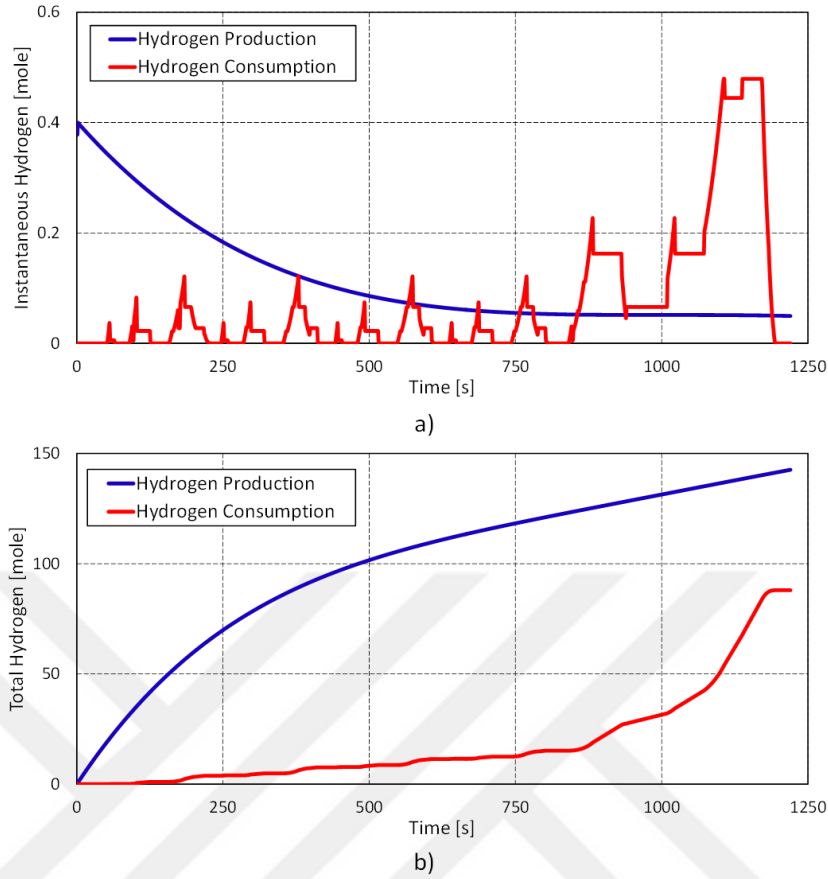


Figure 5.6 a) Instantaneous and b) total hydrogen productions and consumptions during the drive cycle simulation period for 10 liters NaBH_4 solution used as the hydrogen source

When Figure 5.6b is examined, it can be seen that the total produced hydrogen in the reactor is 142.53 moles at the end of the reaction. Until the 500th second of the cycle, the hydrogen production is very fast, but after this second, the hydrogen production slows down since the fuel in the reactor decreases. On the other hand, total hydrogen consumption up to the 750th second of the cycle is very low, below 15 moles. After this moment, there is a fluctuating increase in consumption due to the increased hydrogen demand associated with the acceleration of the vehicle, and 87.95 moles of hydrogen were consumed at the end of the cycle.

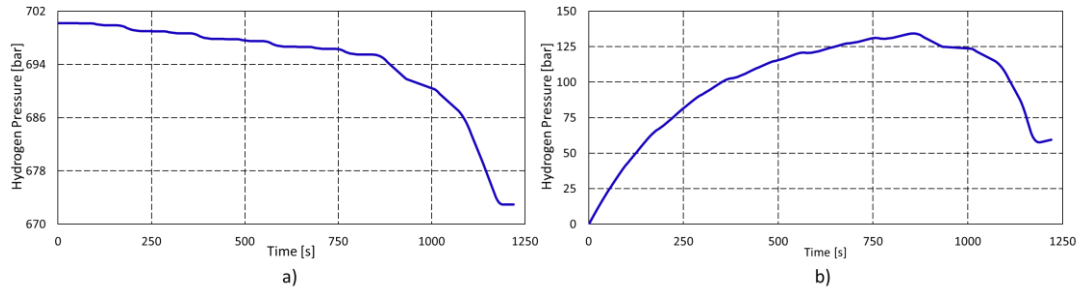


Figure 5.7 Hydrogen pressure of a) the HPHS tank and b) LPHS tank during the drive cycle simulation period

In Figure 5.7a, the pressure drop in the HPHS is given. Accordingly, due to the low hydrogen demand at the beginning of the cycle, the pressure drop in the HPHS tank is also low, and the pressure of the tank is 696.25 bar at the 750th second. On the other hand, in the last part of the cycle in which extra-urban driving conditions are examined, the pressure drop of the HPHS tank increases with the rising hydrogen demand. Therefore, between the 890th and 1000th seconds of the cycle, there is a 10 bar decrease in the tank pressure. After the 1000th second, the tank pressure tends to drop rapidly due to the increase in vehicle speed. HPHS tank pressure at the end of the cycle is approximately 673 bar and the total pressure drop in the tank is 27.25 bar throughout the cycle. Figure 5.7b shows the pressure change of the LPHS throughout the cycle. In the 20th second of the cycle, the pressure reaches 10 bar, which is the empty pressure value of the tank, and does not fall below this value until the end of the cycle. On the other hand, the movement of the vehicle and consequently the hydrogen consumption starts in the 52nd second of the cycle and the pressure of the LPHS for this moment is 23.91 bar. In addition, the pressure of the LPHS is 67.72 bar at the end of the cycle. Accordingly, it can be said that hydrogen can be easily drawn from the tank during the cycle.

Table 5.3 compares two different types of hydrogen storage systems in terms of the storage volume, the vehicle range, and the consumed hydrogen. The LPHS tank has the advantage of providing 60 liters less volume and 550 bar less pressure compared to the compressed gas tank. Accordingly, the NaBH₄ based H₂ storage system provides safer storage in case of a possible accident since the components are operating at lower pressure in the system. The compressed gas tank can supply the fuel cell stack in the

vehicle until the tank pressure drops to 30 bar, whereas there is no pressure restriction for the NaBH_4 hydrogen storage system. However, in the system considered, excess hydrogen in the hydrogen reactor is stored in a low-pressure storage tank and the empty pressure for this tank is 10 bar. On the other hand, since the LPHS pressure does not drop to the empty tank pressure value, it can supply hydrogen until the end of the cycle. Accordingly, the NaBH_4 system can supply hydrogen until the fuel tank is completely depleted and the pressure of the LPHS drops to 10 bar and has a range of 273.94 km; whereas the range of the vehicle fed by the compressed hydrogen tank is 262.35 km. In addition, as can be seen in Figure 5.7a, the compressed gas tank provides a total pressure drop of 27.25 bar at the end of a cycle and the corresponding mole of consumed hydrogen is 87.95. In addition, at the end of a cycle, the content of hydrogen tanks decreases by 3.89%. Accordingly, the occupancy rate of the storage systems is calculated as 96.11%.

Table 5.3 Comparison of the results for two different storage methods

Parameter	NaBH_4	Compressed H_2
Hydrogen Storage Tank Volume	20 liters	80 liters
Hydrogen Storage Tank Pressure	150 bars	700 bars
Vehicle Range	273.94 km	262.35 km
Consumed Hydrogen and Pressure Drop in One Cycle	87.95 mole	27.25 bar
Hydrogen Changing in One Cycle	%3.89	%3.89

CHAPTER SIX

ECONOMIC AND ENVIRONMENTAL ASSESSMENT OF HYDROGEN POWERED VEHICLES

6.1 Economic and Environmental Effects of Fuels and Vehicles

It is known that pollutants originating from vehicle systems and fuels have harmful effects on the environment and human health, and the transition to electric vehicles is considered as a solution to minimize these effects. (Huo, Wu & Wang, 2009). Although FCVs are known as zero-emission vehicles, they should be evaluated in terms of greenhouse gas production and other environmental impacts when the production stage of the hydrogen fuel is taken into account. In order to determine the environmental effects of a fuel cell vehicle, an analysis called well-to-wheel (WTW) can be done. WTW analysis covers the process from the production of the fuel until it is delivered to the vehicle. (Huang & Zhang, 2006). The GREET software, developed by the Argonne National Laboratory (ANL) under the sponsorship of the US Energy Ministry, is used as an effective tool to estimate emissions and there are many studies using this software in the literature (Huang & Zhang, 2006). On the other hand, despite the policies encouraging the use of fuel cell vehicles, it is thought that there are economic obstacles to the widespread use of these vehicles yet (Wróblewski et al., 2021). In many studies in the literature, it has been stated that a realistic economic analysis is needed to determine the costs and benefits associated with the purchase and use of zero emission vehicles (Ellram, 1995). For this purpose, the total cost of ownership (TCO) method can be used. In this study, AFLEET Tool, which was created by ANL based on GREET software, was used to evaluate a FCV for two different fuel, compressed gas H₂ and SBH based H₂, from an economic and environmental point of view and to compare it with an ICEV using gasoline.

