**ÇUKUROVA UNIVERSITY**
**INSTITUTE OF NATURAL AND APPLIED SCIENCES**

**MSc THESIS**

**Ali Cem YAKARYILMAZ**

# ENERGY AND EXERGY ANALYSIS OF A PROTON EXCHANGE MEMBRANE FUEL CELL (PEMFC)

**DEPARTMENT OF AUTOMOTIVE ENGINEERING**

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# ÇUKUROVA UNIVERSITY

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We certify that the thesis titled above was reviewed and approved for the award of degree of the Master of Science by the board of jury on 23/05/2018

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**ABSTRACT**

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This study investigates the thermodynamic performance of a 1 kW self-humidified Proton Exchange Membrane (PEM) fuel cell. The first law analysis of thermodynamic is performed both experimentally and theoretically and the second law analysis or thermodynamic is performed at different operating temperature ratio ($T/T_0$) varies from 1 to 1.2 and operating pressure ratio ($P/P_0$) varies from 1 to 2 for different power output. Hydrogen is used as a fuel and in order to perform the thermodynamic analysis hydrogen, air, product water and exit air flow rates and specific physical are calculated. The energy and exergy balances for the control volume are used to calculate the efficiencies of energy and exergy of the PEM fuel cell. All results were compared with each other to see the effects of operating temperature and pressure on performance. As a result, it was observed that both increment in operating pressure and operating temperature improves the exergetic performance.

**Keywords:** Energy; Exergy; PEM Fuel Cell; Operating Temperature; Operating Pressure

# ÖZ

## YÜKSEK LİSANS TEZİ

**PROTON DEĞİŞİM MEMBRANLI BİR YAKIT PİLİNİN ENERJİ VE EKSERJİ ANALİZİ**

**Ali Cem YAKARYILMAZ**

**ÇUKUROVA ÜNİVERSİTESİ**
**FEN BİLİMLERİ ENSTİTÜSÜ**
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Bu çalışma da 1 kW kendinden nemlendirilmiş Proton Değişim Membranlı yakıt hücresinin termodinamik performansı incelenmiştir. Termodinamiğin birinci yasası hem deneysel olarak hem de teorik olarak gerçekleştirilmiştir ve termodinamiğin ikinci yasası 1'den 1.2'ye değişkenlik gösteren çalışma sıcaklığı oranlarında ($T/T_0$) ve 1 ve 2 olmak üzere değişen çalışma basıncı oranlarında ($P/P_0$) farklı güç çıkış değerleri için gerçekleştirilmiştir. Yakıt olarak hidrojen kullanılmıştır ve yakıt, hava, su ve çıkış hava debileri ve özgül fiziksel ekserjileri hesaplanmıştır. Enerji ve ekserji dengeleri kontrol hacmi için kullanılarak enerji ve ekserji verimleri bulunmuştur. Enerji ve ekserji performanslarına çalışma sıcaklığı ve basıncı etkilerini görebilmek için bütün sonuçlar birbirleri ile karşılaştırılmıştır. Sonuç olarak hem çalışma sıcaklığındaki artışın hem de çalışma basıncındaki artışın ekserji performansını artırdığı gözlenmiştir.

**Anahtar Kelimeler:** Enerji, Ekserji, PEM Yakıt Hücresi, Çalışma Sıcaklığı; Çalışma Basıncı

## GENİŞLETİLMİŞ ÖZET

Tüm dünyada fosil yakıtlar ve fosil yakıt tabanlı enerji sistemleri, artan dünya nüfusu ve enerji talepleri ile son derece yüksek düzeyde kullanılmaktadır. Bu yakıtlar ve sistemler, yolcu ve eşya taşımacılığı, ısıtma gibi hayatın her bölümünde özel bir öneme sahiptir. Ama fosil yakıtların en çok kullanıldığı alan doğal olarak taşıtlardır.

Fosil yakıtlar, hava kirliliği gibi çevresel hasarlara neden olmaktadır. Son yıllarda fosil yakıtların bu olumsuz etkileri daha önce olmadığı kadar açıkça görülmektedir. Ayrıca fosil yakıtlar hızla azalmakta ve er ya da geç tükenecektir. Bu durum ve insanoğlunun enerji talepleri nedenleriyle gelecek için büyük bir problem ortaya çıkmaktadır. Günümüzde yeni alternatif enerji kaynakları (rüzgâr, güneş, hidroelektrik, jeotermal vb.) ve nükleer enerji ele alınmıştır. Ancak bu enerji kaynaklarının hiçbiri fosil yakıtların en çok kullanıldığı alan olan araçlar için bir alternatif olamaz.

1800'lü yıllarda, yakıt hücreleri ortaya çıktı ama içten yanmalı motorların keşfi ile yakıt hücreleri uzay uygulamalarında doğan yüksek enerji ihtiyacının ortaya çıkmasına kadar ihmal edildi.

Yakıt hücreleri yakıt olarak hidrojen kullanır ve genellikle havanın içerisinde bulunan oksijeni kullanarak enerji üretmektedir. Hidrojen geleceğin enerji kaynağı olarak görülmektedir ve yakıt hücreleri hidrojenin kimyasal enerjisini birçok alanda kullanılabilecek elektrik enerjisine dönüştüren cihazlardır. Yakıt hücreleri temiz enerji dönüşüm birimleridir ve güvenlik, yüksek verim ve neredeyse sıfır emisyon seviyelerinin avantajları sayesinde yoğun ilgiye sahiptirler.

Yakıt hücrelerinin avantajlarının yanında yakıt olarak kullanılan hidrojenin Dünya üzerinde hazır olarak bulunmaması ve fosil kaynaklı (doğal gaz ve kömür) ya da yenilebilir kaynaklı (su, odun ve yosun) hammaddelerden elde edilmesi gerekmektedir.

Hidrojen düşük viskozite, düşük yoğunluk ve yüksek ısıl iletkenliği nedenleriyle küçük boşluklardan dahi sızıntı yapabilmektedir. Bu nedenle hidrojenin üretilmesinden sonra depolanmasının dikkatli yapılması gerekmektedir. Hidrojenin depolama yöntemleri genel olarak katı, sıvı ve gaz olarak yapılmaktadır. Bu üç yöntem içerisinde katı depolama yöntemi daha düşük hacim, düşük basınçta yüksek verim ve daha saf hidrojen kullanımına izin vermesinden dolayı sıvı ve gaz olarak depolama yöntemlerinden daha avantajlıdır.

Yakıt hücrelerinin çalışma prensibi temelde suyun elektrolizinin tersine dayanmaktadır. Daha önce elektrik enerjisi verilerek hidrojen ve oksijen iyonları, verilen elektrik enerjinin yerine ampermetre koyularak tekrardan gözlendiğinde iyonların birleşip tekrar suyu oluştururken ampermetreden akım geçtiği gözlenebilmiştir.

Yakıt hücreleri hidrojenin kimyasal enerjisini doğrudan elektrik enerjisine dönüştüren umut verici cihazlardır. Günümüzde kullanılan birçok yakıt hücresi bulunmaktadır. Yakıt hücreleri geleneksel olarak sistemde kullanılan elektrolit malzemesine göre sınıflandırılır. Alkali yakıt hücresi, fosforik asit yakıt hücresi, proton değişim membranlı yakıt hücresi, katı oksit yakıt hücresi, eriyik karbonat yakıt hücresi ve doğrudan alkol yakıt hücreleri olarak toplamda altı ana başlıkta sıralanabilir. Bütün bu yakıt hücreleri arasında proton değişim membranlı yakıt hücreleri hızlı başlatma süresi, yüksek verim, düşük çalışma sıcaklığı, yüksek güç yoğunluğu ve kolay ve güvenli kullanımı sayesinde ulaşım için en umut verici adaydır.

Bir enerji dönüşüm sürecinin verimliliği, bu dönüşümün en önemli yönlerinden biridir. Enerji ve verimlilik, bir sistemi kullanım için seçmek durumunda oldukça etkili iki anahtar faktördür. Ancak, geleneksel termodinamiğin ilk yasa analizinin, bir sistemin performansını belirlemek için tek başına yeterli olduğu çoğu zaman yanlış anlaşılmıştır. Bir sistem performansını analiz etmek için, çeşitli durumlarla ilişkili sistemin verimsizliğini değerlendirmek gerekmektedir ve sisteme ikinci yasa analizini uygulamakla mümkündür. İkinci yasa

“kullanılabilirlik” terimine dayanır ve kullanılabilirlik, sistemin iş yapması için potansiyelini ifade eder. Enerji tersine, kullanılabilirlik yok edilebilir. Kullanılabilirliğin yıkımı genellikle tersinmezlik olarak adlandırılır ve tersinmezliklerin azaltılması daha iyi sistem performansına yol açabilir. Bu durumda, PEM yakıt hücresi, geleneksel sisteme kıyasla oldukça verimli bir sistemdir. Ayrıca, enerji üretildikten sonra, önemli miktarda olmayan azot dışında hiçbir emisyon ortaya çıkmamaktadır.