6.2 Environmental Assessment

Within the scope of this thesis, WTW analysis was performed for three different vehicles, the conventional ICEV, the FCV using compressed gas H₂ tank and the FCV using sodium borohydride hydrogen storage system, and the vehicles were evaluated from an environmental point of view by AFLEET Tool. Petroleum use, greenhouse gas emissions and air pollutants (carbon monoxide (CO), nitrogen oxide (NO_x), particulate matter (PM₁₀ with a diameter of less than 10 µm and PM_{2.5} with a diameter of less than 2.5 µm), volatile organic compounds (VOC) and sulfur oxide (SO_x)) were investigated.

VOC emissions are the exhaust and evaporative emissions, while PM, NO_x and CO emissions are exhaust emissions only (Wang et al., 2020). VOC and NO_x have been reported as two pollutants responsible for ozone depletion (Huo, Wu & Wang, 2009). SO_x, on the other hand, is quite harmful to the environment because it causes air pollution and pollutes soil and water with acid rain. Particulate matter is known to increase respiratory diseases and the negative effects of CO on human health have been known for many years.

For the WTW analysis, the energy consumption is affected by parameters such as the fuel economy of the vehicle, the lower heating value of the fuel and the density of the fuel, and is determined as follows (Wang et al., 2020);

$$EC_j = (LHV_j \cdot \rho_j) / (FE_j \cdot 100) \quad (6.1)$$

where j is the fuel type, EC_j is the energy consumption for fuel, LHV_j is the lower heating value of fuel, ρ_j is the density of the fuel, and FE_j is the fuel economy of the vehicle.

In the calculation of the emissions mentioned above, the following equation is used (Wang et al., 2020);

$$EM_i = \sum j \sum k EF_{i,j,k} \cdot FC_{j,k} \quad (6.2)$$

where i is the pollutant, k is the fuel production technology, EM_i is the emission of a pollutant, $EF_{i,j,k}$ is the emission factor of a burned fuel, $FC_{j,k}$ is the fuel consumption.

Fuel economies for vehicles using gasoline, compressed gas hydrogen and SBH-based hydrogen have been accepted as 30.93, 73.49 and 73.49 miles per gasoline gallon equivalent (MPGGE), respectively. The annual and lifetime pollutant values obtained as a result of the analysis are presented in the graphs below.

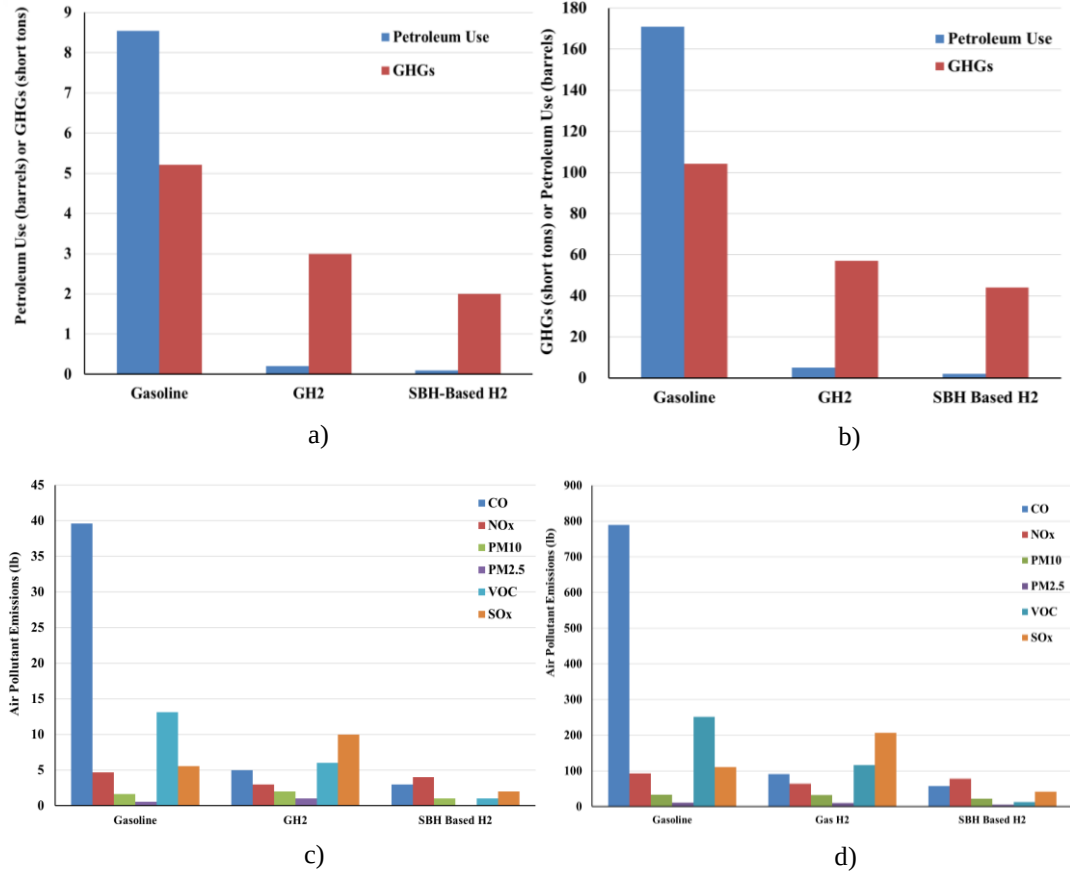


Figure 6.1 Petroleum use, GHGs and air pollutants emissions for three different fuels a) annual petroleum use and GHGs emissions, b) lifetime petroleum use and GHGs emissions, c) annual air pollutants emissions, d) lifetime air pollutants emissions

For FCVs that have zero emissions during the use of the vehicle, the amount of greenhouse gas (GHG) released, petroleum use and air pollutants emissions rates are

considerably lower than gasoline vehicles. The source of the emissions seen in Figure 6.1 is the need for electricity and oil during hydrogen production, compression and transport, and electricity is produced by natural gas or coal. In this study, it is assumed that compressed gas hydrogen production is made by steam methane reforming, and SBH-based hydrogen production is made by catalytic hydrolysis of SBH. In order to take into account the pollutants caused by the electricity used in the SBH production process, it is assumed that 0.5 kWh of electricity is used per kg of SBH (Law et al, 2013). Less environmental impacts in the hydrogen production phase have resulted in fewer emissions in SBH-based hydrogen production. Although all emissions are lower for hydrogen vehicles than for gasoline vehicles, the PM emission values for gasoline vehicles and hydrogen vehicles are similar since PM emissions are also caused by tire and brake wear (Winkler et al., 2018).

6.3 Economic Evaluation

TCO basically consists of two parameters: the total costs of the vehicle in use and the loss of value that will occur if the vehicle is resold (Guo & Zhou, 2019). These costs vary depending on where the vehicle is used. Within the scope of this thesis, an economic analysis has been made for a passenger vehicle used in New York City. Some features of the vehicle and parameters used in TCO analysis are given in Table 6.1 and Table 6.2.