Bu çalışmada 1 kW'lık kendinden nemlendirilmiş 50 hücreli bir PEM yakıt hücresinin deneysel verilerine enerji ve ekserji analizi uygulanmıştır. 1. ve 2. yasalar, miktar ve kalite ile ilgili termodinamik verim, farklı çalışma sıcaklıkları ve çalışma basıncı koşulları için belirlenmiş ve karşılaştırılmıştır.

Termodinamiğin birinci yasası hem deneysel olarak hem de teorik olarak gerçekleştirilmiştir ve termodinamiğin ikinci yasası 1’den 1.2’ye değişkenlik gösteren çalışma sıcaklığı oranlarında ($T/T_0$) ve 1’den 2’e değişkenlik gösteren çalışma basıncı oranlarında ($P/P_0$) farklı güç çıkış değerleri için gerçekleştirilmiştir. Yakıt olarak hidrojen sıkıştırılmış gaz olarak temin edilip kullanılmıştır. Kullanılan hidrojen saflığı %99,99’dur ve yakıt, hava, su ve çıkış hava debileri ve özgül fiziksel ekserjileri hesaplanmıştır. Enerji ve ekserji dengeleri kontrol hacmi için kullanılarak enerji ve ekserji verimleri bulunmuştur. Enerji ve ekserji performanslarına çalışma sıcaklığı ve basıncı etkilerini görebilmek için bütün sonuçlar birbirleri ile karşılaştırılmıştır.

Deneysel olarak elde edilen hidrojen debisi sayesinde ve literatürde yer alan hidrojenin debisini bulmakta kullanılan formülün yardımı ile enerji verimliliği sistemin farklı güç çıkış değerlerinde hesaplanmıştır. Daha sonra verim değerleri birbirleri arasında karşılaştırılmıştır.

Termodinamiğin ikinci yasası denge denklemi kontrol hacmi için yazılmış ekserji verimi hesabı için gerekli olan tepkimeye giren ve tepkimeden çıkan (ürün) maddelerin fiziksel ekserjileri 100 W’tan 1000 W’a kadar her çalışma sıcaklığı oranı ($T/T_0$) 1’den 1.2’ye kadar 0.05 aralıklar ve her çalışma basıncı oranı ($P/P_0$) 1

ve 2 için hesaplanmıştır. Özgül kimyasal ekserji değerleri literatürden alınarak ekserji verimleri belirlenmiştir. Son olarak tüm elde edilen verilerin birbirlerine göre değişimleri incelenmiştir.

Sonuç olarak, deneysel ve teorik enerji verim değerleri incelendiğinde deneysel verilerden elde edilen verimin teorik hesaplamalar kullanılarak elde edilen enerji veriminden daha yüksek çıktığı ve bu durumun doğrudan etkisi olan kullanılan hidrojen miktarlarının farklılığından kaynaklandığı bulunmuştur. Ayrıca, çalışma basıncı ve çalışma sıcaklığının artırıldığında tepkimeye giren ve çıkan maddelerin özgül fiziksel ekserjilerinin artığı bulunmuştur. Bununla beraber, çalışma basıncı sabit tutulup çalışma sıcaklığı artırıldığında yakıt pilinin ekserji verimini arttığı gözlenmiştir. Fakat, çalışma sıcaklığı sabit tutulup çalışma basıncının artırılması sistem ekserji verimine etkisi olmakla birlikte sürekli bir artışa sebep olmadığı bulunmuştur. Enerji ve ekserji verimlerinin sistem gücünün artırılması ile birlikte düşme eğilimi gösterdiği bulunmuştur.

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**LIST OF ABBREVIATIONS AND NOMENCLATURE**

| | | |
|---|---|---|
| etc | : | et cetera |
| R&D | : | Research and Development |
| C | : | Celsius |
| K | : | Kelvin |
| kg | : | Kilogram |
| m | : | Meter |
| cm | : | Centimeter |
| mm | : | Millimeter |
| ICE | : | Internal Combustion Engine |
| PEFC | : | Polymer Electrolyte Fuel Cell |
| PEMFC | : | Proton Exchange Membrane Fuel Cell |
| AFC | : | Alkaline Fuel Cell |
| SOFC | : | Solid Oxide Fuel Cell |
| MCFC | : | Molten Carbonate Fuel Cell |
| PAFC | : | Phosphoric Acid Fuel Cell |
| DMFC | : | Direct Methanol Fuel Cell |
| CO | : | Carbon Monoxide |
| $CO_2$ | : | Carbon Dioxide |
| $H_2O$ | : | Water |
| $H_2$ | : | Hydrogen |
| $NaBH_4$ | : | Sodium Borohydride |
| $CH_3OH$ | : | Methanol |
| $H_3PO_4$ | : | Phosphoric Acid |
| $LiAlO_2$ | : | Lithium Aluminate |
| $CO_3^{2-}$ | : | Carbonate |
| $ZrO_2$ | : | Zirconium Dioxide |
| $Y_2O_3$ | : | Yttrium Oxide |

| | | |
|---|---|---|
| kJ | : | Kilojoule |
| W | : | Watt |
| kW | : | Kilowatt |
| MW | : | Megawatt |
| CHP | : | Combined Heat and Power |
| RH | : | Relative Humidity |
| V | : | Voltage |
| A | : | Ampere |
| mA | : | Milliampere |
| atm | : | Atmosphere |
| P | : | Pressure, atm |
| $P_0$ | : | Pressure of Standard, 1 atm |
| T | : | Temperature, K |
| $T_0$ | : | Temperature of Standard, 298.15 K |
| % | : | Percentage |
| psi | : | Pound Per Square Inch |
| SLPM | : | Standard Liter Per Minute |
| LFL | : | Lower Flammability Level |
| DC | : | Direct Current |
| F | : | Farad |
| l | : | Liter |
| vpm | : | Volume Per Million |
| FLT | : | First Law of Thermodynamics |
| SLT | : | Second Law of Thermodynamics |
| PE | : | Potential Energy |
| KE | : | Kinetic Energy |
| $c_p$ | : | Specific Heat |
| $\dot{m}$ | : | Mass Flow Rate |

| | | |
|---|---|---|
| k | : | Specific Heat Ratio |
| h | : | Specific Enthalpy |
| s | : | Specific Entropy |
| $\dot{Q}$ | : | Heat Transfer Rate |
| $\dot{W}$ | : | Work Rate |
| $\dot{E}x$ | : | Exergy Rate |
| ex | : | Specific Exergy |
| x | : | Mass Fraction |
| R | : | Universal Gas Constant |
| $\eta$ | : | First Law Efficiency |
| $\psi$ | : | Second Law Efficiency |
| λ | : | Stoichiometry of Air |
| *0* | : | Standard Condition |
| *s* | : | Solid |
| *l* | : | Liquid |
| *g* | : | Gaseous |
| *R* | : | Reactant |
| *P* | : | Product |
| *in* | : | Inlet |
| *out* | : | Outlet |
| *dest* | : | Destruction |
| ch | : | Chemical |
| ph | : | Physical |
| kn | : | Kinetic |
| pt | : | Potential |

# 1. INTRODUCTION

All over the world fossil fuels and fossil fuels-based energy systems have been using extremely high levels with growing world population and energy demands of the population. These fuels and systems has unique importance in every part of life such as transportation of goods and passengers, heating etc. But the most used field of fossil fuels is naturally in vehicles.

Fossil fuels causes air pollution and damage to the world. Last years these negative impacts of fossil fuels are seen more clearly than ever before. Also, fossil fuel resources diminish rapidly and soon or later will vanish. This situation and energy demands of the human being come out a big problem for the future.

Nowadays, new natural alternative energy sources (sun, wind, geothermal, hydroelectric etc.) and nuclear energy have been handled. But none of these sources can be a substitute for the most critic field which is using in vehicles. In 1800s, fuel cells have been found out but with the discovering of the internal combustion engines (ICE), fuel cells have been neglected until needs of space applications (Oğuz, 2006).

Fuel cells use oxygen generally taken from air and hydrogen as a fuel. Hydrogen energy is seen that the future energy source and the fuel cells are the apparatuses that converts the chemical energy of hydrogen into electricity that can be used many fields. Fuel cells are clean energy conversion units and thanks to advantages of safety, high efficiency and nearly zero emission levels, fuel cells has great interest (Chandan et al., 2013).

Besides the advantages of hydrogen as a fuel, there are also disadvantages of hydrogen. Hydrogen is not readily available on Earth and it must be turned out from some feedstock like fossil based (natural gas, coal) or renewable sources (water, algae, wood). Figure 1.1. shows some hydrogen feedstocks and process alternatives.