Table 6.1 Specifications of the vehicles

Fuel Type	Annual Mileage	Fuel Economy (MPGGE)	Purchase Price (\$/vehicle)	Maintenance&Repair (\$/mi)	Ref.
Gasoline	12400	30.93	20000	0.15	Burnham, 2016
Compressed Gas H ₂	12400	73.49	50000	0.09	Burnham, 2016
SBH based H ₂	12400	73.49	50000	0.09	Burnham, 2016

Table 6.2 TCO analysis parameters

Parameters	Value	Ref.
Gasoline price	2.41 \$/gallon	Burnham, 2016
Compressed Gas H ₂ Price	12.0 \$/kg	Law et al, 2013
SBH based H ₂ Price	10.4 \$/kg	Law et al, 2013
Years of planned ownership	20 years	Assumed
Loan term	5 years	Burnham, 2016
Interest rate	4.20%	Burnham, 2016
Percent down payment	12%	Burnham, 2016
Escalation rate for H ₂	1.8%	Burnham, 2016
Escalation rate for Gasoline	3.5%	Burnham, 2016

Five types of cost calculations, license and registration, insurance, maintenance and repair, fuel and depreciation, are considered in this study. License and registration costs have to be paid each year, and for the vehicles mentioned, this cost was assumed to be \$24/vehicle.

Insurance costs, which are legally obligatory to pay for the damage caused to the other vehicle in the event of an accident, vary each year depending on the class and type of vehicle and the age and driving history of the driver. Within the scope of this study, the insurance is considered as \$924 for the first year for the gasoline vehicle and \$944 for the fuel cell vehicles and an increase of 2.2% is foreseen for each subsequent year (Burnham, 2016).

Maintenance and repair costs depend on the vehicle type and annual mileage and include all maintenance, such as periodic maintenance, battery replacement, and tire replacement, throughout the vehicle's life. These costs are given in Table 6.1 as \$/mi.

Fuel costs depend on the fuel economy of the vehicle and the price of the fuel it uses. Information on the parameters used to calculate these costs are given in Tables 6.1 and 6.2.

Since vehicles lose value over time, depreciation costs must also be taken into account in the calculations. While the depreciation cost of the vehicle is high in the

first year, it gradually decreases later on (Lebeau et al., 2013). The depreciation rate of the vehicle was taken as 29% for the first year and 11% for each subsequent year.

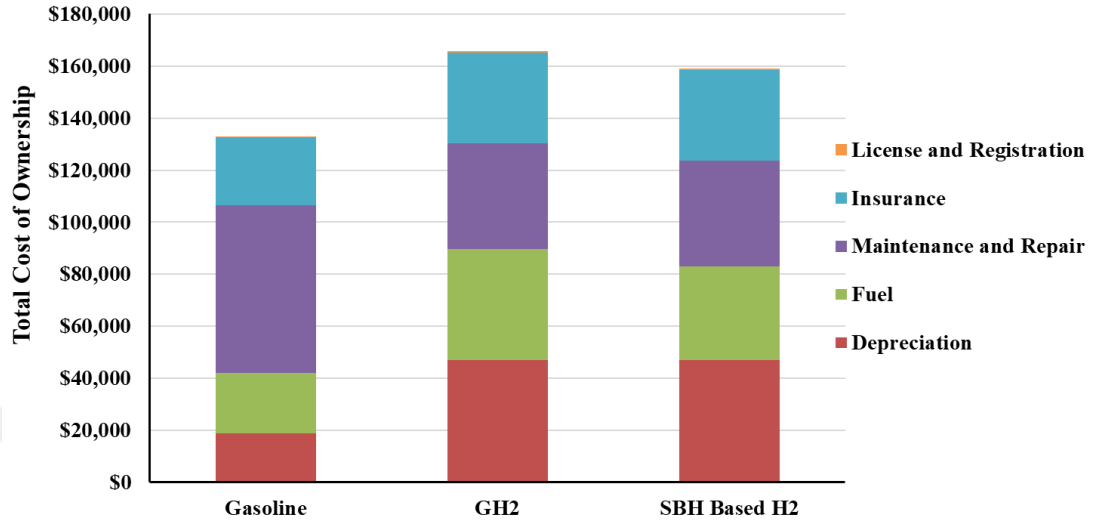


Figure 6.2 Total cost of ownership values of vehicles

Since the fuel cell vehicles have degradable parts such as fuel cell stack and battery, the depreciation costs of the hydrogen-powered vehicles are much higher than the gasoline vehicle as can be seen in Figure 6.2. Similarly, fuel prices are higher for fuel cell vehicles than for gasoline vehicles due to the costs of the hydrogen production and storage process. However, since the engines of electric vehicles have fewer parts to wear out and do not need oil changes, maintenance and repair costs are lower than internal combustion engines. License and registration costs are similar for all three vehicles.

The total cost of ownership for 20 years is calculated as \$133011 for a gasoline vehicle, \$165646 for a fuel cell vehicle using a compressed gas tank, and \$159028 for a fuel cell vehicle using an SBH-based hydrogen tank. Although gasoline vehicles seem to be advantageous in terms of cost, the total cost of ownership of fuel cell vehicles reveals that they are at a competitive level with gasoline vehicles. On the other hand, the SBH-based hydrogen production method, which enables the hydrogen fuel to be supplied more cheaply, provided an improvement of \$6618 in the total cost of ownership of the vehicle compared to the traditional steam methane reforming

(SMR) hydrogen production method. It can be predicted that fuel cell vehicles are expected to replace internal combustion engine vehicles in the future with further studies to reduce the costs of hydrogen fuel and fuel cell vehicle components.



CHAPTER SEVEN

CONCLUSIONS

In this thesis, hydrogen production from solid hydrogen storage materials and its use in fuel cell vehicles are experimentally and numerically investigated and an economic and environmental evaluation is presented. In the third chapter, the catalytic hydrolysis of morpholine borane in the presence of PSSA stabilized PdAg catalyst was investigated experimentally. The conclusions reached from this chapter are as follows:

- Among the PSSA stabilized bimetallic catalysts, PdAg was the catalyst that showed the best catalytic activity for the catalytic hydrolysis of morpholine borane at room temperature, and the optimum [metal]/[PSSA] ratio and metal ratios were 1/4 and Pd₅₀Ag₅₀, respectively.
- As a result of the kinetic studies, it was determined that the reaction was first order according to the catalyst and zero order according to the substrate.
- The activation energy and the enthalpy of the hydrolysis reaction of morpholine borane in the presence of PSSA stabilized Pd₅₀Ag₅₀ was calculated as 55.68 kJ/mol and -53.22 kJ/mol respectively.
- It was concluded that the PSSA stabilized PdAg catalyst maintained its stability during the first 10 cycles, showed 100% catalytic activity in the first two cycles, and retained more than 70% of its activity at the end of the twentieth cycle.

A 3D batch reactor and a 3D continuous porous reactor were modeled in Comsol Multiphysics environment to produce hydrogen from ammonia borane in chapter four, and the following conclusions were derived.

- When the initial concentrations of the species are known, the variation of the concentration of each species over time was obtained with the batch reactor model.
- With the continuous porous reactor model, information about the concentrations of the species can be obtained depending on the location in the reactor.

In the fifth chapter, a system model was developed in MATLAB Simulink® environment for a fuel cell vehicle using two different hydrogen storage systems, compressed gas and sodium borohydride-based hydrogen storage system, and the following conclusions were obtained;

- The required cell voltage is over 300 V for the first 1000 seconds of the cycle, and after this time, the current increases and the voltage decreases due to the acceleration of the vehicle.
- The state of charge of the battery is over 80% throughout the cycle. After the 1200th second of the cycle, there is a 12% decrease in the battery charge.
- The total hydrogen produced in the NaBH₄ reactor is 142.53 moles and 87.95 moles of hydrogen is consumed at the end of the cycle.
- The vehicle's maximum hydrogen consumption rate is at the 1105th second of the cycle and has a value of 0.48 mol/s.
- The total pressure drop in the HPHS tank at the end of the cycle is 27.25 bar.
- At the end of the cycle, the occupancy rate of both storage systems is 96.11%.
- In the case of using a compressed gas tank and a NaBH₄ based H₂ storage system, the vehicle range is 262.35 km and 273.94 km, respectively.