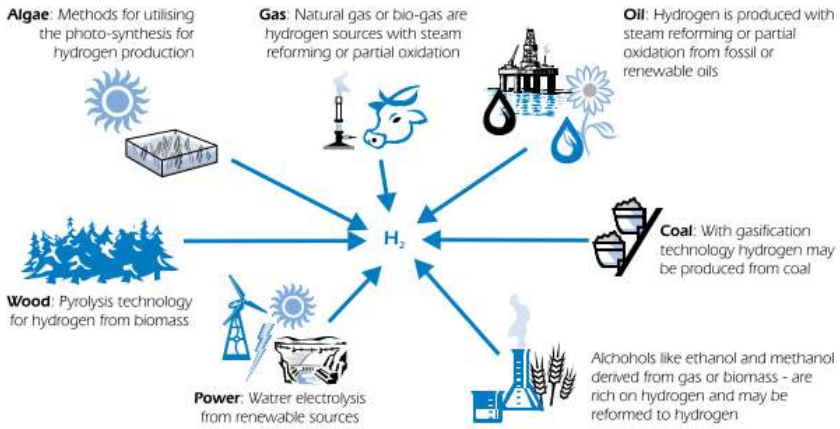


Figure 1.1. Some feedstock and production process alternatives (Adapted from International Energy Agency, 2006)

For an example hydrogen production from natural gas which is also called methane, it is known that chemical formula of methane is $CH_4$. Hydrogen is derived from methane via three process which are auto-thermal reforming, partial oxidation and steam reforming. The production of hydrogen from methane by means of steam reforming process equations are given below:

$$CH_4 + H_2O + heat \rightarrow CO + 3H_2O \quad (0.1.)$$

$$CO + H_2O \rightarrow CO_2 + H_2 + heat \quad (0.2.)$$

It is seen from the equations that after producing hydrogen from methane there is formation of carbon dioxide which is not a good thing for air so capturing and storing of this formation are needed. Conversion of energy of hydrogen energy into electric energy is an environmentally friendly, but the production of hydrogen sometimes can be opposite of it. These two situations should not confuse each other.

Since hydrogen has higher thermal conductivity, lower viscosity and lower density among all other gases, it can leak very small space. Thus, the storage of the hydrogen must be done very carefully. There are three types of hydrogen and these are gaseous, liquid and solid.

Gaseous hydrogen is compressed at high pressure to store. The storage of hydrogen in gaseous form uses steel, composite and glass microspheres as tank. But the most common storage method is in steel tanks. Nevertheless, design of composite tanks is becoming more common because of higher pressure levels. Low weight of composite tanks is the main advantages to store hydrogen in gaseous from with high pressure ranges (300-700 bar). Besides, there are still needs for more research and developments (R&D) such as; research on material embrittlement, development of lower cost and stronger materials that should be used in construction (especially carbon fibres), development of a clean and efficient compressor and development of reduction of compression energy. The storage of hydrogen in glass microspheres has three steps. First step is charging: hollow spheres are filled with hydrogen at high temperature about 300℃ and high pressure between 350-700 bar by passage in a vessel that has high pressure. The second step is filling: the temperatures of microspheres are decreased to room temperature and transferred to the tank which is at low pressure. Last step is discharging: the temperatures of microspheres are increased to 200-300℃ to liberate hydrogen in a controlled way. The primary problem of microspheres of glass is low volumetric density. Furthermore, some research and development studies are needed like composite tanks. Reduction of cost of production and coating methodes for optimization of hydrogen permeability and stronger glasses.

Decreasing of the temperature of hydrogen till cryogenic temperature (22 K ~ -253˚C) is used to store hydrogen in liquid form. This type of storage is the most common technique. Other techniques store hydrogen as a component in other liquids, for example; rechargeable organic fluids or sodium borohydride ($NaBH_4$) solutions. These three methods that is mentioned above are the most encouraging

techniques. Density of cryogenic hydrogen is 70.8 kg/m$^3$ at normal boiling point (-253℃) and cryogenic hydrogen is simply referred to as liquid hydrogen ($LH_2$). Critical temperature is -240˚C and pressure is 13 bar. It is important to control boiling-off loss during quiescence and to insulate the containers. The main advantage of cryogenic hydrogen is high storage density. But, new developments of more efficient processes of liquefaction, search of lower cost and improved the insulated containers and developed systems that capture the boil-off and re-liquefy the fuel automatically are the tasks of the research and development studies. Another liquid storage method which is used for hydrogen is borohydride ($NaBH_4$) solutions. The reaction is:

$$NaBH_4(l) + 2H_2O(l) \rightarrow 4H_2(g) + NaBO_2(s) \quad (0.3.)$$

The primary advantage of using $NaBH_4$ solutions is that it permits controllable and safe for production of hydrogen. The regenerating of reaction product $NaBO_2$ back to $NaBH_4$ is the main disadvantage of using $NaBH_4$ solution. Development of a direct borohydride fuel cell is identified for a R&D task.