- NaBH₄ based H₂ storage system provides 11.59 km more vehicle range than the compressed gas tank. Accordingly, it can be concluded that the NaBH₄ based hydrogen storage system can be an alternative to the compressed hydrogen gas storage method.

The sixth chapter included economic and environmental analyzes for three passenger vehicles using gasoline, compressed gas hydrogen and sodium borohydride-based hydrogen as fuel. As a result of the chapter, the following conclusions were derived.

- Among the vehicles examined in terms of the amount of GHGs released into the environment, the vehicle using SBH-based hydrogen storage has the lowest environmental impact, and the hydrogen production based on solid hydrogen storage material can reduce emissions by more than 50% compared to gasoline.
- For vehicles using SBH-based hydrogen and compressed gas hydrogen tanks, most of their emissions come from the production, compression and transport stages of hydrogen. When examined in terms of air pollutants, the use of SBH-based hydrogen is very advantageous, especially in terms of CO and VOC emissions.
- PM_{2.5} and PM₁₀ emissions are at similar levels for all vehicles, since these emissions are mostly caused by brake and tire wear.
- The total cost of ownership for 20 years is calculated as \$133011 for a gasoline vehicle, \$165646 for a fuel cell vehicle using a compressed gas tank, and \$159028 for a fuel cell vehicle using an SBH-based hydrogen tank. It is concluded that in the end, FCVs are expected to be in an economically competitive position compared to ICEVs.

REFERENCES

- Abdalla, A. M., Hossain, S., Nisfindy, O. B., Azad, A. T., Dawood, M., & Azad, A. K. (2018). Hydrogen production, storage, transportation and key challenges with applications: A review. *Energy Conversion and Management*, 165, 602-627.
- Aceves, S. M., Berry, G., Petitpas, G., & Ross, T. (2011). Thermodynamic modeling of rapid low loss cryogenic hydrogen refueling. *DOE Hydrogen and Fuel Cells Program FY 2011 Annual Progress Report*, 358-361.
- Ahluwalia, R. K., Peng, J. K., Roh, H. S., Hua, T. Q., Houchins, C., & James, B. D. (2018). Supercritical cryo-compressed hydrogen storage for fuel cell electric buses. *International Journal of Hydrogen Energy*, 43(22), 10215-10231.
- Ahluwalia, R. K., Peng, J. K., & Hua, T. Q., (2011). Cryo-compressed hydrogen storage: Performance and cost review. *Compressed and Cryo-compressed Hydrogen Storage Workshop*, February 14-15, 2011.
- Aiello, R., Sharp, J. H., & Matthews, M. A. (1999). Production of hydrogen from chemical hydrides via hydrolysis with steam. *International Journal of Hydrogen Energy*, 24(12), 1123-1130.
- Ajanovic, A., & Haas, R. (2019). Economic and environmental prospects for battery electric-and fuel cell vehicles: a review. *Fuel Cells*, 19(5), 515-529.
- Akbayrak, S., Özçifçi, Z., & Tabak, A. (2019). Noble metal nanoparticles supported on activated carbon: highly recyclable catalysts in hydrogen generation from the hydrolysis of ammonia borane. *Journal of colloid and interface science*, 546, 324-332.
- Asghar, R., Rehman, F., Ullah, Z., Qamar, A., Ullah, K., Iqbal, K., Aman, A., & Nawaz, A. A. (2020). Electric vehicles and key adaptation challenges and

- prospects in Pakistan: A comprehensive review. *Journal of Cleaner Production*, 123375.
- Ba, Q., He, Q., Zhou, B., Chen, M., Li, X., & Cheng, L. (2020). Modeling of cryogenic hydrogen releases. *International Journal of Hydrogen Energy*, 45(55), 31315-31326.
- Baetcke, L., & Kaltschmitt, M. (2018). Hydrogen storage for mobile application: Technologies and their assessment. *Hydrogen Supply Chains*, 2018, 167-206.
- Bairabathina, S., & Balamurugan, S. (2020). Review on non-isolated multi-input step-up converters for grid-independent hybrid electric vehicles. *International Journal of Hydrogen Energy*, 45(41), 21687-21713.
- Balali, Y., & Stegen, S. (2021). Review of energy storage systems for vehicles based on technology, environmental impacts, and costs. *Renewable and Sustainable Energy Reviews*, 135, 110185.
- Baricco, M., Bang, M., Fichtner, M., Hauback, B., Linder, M., Luetto, C., Moretto, P., & Sgroi, M. (2017). SSH2S: Hydrogen storage in complex hydrides for an auxiliary power unit based on high temperature proton exchange membrane fuel cells. *Journal of Power Sources*, 342, 853-860.
- Baskar, S., Vijayan, V., Premkumar, I. I., Arunkumar, D., & Thamaran, D. (2021). Design and material characteristics of hybrid electric vehicle. *Materials Today: Proceedings*, 37, 351-353.
- Basu, S., Brockman, A., Gagare, P., Zheng, Y., Ramachandran, P. V., Delgass, W. N., & Gore, J. P. (2009). Chemical kinetics of Ru-catalyzed ammonia borane hydrolysis. *Journal of Power Sources*, 188(1), 238-243.
- Basu, S., Zheng, Y., Varma, A., Delgass, W. N., & Gore, J. P. (2010). Catalytic

- hydrolysis of ammonia borane: Intrinsic parameter estimation and validation. *Journal of Power Sources*, 195(7), 1957-1963.
- Boettner, D. D., Paganelli, G., Guezennec, Y. G., Rizzoni, G., & Moran, M. J. (2002). Proton exchange membrane fuel cell system model for automotive vehicle simulation and control. *Journal of Energy Resources Technology*, 124(1), 20-27.
- Brooks, K. P., Sprik, S. J., Tamburello, D. A., & Thornton, M. J. (2018). Design tool for estimating chemical hydrogen storage system characteristics for light-duty fuel cell vehicles. *International Journal of Hydrogen Energy*, 43(18), 8846-8858.
- Brooks, K. P., Sprik, S. J., Tamburello, D. A., & Thornton, M. J. (2020). Design tool for estimating metal hydride storage system characteristics for light-duty hydrogen fuel cell vehicles. *International Journal of Hydrogen Energy*, 45(46), 24917-24927.
- Burnham, A. (2018). User guide for AFLEET Tool 2018. Chicago: Argonne National Laboratory
- Cai, Z., Ou, X., Zhang, Q., & Zhang, X. (2012). Full lifetime cost analysis of battery, plug-in hybrid and FCEVs in China in the near future. *Frontiers in Energy*, 6(2), 107-111.
- Can, H., & Metin, Ö. (2019). Hydrogen generation via the catalytic hydrolysis of morpholine-borane: A new, efficient and cost-effective hydrogen storage medium. *International Journal of Hydrogen Energy*, 44(47), 25642-25651.
- Casolari, B. L., Ellington, M. A., Oros, J. M., Schuttinger, P., Radley, C. J., Kiley, K. A., & Klebanoff, L. E. (2014). Model study of a fuel cell range extender for a neighborhood electric vehicle (NEV). *International Journal of Hydrogen Energy*, 39(20), 10757-10787.