Both for mobile and stationary applications the solid storage of hydrogen has the potential to be an efficient and safe way for energy storage. There are four main groups of suitable materials: thermal chemical hydrides, carbon and other high surface area materials rechargeable hydrides and $H_2O$-reactive chemical hydrides. In rechargeable hydrides, the granules of hydrogen are stored between spaces of metal atoms. Solid hydrogen needs less energy than liquid and gaseous hydrogen storage techniques.

Comparison between the basic storage techniques presents that the possible benefits of storage of hydrogen as solid compared to gaseous and liquid hydrogen storage are: higher purity of hydrogen output, lower pressure and lower volume but greater energy efficiency and (International Energy Agency, 2006).

The basic principle of operation of fuel cells was noticed in 1839 by scientist and lawyer William Grove, he was make an experiment that shown in Figures 1.2a and 1.2b. In Figure 1.2a, firstly, water was being seperated into hydrogen and oxygen thanks to electrolyzing. In Figure 1.2b, the power supply was changed with an ammeter, and a small current was flowing. It was concluded that the electrolysis was reversed, the hydrogen and oxygen was recombined, and an electric current was produced. The reasons of the small current rate are the low contact area between the electrode, the electrolyte and the gas and large distance between the electrodes. This large distance causes resistance of the flow of electric current. In order to defeat problems, the electrodes are generally made flat, with a thin layer of electrolyte.

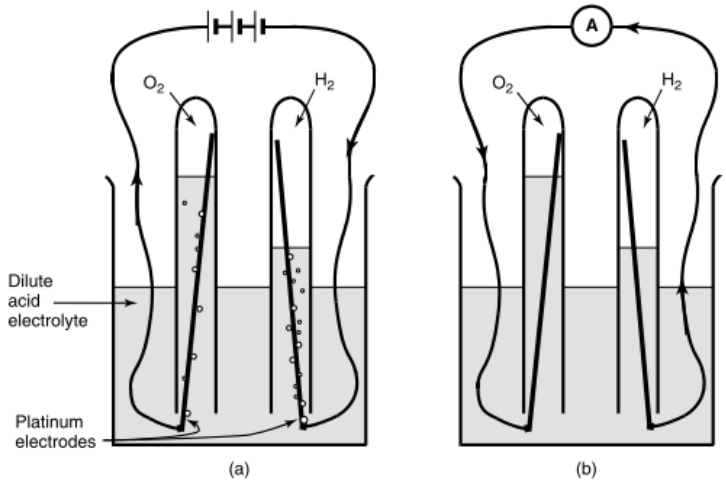


Figure 1.2. (a) The electrolysis of water. (b) Current flow. The hydrogen and oxygen are recombining (Larminie and Dicks, 2001)

Fuel cells are the promising apparatuses that convert chemical energy of hydrogen into electricity directly. There are several types of fuel cells that are used today. Fuel cells are traditionally classified in accordance with material of electrolyte. These are classified as; alkaline fuel cell (AFC), proton exchange membrane fuel cell (PEMFC) or polymer electrolyte fuel cell (PEFC), phosphoric

acid fuel cell (PAFC), direct methanol fuel cell (DMFC), solid oxide fuel cell (SOFC) and molten carbonate fuel cell (MCFC). They are separated their operating temperatures, electrical efficiencies, typical applications and power outputs (EG&G Technical Services, 2004).

Alkaline fuel cell's electrolyte needs to be an alkaline solution. Sodium hydroxide (NaOH) and potassium hydroxide solution are being highly soluble, lowest cost and not excessively corrosive are the important candidates. The reactions of anode and cathode are as follows:

$$\text{Anode: } 2H_2 + 4OH^- \rightarrow 4H_2O + 4e^- \tag{0.4.}$$

$$\text{Cathode: } O_2 + 4e^- + 2H_2O \rightarrow 4OH^- \tag{0.5.}$$

The AFC operates between 50˚C and 250˚C temperature range. The beginning in 1960s, the AFC is the one of the first contemporary fuel cells but the studies data back to 1900s. The application of the AFC which is the success of AFC was to supply electric power for space vehicle Apollo. The fuel cell needs highly pure hydrogen as a fuel since the precision of the electrolyte to $CO_2$. The $CO_2$ in the air must be removed if ambient air is used as the oxidant.