- Chabane, D., Ibrahim, M., Harel, F., Djerdir, A., Candusso, D., & Elkedim, O. (2019). Energy management of a thermally coupled fuel cell system and metal hydride tank. *International Journal of Hydrogen Energy*, 44(50), 27553-27563.
- Chan, C. C., Bouscayrol, A., & Chen, K. (2009). Electric, hybrid, and fuel-cell vehicles: Architectures and modeling. *IEEE Transactions on Vehicular Technology*, 59(2), 589-598.
- Chang, K. Y. (2011). The optimal design for PEMFC modeling based on Taguchi method and genetic algorithm neural networks. *International Journal of Hydrogen Energy*, 36(21), 13683-13694.
- Changizian, S., Ahmadi, P., Raeesi, M., & Javani, N. (2020). Performance optimization of hybrid hydrogen fuel cell-electric vehicles in real driving cycles. *International Journal of Hydrogen Energy*, 45(60), 35180-35197.
- Chen, F. Q., Zhang, M., Qian, J. Y., Chen, L. L., & Jin, Z. J. (2017). Pressure analysis on two-step high pressure reducing system for hydrogen fuel cell electric vehicle. *International Journal of Hydrogen Energy*, 42(16), 11541-11552.
- Chen, J., Hu, M., Ming, M., Xu, C., Wang, Y., Zhang, Y., Wu, J., Gao, D., Bi, J., & Fan, G. (2018). Carbon-supported small Rh nanoparticles prepared with sodium citrate: Toward high catalytic activity for hydrogen evolution from ammonia borane hydrolysis. *International Journal of Hydrogen Energy*, 43(5), 2718-2725.
- Chen, J., Veenstra, M., Purewal, J., Hobein, B., & Papasavva, S. (2019). Modeling a hydrogen pressure regulator in a fuel cell system with Joule–Thomson effect. *International Journal of Hydrogen Energy*, 44(2), 1272-1287.
- Chen, K., Laghrouche, S., & Djerdir, A. (2019). Degradation model of proton exchange membrane fuel cell based on a novel hybrid method. *Applied Energy*, 252, 113439.

- Conte, M., Iacobazzi, A., Ronchetti, M., & Vellone, R. (2001). Hydrogen economy for a sustainable development: state-of-the-art and technological perspectives. *Journal of Power Sources*, 100(1-2), 171-187.
- Dai, P., Zhao, X., Xu, D., Wang, C., Tao, X., Liu, X., & Gao, J. (2019). Preparation, characterization, and properties of Pt/Al₂O₃/cordierite monolith catalyst for hydrogen generation from hydrolysis of sodium borohydride in a flow reactor. *International Journal of Hydrogen Energy*, 44(53), 28463-28470.
- Dang, T. M. D., Le, T. T. T., Fribourg-Blanc, E., & Dang, M. C. (2011). Synthesis and optical properties of copper nanoparticles prepared by a chemical reduction method. *Advances in Natural Sciences: Nanoscience and Nanotechnology*, 2(1), 015009.
- Das, H. S., Tan, C. W., & Yatim, A. H. M. (2017). Fuel cell hybrid electric vehicles: A review on power conditioning units and topologies. *Renewable and Sustainable Energy Reviews*, 76, 268-291.
- Davids, M. W., Lototsky, M., Malinowski, M., van Schalkwyk, D., Parsons, A., Pasupathi, S., Swanepoel, D., & van Niekerk, T. (2019). Metal hydride hydrogen storage tank for light fuel cell vehicle. *International Journal of Hydrogen Energy*, 44(55), 29263-29272.
- Demirci, U. B. (2018). About the technological readiness of the hydrogen generation by hydrolysis of B (– N)– H compounds. *Energy Technology*, 6(3), 470-486.
- Dinc, A., & Otkur, M. (2020, July). Optimization of electric vehicle battery size and reduction ratio using genetic algorithm. *11th International Conference on Mechanical and Aerospace Engineering (ICMAE)*, 281-285.
- Durbin, D. J., & Malardier-Jugroot, C. (2013). Review of hydrogen storage

- techniques for on board vehicle applications. *International Journal of Hydrogen Energy*, 38(34), 14595-14617.
- Ellram, L. M. (1995). Total cost of ownership: an analysis approach for purchasing. *International Journal of Physical Distribution & Logistics Management*, 25(8), 4-23.
- Fakioğlu, E., Yürüm, Y., & Veziroğlu, T. N. (2004). A review of hydrogen storage systems based on boron and its compounds. *International Journal of Hydrogen Energy*, 29(13), 1371-1376.
- Fernández, R. Á., Cilleruelo, F. B., & Martínez, I. V. (2016). A new approach to battery powered electric vehicles: A hydrogen fuel-cell-based range extender system. *International Journal of Hydrogen Energy*, 41(8), 4808-4819.
- Feroldi, D., & Carignano, M. (2016). Sizing for fuel cell/supercapacitor hybrid vehicles based on stochastic driving cycles. *Applied Energy*, 183, 645-658.
- Francia, C., Ijeri, V. S., Specchia, S., & Spinelli, P. (2011). Estimation of hydrogen crossover through Nafion® membranes in PEMFCs. *Journal of Power Sources*, 196(4), 1833-1839.
- Gangloff, J. J., Kast, J., Morrison, G., & Marcinkoski, J. (2017). Design space assessment of hydrogen storage onboard medium and heavy-duty fuel cell electric trucks. *Journal of Electrochemical Energy Conversion and Storage*, 14(2), 1-8.
- Gao, D., Jin, Z., Zhang, J., Li, J., & Ouyang, M. (2016). Comparative study of two different powertrains for a fuel cell hybrid bus. *Journal of Power Sources*, 319, 9-18.
- Gardiner, M. (2009). Energy requirements for hydrogen gas compression and liquefaction as related to vehicle storage needs. *DOE hydrogen and fuel cells*

program record, 9013.

- Ghosh, A. (2020). Possibilities and challenges for the inclusion of the Electric Vehicle (EV) to reduce the carbon footprint in the transport sector: A review. *Energies*, 13(10), 2602.
- Gröger, O., Gasteiger, H. A., & Suchsland, J. P. (2015). Electromobility: Batteries or fuel cells?. *Journal of the Electrochemical Society*, 162(14), 2605-2615.
- Guo, J., Yang, J., Zhao, Y., Pan, X., Zhang, L., Zhao, L., & Zheng, J. (2014). Investigations on temperature variation within a type III cylinder during the hydrogen gas cycling test. *International Journal of Hydrogen Energy*, 39(25), 13926-13934.
- Guo, Z., & Zhou, Y. (2019). Residual value analysis of plug-in vehicles in the United States. *Energy Policy*, 125, 445-455.
- Gye, H. R., Seo, S. K., Bach, Q. V., Ha, D., & Lee, C. J. (2019). Quantitative risk assessment of an urban hydrogen refueling station. *International Journal of Hydrogen Energy*, 44(2), 1288-1298.
- Hong, B. K., & Kim, S. H. (2018). Recent advances in fuel cell electric vehicle technologies of Hyundai. *ECS Transactions*, 86(13), 3-18.
- Hua, T. Q., Roh, H. S., & Ahluwalia, R. K. (2017). Performance assessment of 700-bar compressed hydrogen storage for light duty fuel cell vehicles. *International Journal of Hydrogen Energy*, 42(40), 25121-25129.
- Huang, P. H., Kuo, J. K., & Han, C. Y. (2017). Numerical investigation into slope-climbing capability of fuel cell hybrid scooter. *Applied Thermal Engineering*, 110, 921-930.

- Huang, Z., & Zhang, X. (2006). Well-to-wheels analysis of hydrogen based fuel-cell vehicle pathways in Shanghai. *Energy*, 31(4), 471-489.
- Huo, H., Wu, Y., & Wang, M. (2009). Total versus urban: Well-to-wheels assessment of criteria pollutant emissions from various vehicle/fuel systems. *Atmospheric Environment*, 43(10), 1796-1804.
- Jepsen, L. H., Ley, M. B., Lee, Y. S., Cho, Y. W., Dornheim, M., Jensen, J. O., Flinchuk, Y., Jorgensen, J. E., Besenbacher, F., & Jensen, T. R. (2014). Boron–nitrogen based hydrides and reactive composites for hydrogen storage. *Materials Today*, 17(3), 129-135.
- Kandidayeni, M., Macias, A., Khalatbarisoltani, A., Boulon, L., & Kelouwani, S. (2019). Benchmark of proton exchange membrane fuel cell parameters extraction with metaheuristic optimization algorithms. *Energy*, 183, 912-925.
- Kang, S., & Min, K. (2016). Dynamic simulation of a fuel cell hybrid vehicle during the federal test procedure-75 driving cycle. *Applied Energy*, 161, 181-196.
- Karaoğlu, M. U., İnce, A. C., Colpan, C. O., Glösen, A., Kuralay, N. S., Müller, M., & Stolten, D. (2019). Simulation of a hybrid vehicle powertrain having direct methanol fuel cell system through a semi-theoretical approach. *International Journal of Hydrogen Energy*, 44(34), 18981-18992.
- Kim, S. C., Lee, S. H., & Yoon, K. B. (2010). Thermal characteristics during hydrogen fueling process of type IV cylinder. *International Journal of Hydrogen Energy*, 35(13), 6830-6835.
- Klebanoff, L. E., Ott, K. C., Simpson, L. J., O'Malley, K., & Stetson, N. T. (2014). Accelerating the understanding and development of hydrogen storage materials: a review of the five-year efforts of the three DOE hydrogen storage materials centers of excellence. *Metallurgical and Materials Transactions*, 1(2), 81-117.

- KoteswaraRao, K, V., & Naga Srinivasulu, G. (2019). Modeling, downsizing, and performance comparison of a fuel cell hybrid mid-size car with FCEV for urban and hill road driving cycles. *International Journal of Green Energy*, 16(2), 115-124.
- Kumar, D., Nema, R. K., & Gupta, S. (2020). A comparative review on power conversion topologies and energy storage system for electric vehicles. *International Journal of Energy Research*, 44(10), 7863-7885.
- Lai, Q., Paskevicius, M., Sheppard, D., Buckley, C., Thornton, A., Hill, M., Gu, Q., Mao, J., Huang, Z., Liu, H. K., Guo, Z., Banerjee, A., Chakraborty, S., Ahuja, R., & Aguey-Zinsou, K. (2015). Hydrogen storage materials for mobile and stationary applications: current state of the art. *ChemSusChem*, 8(17), 2789-2825.
- Law, K., Rosenfeld, J., Han, V., Chan, M., Chiang, H., & Leonard, J. (2013). *US Department of Energy Hydrogen Storage Cost Analysis*. California: U.S. Department of Energy
- Lebeau, K., Lebeau, P., Macharis, C., & Van Mierlo, J. (2013, November). How expensive are electric vehicles? A total cost of ownership analysis. *2013 World Electric Vehicle Symposium and Exhibition (EVS27)*, 1-12.
- Lekshmi, S., & PS, L. P. (2019). Mathematical modeling of Electric vehicles-A survey. *Control Engineering Practice*, 92, 104138.
- Li, F., Yang, T., Xiao, J., Bénard, P., & Chahine, R. (2019). Numerical solution for thermodynamic model of charge-discharge cycle in compressed hydrogen tank. *Energy Procedia*, 158, 2145-2151.
- Li, M., Bai, Y., Zhang, C., Song, Y., Jiang, S., Grouset, D., & Zhang, M. (2019). Review on the research of hydrogen storage system fast refueling in fuel cell

- vehicle. *International Journal of Hydrogen Energy*, 44(21), 10677-10693.
- Li, S. C., & Wang, F. C. (2016). The development of a sodium borohydride hydrogen generation system for proton exchange membrane fuel cell. *International Journal of Hydrogen Energy*, 41(4), 3038-3051.
- Li, T., Liu, H., Zhao, D., & Wang, L. (2016). Design and analysis of a fuel cell supercapacitor hybrid construction vehicle. *International Journal of Hydrogen Energy*, 41(28), 12307-12319.
- Li, Y. T., Zhang, X. L., Peng, Z. K., Liu, P., & Zheng, X. C. (2020). Hierarchical porous g-C₃N₄ coupled ultrafine RuNi alloys as extremely active catalysts for the hydrolytic dehydrogenation of ammonia borane. *ACS Sustainable Chemistry & Engineering*, 8(22), 8458-8468.
- Lim, K. L., Kazemian, H., Yaakob, Z., & Daud, W. W. (2010). Solid-state materials and methods for hydrogen storage: a critical review. *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology*, 33(2), 213-226.
- Lü, X., Qu, Y., Wang, Y., Qin, C., & Liu, G. (2018). A comprehensive review on hybrid power system for PEMFC-HEV: Issues and strategies. *Energy Conversion and Management*, 171, 1273-1291.
- Ma, S., Lin, M., Lin, T. E., Lan, T., Liao, X., Maréchal, F., Van herle, J., Yang, Y., Dong, C., & Wang, L. (2021). Fuel cell-battery hybrid systems for mobility and off-grid applications: A review. *Renewable and Sustainable Energy Reviews*, 135, 110119.
- Manoharan, Y., Hosseini, S. E., Butler, B., Alzhahrani, H., Senior, B. T. F., Ashuri, T., & Krohn, J. (2019). Hydrogen fuel cell vehicles; current status and future prospect. *Applied Sciences*, 9(11), 2296.

Markert, F., Melideo, D., & Baraldi, D. (2014). Numerical analysis of accidental hydrogen releases from high pressure storage at low temperatures. *International Journal of Hydrogen Energy*, 39(14), 7356-7364.

Mench, M. M., (2008). *Fuel cell Engines*, (1st Ed.). New York: John Wiley & Sons.

Mercedes-Benz GLC F-CELL, Special hybrid with fuel cell. (2019). Retrieved August 10, 2020 from <https://www.daimler.com/products/passenger-cars/mercedes-benz/glc-f-cell.html>.

Mohammadi, A., Guilbert, D., Gaillard, A., Bouquain, D., Khaburi, D., & Djerdir, A. (2013). Faults diagnosis between PEM fuel cell and DC/DC converter using neural networks for automotive applications. *IECON 2013-39th Annual Conference of the IEEE Industrial Electronics Society*, 8186-8191.

Mohammadshahi, S. S., Gray, E. M., & Webb, C. J. (2016). A review of mathematical modelling of metal-hydride systems for hydrogen storage applications. *International Journal of Hydrogen Energy*, 41(5), 3470-3484.

Moradi, R., & Groth, K. M. (2019). Hydrogen storage and delivery: Review of the state of the art technologies and risk and reliability analysis. *International Journal of Hydrogen Energy*, 44(23), 12254-12269.

Moreno-Blanco, J., Petitpas, G., Espinosa-Loza, F., Elizalde-Blancas, F., Martinez-Frias, J., & Aceves, S. M. (2019). The fill density of automotive cryo-compressed hydrogen vessels. *International Journal of Hydrogen Energy*, 44(2), 1010-1020.

Moreno-Blanco, J., Petitpas, G., Espinosa-Loza, F., Elizalde-Blancas, F., Martinez-Frias, J., & Aceves, S. M. (2019). The storage performance of automotive cryo-compressed hydrogen vessels. *International Journal of Hydrogen Energy*, 44(31), 16841-16851.

- Mori, D., & Hirose, K. (2009). Recent challenges of hydrogen storage technologies for fuel cell vehicles. *International Journal of Hydrogen Energy*, 34(10), 4569-4574.
- Moury, R., Moussa, G., Demirci, U. B., Hannauer, J., Bernard, S., Petit, E., van der Lee, A., & Miele, P. (2012). Hydrazine borane: synthesis, characterization, and application prospects in chemical hydrogen storage. *Physical Chemistry Chemical Physics*, 14(5), 1768-1777.
- Muthukumar, M., Rengarajan, N., Velliyangiri, B., Omprakas, M. A., Rohit, C. B., & Raja, U. K. (2021). The development of fuel cell electric vehicles—A review. *Materials Today: Proceedings*, 45, 1181-1187.
- Nassif, G. G., & de Almeida, S. C. (2020). Impact of powertrain hybridization on the performance and costs of a fuel cell electric vehicle. *International Journal of Hydrogen Energy*, 45(41), 21722-21737.
- Niaz, S., Manzoor, T., & Pandith, A. H. (2015). Hydrogen storage: Materials, methods and perspectives. *Renewable and Sustainable Energy Reviews*, 50, 457-469.
- O'Malley, K., Ordaz, G., Adams, J., Randolph, K., Ahn, C. C., & Stetson, N. T. (2015). Applied hydrogen storage research and development: a perspective from the US Department of Energy. *Journal of Alloys and Compounds*, 645, 419-422.
- Ogumerem, G. S., & Pistikopoulos, E. N. (2019). Parametric optimization and control toward the design of a smart metal hydride refueling system. *AIChE Journal*, 65(10), 16680.
- Olabi, A. G., Wilberforce, T., & Abdelkareem, M. A. (2021). Fuel cell application in the automotive industry and future perspective. *Energy*, 214, 118955.