The PEM fuel cell's electrolyte is an ion exchange membrane which is perfect proton conductor. Water is the only liquid in the fuel cell, so wearing out problems are minimal. Platinum is used for both cathode and anode as a catalyst. The reactions of anode and cathode are given below:

$$\text{Anode: } 2H_2 + 4H^+ + 4e^- \tag{0.6.}$$

$$\text{Cathode: } O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \tag{0.7.}$$

The PEMFC operates between 30˚C and 100˚C operating temperature range. The PEMFC are used for a wide variety of applications, especially in fuel cell vehicles. The fuel cell has a solid electrolyte that ensures perfect resistance to crossover of gas. The narrow and low temperature of operation range makes thermal management difficult.

The DMFC uses alcohol without reforming. Fuel cells are mostly used for portable applications because of low power range. The overall reaction in the DMFC is represented by the equation is:

$$\text{Overall: } CH_3OH + 1/2\,O_2 \rightarrow 2H_2O + CO_2 \qquad (0.8.)$$

The DMFC operates between 20 and 90˚C temperature range. The main advantage of the direct methanol fuel cell is usage of methanol directly in the system.

The PAFC uses phosphoric acid ($H_3PO_4$) as electrolyte which typically operates about 220 ˚C. Phosphoric acid is a poor ionic conductor at lower temperature. The operation of the PAFC is the same as the PEMFC, so the reactions that occur in anode and cathode are the same as given above. It is safe and operates for a long time without any maintenance.

The MCFC's electrolyte is usually mixture of alkali carbonates, that is kept in a ceramic matrix of $LiAlO_2$. Carbonate ions provides ionic conduction and the fuel cell operates about 650˚C. The reactions of the MCFC is given below:

$$\text{Anode: } 2H_2 + 2CO_3^{2-} \rightarrow 2H_2O + 2CO_2 + 4e^- \qquad (0.9.)$$

$$\text{Cathode: } O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2-} \qquad (0.10.)$$

The mobile ions go through electrolyte from cathode to anode. The system requires $CO_2$ unlike AFC. Methane can be used directly in the fuel cell. The comparatively high temperature of the MCFC eventuate in several benefits: both certain hydrocarbons and CO also used in the system and no expensive electro-catalyst is required as the nickel electrodes ensure adequate activity. The main difficulty for MCFC is the corrosivity and mobile electrolyte, which needs use of nickel and high-grade stainless steel. The higher temperatures cause affecting of mechanical stability and stack life and material problems.

The SOFC uses an oxide ion-conducting ceramic material that is generally $Y_2O_3$-stabilized $ZrO_2$ (zirconia) as electrolyte but it is hard to manufacture of ceramic materials and the cost of fuel cell is rather high. The SOFC uses both hydrogen and carbon monoxide as fuel. The anode and cathode reactions of the SOFC are as follows for the hydrogen fuel:

$$\text{Anode: } 2H_2 + 2O^{=} \rightarrow 2H_2O + 4e^{-} \qquad (0.11.)$$

$$\text{Cathode: } O_2 + 4e^{-} \rightarrow 2O^{=} \qquad (0.12.)$$

The anode and cathode reactions of the SOFC are as follows for the carbon monoxide fuel:

$$\text{Anode: } 2CO + 2O^{=} \rightarrow 2CO_2 + 4e^{-} \qquad (0.13.)$$

$$\text{Cathode: } O_2 + 4e^{-} \rightarrow 2O^{=} \qquad (0.14.)$$

The solid construction of ceramic eliminates any corrosion problems in the fuel cell. Since the fuel cell operates at high operating temperature range above 500

˚C, system efficiency ranges between 60-75%. It has advantages thanks to high operating temperatures, it has some disadvantages too. The high operating temperature causes strict limitations on selection of materials and ends up with difficult processes of fabrication.