- Pinto, P. J. R., Sousa, T., Fernandes, V. R., Pinto, A. M. F. R., & Rangel, C. M. (2013). Simulation of a stand-alone residential PEMFC power system with sodium borohydride as hydrogen source. *International Journal of Electrical Power & Energy Systems*, 49, 57-65.
- Pornea, A. M., Abebe, M. W., & Kim, H. (2019). Ternary NiCoP urchin like 3D nanostructure supported on nickel foam as a catalyst for hydrogen generation of alkaline NaBH₄. *Chemical Physics*, 516, 152-159.
- Preuster, P., Alekseev, A., & Wasserscheid, P. (2017). Hydrogen storage technologies for future energy systems. *Annual Review of Chemical and Biomolecular Engineering*, 8, 445-471.
- Rajabzadeh, M., Bathaee, S. M. T., & Golkar, M. A. (2016). Dynamic modeling and nonlinear control of fuel cell vehicles with different hybrid power sources. *International Journal of Hydrogen Energy*, 41(4), 3185-3198.
- Rakap, M. (2020). Synthesis and characterization of bimetallic cobalt-rhodium nanoclusters as effective catalysts to produce hydrogen from ammonia borane hydrolysis. *Renewable Energy*, 154, 1076-1082.
- Rashidi, A. M., Nouralishahi, A., Khodadadi, A. A., Mortazavi, Y., Karimi, A., & Kashefi, K. (2010). Modification of single wall carbon nanotubes (SWNT) for hydrogen storage. *International Journal of Hydrogen Energy*, 35(17), 9489-9495.
- Reed, R. P., & Golda, M. (1994). Cryogenic properties of unidirectional composites. *Cryogenics*, 34(11), 909-928.
- Ren, J., Musyoka, N. M., Langmi, H. W., Mathe, M., & Liao, S. (2017). Current research trends and perspectives on materials-based hydrogen storage solutions: a critical review. *International Journal of Hydrogen Energy*, 42(1), 289-311.

- Ren, X., Dong, L., Xu, D., & Hu, B. (2020). Challenges towards hydrogen economy in China. *International Journal of Hydrogen Energy*, 45(59), 34326-34345.
- Rivard, E., Trudeau, M., & Zaghib, K. (2019). Hydrogen storage for mobility: a review. *Materials*, 12(12), 1973.
- Rusman, N. A. A., & Dahari, M. (2016). A review on the current progress of metal hydrides material for solid-state hydrogen storage applications. *International Journal of Hydrogen Energy*, 41(28), 12108-12126.
- Samsun, R. C., Krupp, C., Baltzer, S., Gnörich, B., Peters, R., & Stolten, D. (2016). A battery-fuel cell hybrid auxiliary power unit for trucks: Analysis of direct and indirect hybrid configurations. *Energy Conversion and Management*, 127, 312-323.
- Sanli, A. E., Yilmaz, E. S., Ozden, S. K., Gordesel, M., & Gunlu, G. (2018). A direct borohydride–peroxide fuel cell–LiPO battery hybrid motorcycle prototype–II. *International Journal of Hydrogen Energy*, 43(2), 992-1005.
- Shimpalee, S., Beuscher, U., & Van Zee, J. W. (2006). Investigation of gas diffusion media inside PEMFC using CFD modeling. *Journal of Power Sources*, 163(1), 480-489.
- Shusheng, X., Qiujie, S., Baosheng, G., Encong, Z., & Zhankuan, W. (2020). Research and development of on-board hydrogen-producing fuel cell vehicles. *International Journal of Hydrogen Energy*, 45(35), 17844-17857.
- Song, K., Li, F., Hu, X., He, L., Niu, W., Lu, S., & Zhang, T. (2018). Multi-mode energy management strategy for fuel cell electric vehicles based on driving pattern identification using learning vector quantization neural network algorithm. *Journal of Power Sources*, 389, 230-239.

Spiegel, C. (2011). *PEM fuel cell modeling and simulation using MATLAB*, (2nd Ed.). Massachusetts: Academic Press.

Stroman, R. O., Schuette, M. W., Swider-Lyons, K., Rodgers, J. A., & Edwards, D. J. (2014). Liquid hydrogen fuel system design and demonstration in a small long endurance air vehicle. *International Journal of Hydrogen Energy*, 39(21), 11279-11290.

Sulaiman, N., Hannan, M. A., Mohamed, A., Majlan, E. H., & Daud, W. W. (2015). A review on energy management system for fuel cell hybrid electric vehicle: Issues and challenges. *Renewable and Sustainable Energy Reviews*, 52, 802-814.

Tanç, B., Arat, H. T., Baltacıoğlu, E., & Aydın, K. (2019). Overview of the next quarter century vision of hydrogen fuel cell electric vehicles. *International Journal of Hydrogen Energy*, 44(20), 10120-10128.

Technical targets for fuel cell systems and stacks for transportation applications. (n.d.). Retrieved August 10, 2020 from <https://www.energy.gov/eere/fuelcells/doe-technical-targets-fuel-cell-systems-and-stacks-transportation-applications>

The powertrain for the BMW i Hydrogen NEXT : BMW Group reaffirms its ongoing commitment to hydrogen fuel cell. (n.d). Retrieved August 10, 2020 from <https://www.press.bmwgroup.com/global/article/detail/T0306930EN/>

Tomoda, K., Katayama, N., Hoshi, N., Yoshizaki, A., & Hirata, K. (2015). Modeling of sodium tetrahydroborate power system for fuel cell vehicle. *ECS Transactions*, 65(1), 33.

Toyota 2020 Mirai. (n.d.). Retrieved August 10, 2020 from <https://www.toyota.com/mirai/assets/modules/carpagehowitworks/>

- Tran, D. D., Vafaeipour, M., El Baghdadi, M., Barrero, R., Van Mierlo, J., & Hegazy, O. (2020). Thorough state-of-the-art analysis of electric and hybrid vehicle powertrains: Topologies and integrated energy management strategies. *Renewable and Sustainable Energy Reviews*, 119, 109596.
- Trencher, G. (2020). Strategies to accelerate the production and diffusion of fuel cell electric vehicles: Experiences from California. *Energy Reports*, 6, 2503-2519.
- Trencher, G., Taeihagh, A., & Yarime, M. (2020). Overcoming barriers to developing and diffusing fuel-cell vehicles: Governance strategies and experiences in Japan. *Energy Policy*, 142, 111533.
- Uzundurukan, A., & Devrim, Y. (2019). Hydrogen generation from sodium borohydride hydrolysis by multi-walled carbon nanotube supported platinum catalyst: A kinetic study. *International Journal of Hydrogen Energy*, 44(33), 17586-17594.
- Vamvuka, D. (1999). Gasification of coal. *Energy Exploration & Exploitation*, 17(6), 515-581.
- Vehicle Specifications of Honda Clarity Fuel Cell*, (n.d). Retrieved August 10, 2020 from <https://owners.honda.com/vehicles/information/2019/Clarity>
- Veziroğlu, T. N. (1987). Hydrogen technology for energy needs of human settlements. *International Journal of Hydrogen Energy*, 12(2), 99-129.
- Wang, F. C., & Fang, W. H. (2017). The development of a PEMFC hybrid power electric vehicle with automatic sodium borohydride hydrogen generation. *International Journal of Hydrogen Energy*, 42(15), 10376-10389.
- Wang, G., Yu, Y., Liu, H., Gong, C., Wen, S., Wang, X., & Tu, Z. (2018). Progress

- on design and development of polymer electrolyte membrane fuel cell systems for vehicle applications: A review. *Fuel Processing Technology*, 179, 203-228.
- Wang, Q., Xue, M., Lin, B. L., Lei, Z., & Zhang, Z. (2020). Well-to-wheel analysis of energy consumption, greenhouse gas and air pollutants emissions of hydrogen fuel cell vehicle in China. *Journal of Cleaner Production*, 275, 123061.
- Whiston, M. M., Lima Azevedo, I. M., Litster, S., Samaras, C., Whitefoot, K. S., & Whitacre, J. F. (2020). Hydrogen Storage for Fuel Cell Electric Vehicles: Expert Elicitation and a Levelized Cost of Driving Model. *Environmental Science & Technology*, 55(1), 553-562.
- Wilberforce, T., El-Hassan, Z., Khatib, F. N., Al Makky, A., Baroutaji, A., Carton, J. G., & Olabi, A. G. (2017). Developments of electric cars and fuel cell hydrogen electric cars. *International Journal of Hydrogen Energy*, 42(40), 25695-25734.
- Winkler, S. L., Anderson, J. E., Garza, L., Ruona, W. C., Vogt, R., & Wallington, T. J. (2018). Vehicle criteria pollutant (pm, no x, co, hcs) emissions: how low should we go?. *Climate and Atmospheric Science*, 1(1), 1-5.
- Winnefeld, C., Kadyk, T., Bensmann, B., Krewer, U., & Hanke-Rauschenbach, R. (2018). Modelling and designing cryogenic hydrogen tanks for future aircraft applications. *Energies*, 11(1), 105.
- Wróblewski, P., Drożdż, W., Lewicki, W., & Dowejko, J. (2021). Total cost of ownership and its potential consequences for the development of the hydrogen fuel cell powered vehicle market in Poland. *Energies*, 14(8), 2131.
- Xia, Z., Shen, Y., Wang, Y., Poh, C. K., & Lin, J. (2014). Development of a portable hydrogen generator with differential pressure-driven control. *International Journal of Hydrogen Energy*, 39(28), 16187-16194.

- Xiao, J., Tong, L., Bénard, P., & Chahine, R. (2020). Thermodynamic analysis for hydriding-dehydriding cycle of metal hydride system. *Energy*, 191, 116535.
- Xiao, J., Bénard, P., & Chahine, R. (2016). Charge-discharge cycle thermodynamics for compression hydrogen storage system. *International Journal of Hydrogen Energy*, 41(12), 5531-5539.
- Xu, W., Li, Q., & Huang, M. (2015). Design and analysis of liquid hydrogen storage tank for high-altitude long-endurance remotely-operated aircraft. *International Journal of Hydrogen Energy*, 40(46), 16578-16586.
- Yan, J. M., Zhang, X. B., Han, S., Shioyama, H., & Xu, Q. (2009). Magnetically recyclable Fe–Ni alloy catalyzed dehydrogenation of ammonia borane in aqueous solution under ambient atmosphere. *Journal of Power Sources*, 194(1), 478-481.
- Yanxing, Z., Maoqiong, G., Yuan, Z., Xueqiang, D., & Jun, S. (2019). Thermodynamics analysis of hydrogen storage based on compressed gaseous hydrogen, liquid hydrogen and cryo-compressed hydrogen. *International Journal of Hydrogen Energy*, 44(31), 16833-16840.
- Yao, G., Du, C., Ge, Q., Jiang, H., Wang, Y., Ait-Ahmed, M., & Moreau, L. (2019). Traffic-Condition-Prediction-Based HMA-FIS Energy-Management Strategy for Fuel-Cell Electric Vehicles. *Energies*, 12(23), 4426.
- Yao, Q., Ding, Y., & Lu, Z. H. (2020). Noble-metal-free nanocatalysts for hydrogen generation from boron-and nitrogen-based hydrides. *Inorganic Chemistry Frontiers*, 7(20), 3837-3874.
- Yersak, T. A., Baker, D. R., Yanagisawa, Y., Slavik, S., Immel, R., Mack-Gardner, A., Herrmann, M., & Cai, M. (2017). Predictive model for depressurization-induced blistering of type IV tank liners for hydrogen storage. *International Journal of Hydrogen Energy*, 42(48), 28910-28917.

Zhu, D., Ait-Amirat, Y., N'Diaye, A., & Djerdir, A. (2019). Active thermal management between proton exchange membrane fuel cell and metal hydride hydrogen storage tank considering long-term operation. *Energy Conversion and Management*, 202, 112187.



APPENDICES

APPENDIX 1: Abbreviations

PSSA	Poly styrenesulfonic acid sodium salt
MB	Morpholine borane
SBH	Sodium borohydride
SLPM	Standart liter per minute
AFLEET	Alternative Fuel Life-Cycle Environmental and Economic Transportation
GREET	Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation
EV	Electric vehicle
FCV	Fuel cell vehicle
BEV	Battery electric vehicle
HEV	Hybrid electric vehicle
EMS	Energy management system
TOF	Turnover frequency
FC	Fuel cell
SC	Supercapacitor
PEMFC	Polymer exchange membrane fuel cell
ICEV	Internal combustion engine vehicle
US DOE	United States Department of Energy
SOC	State of charge
HR	Batch reactor
HPHS	High pressure hydrogen storage
LPHS	Low pressure hydrogen storage
NEDC	New European drive cycle
WTW	Well to wheel
MPGGE	Miles per gasoline gallon equivalent
GHG	Greenhouse gases
SMR	Steam methane reforming

TCO Total cost of ownership



APPENDIX 2: Nomenclature

E_a	Activation energy, kJ/mol
R	Universal gas constant, Latm/molK
ΔH	Enthalpy, kJ/mol
c	Concentration, mol/m ³
D	Diffusion coefficient, m ² /s
R	Reaction rate, mol/m ³ s
V_r	Reactor volume, m ³
C_p	Heat capacity, J/kgK
u	Velocity, m/s
k	Thermal conductivity, W/mK
Q	Heat source of the reaction, kJ
h	Convective heat transfer coefficient, W/m ² K
T_{ext}	External surface temperature, K
T_{amb}	Ambient temperature, K
P	Pressure, bar
V	Volume, m ³
T	Temperature, K
k_r	Reaction rate constant, mol/s
P_{FC}	Power output of the FC stack, W
V_{cell}	Cell voltage, V
i_{cell}	Current density, A/m ²
A_{cell}	Active area of the cell, m ²
n_{cell}	Number of cells in the FC stack
V_{Nernst}	Nernst voltage, V
$V_{activation}$	Activation losses, V
V_{ohmic}	Ohmic losses, V
$V_{concentration}$	Concentration losses, V
V_{other}	Other losses, V
ΔG	Gibbs free energy change, kJ/mol
T_{cell}	Temperature of the cell, K

n_{eq}	Number of electrons transferred per mole of oxidized hydrogen
F	Faraday constant, C/mol
y	Stoichiometric ratio
a	Thermodynamic activity coefficient
RH	Relative humidity
i_x	Crossover current density, A/m ²
i_0	Exchange current density, A/m ²
l	Thickness, m
$R''_{contact}$	Area specific contact resistance, Ω
k_m	Mass transport constant, mol/m ³
i_l	Limiting current density, A/m ²
A	Pre-exponential coefficient, 1/s
K_a	Langmuir-Hinselwood adsorption constant, m ³ /mol
N	Mole numbers of species, mol
M	Molecular weight of species, g/mol
Q_{Bat}	Battery capacity, kWh
P_{Bat}	Battery power, W
F_R	Rolling resistance
F_{St}	Grading resistance
F_L	Air resistance
F_a	Acceleration resistance
m	Vehicle mass, kg
g	Acceleration of gravity, m/s ²
f_R	Coefficient of rolling resistance
C_W	Aerodynamic coefficient of the vehicle
V	Vehicle speed, km/h
a	Acceleration, m/s ²
P_{EM}	Power requirement in the electric motor, kW
I_{EM}	Current output of the electric motor, A
V_{EM}	Constant motor voltage, V
I_{FC}	Current demand of the FC stack, A
I_{Bat}	Battery current, A

APPENDIX 3: Greek Letters

ρ	Density
α	Transfer coefficient
σ	Effective ionic conductivity
α'	Amplification constant
δ	Slope angle
η_M	Mechanical efficiency
η_{EM}	Electric motor efficiency