Table 1.1. Types of fuel cell and their major differences

| | AFC | PEMFC | DMFC | PAFC | MCFC | SOFC |
|---|---|---|---|---|---|---|
| Electrolyte | Potassium hydroxide in asbestos matrix | Polymer ion exchange membrane | Alkaline electrolyte | Liquid phosphoric acid | Liquid molten carbonate | Ceramics |
| Electrodes | Transition metal | Carbon | Carbon | Carbon | Nickel or nickel oxide | Perovskites and perovskite/ metal cermet |
| Catalyst | Platinum | Platinum | Carbon-supported | Platinum | Electrolyte material | Electrolyte material |
| Operating Temperature | 50-200 ℃ | 30-100 ℃ | 20-90 ℃ | ~220 ℃ | ~650 ℃ | 500-1000 ℃ |
| Mobile ion | $OH^-$ | $H^+$ | $H^+$ | $H^+$ | $CO_3^{2-}$ | $O^{2-}$ |
| Applications | Space vehicles | Vehicles and mobile application and lower CHP systems | Portable electronic systems of low power | Large numbers of 200 kW CHP systems | Medium to large scale CHP systems | All sizes of CHP systems 2 kW to multi MW |

Among all these types the PEMFC is the most encouraging nominee for transportation owing to fast start-up time, low operating temperature, high power density, high efficiency, and easy and safe handling (Sharaf and Orhan, 2014). The anode, the electrolyte and the cathode are the main three parts of a fuel cell. These three parts come together and make a stack. In PEM fuel cell, the PEM allows hydrogen ions to pass through it and it is a thin plastic sheet. High degree of dispersed metal alloy particles is used to coat the membrane on both sides these particles are commonly platinum that is active catalysts. Hydrogen atoms release its electrons then, hydrogen ions are occurred on the anode side of fuel cell by means of catalyst that encourages the atoms of hydrogen. The electric current that

is the form of the released electrons can be utilized before it arrives to the cathode side. Moreover, the protons diffuse through the membrane to the cathode, where the hydrogen atoms are rejoined and reacted with oxygen in order to produce water, so overall process is completed (Ibrahim Dincer, 2002).

The efficiency of an energy conversion process is one of the most important aspects of that conversion. Energy and efficiency is the two keys factor that has quite influence to choose a system for utilization. But it had been misunderstood that the traditional first law thermodynamics analysis was enough by itself to determine the performance of a system. In order to analyze a system performance, it is necessary to assess the inefficiency of the system associated with a number of situations that is possible with applying the second law analysis to the system. The second law analysis based on the term “availability” and the availability means potential of the system to do work. Contrast to energy, availability can be destroyed. The destruction of availability is often call irreversibility and the reduction of irreversibilities can lead to better system performance. In this case, PEM fuel cell is rather efficient system compared to conventional system. Additionally, after producing energy there is no emissions occurs except nitrogen which is not considerable amount.

In this study energy and exergy analysis were carried out to a 1 kW self-humidified PEM fuel cell. 1$^{st}$ and 2$^{nd}$ law thermodynamics efficiency related with quantity and quality were determined and compared with each other for different operating temperature and operating pressure conditions.

# 2. PRELIMINARY WORK

## 2.1. PEM Fuel Cell Literature Review

In the middle of the 1800s fuel cell researches had been conducted. But after discovering the internal combustion engines, the fuel cells fallen behind of these engines which are used fossil-based fuels. For the last 20 years, application and the utilization of the fuel cells are mostly taking place instead of internal combustion engine due to decrease of fossil fuels and the negative impacts of these fuels to the environment such as ozone depletion, greenhouse gas effect, global warming etc. providing power in portable and stationary applications (Andújar and Segura, 2009). The fuel cells are conversion devices that convert the chemical energy of hydrogen fuel to the electrical energy directly with zero emission. There are several types of fuel cell which are conducted in the studies. Nevertheless, PEM fuel cells are step forward with fast start-up, high efficiency, high power density, low operating temperature, easy and safe handling. When considered from this point of view many researchers have studied the performance of a PEM fuel cell and the parameters that affects the PEM fuel cell.

Santarelli and Torchio (2007) experimentally investigated the effects of different operation variables on a single cell PEM fuel cell with a 25 $cm^2$ Nafion® 115 membrane with the variation of the values of cell temperature, pressure of reactants and humidification. The experiment tests are conducted with the cell temperatures varies between 50-80˚C and operating pressure 1 and 2 bar, and also humidified or dry the anode and cathode. An increment of the cell temperature results increasing of membrane conductivity and cell performance. The increment in operating pressure enhances stability of tests at high currents and the performance of fuel cell. The humidification is also concerned, an increase in humidification improves the performance at high cell temperature.

Ko et. al. (2018) presented the effect of pressure of operation on the performance of PEMFC and its effect on the water distribution. A PEM fuel cell test cell manufactured with a layer of composed parts including end plates, bipolar plate with channel, silicon gasket, gas diffusion layer and membrane that made of Nafion. The investigation of the performance and water distribution of PEM fuel cell was made four different pressurized condition (anode side or cathode side, none or both sides pressurized) with two different pressure values (0.4 bar and 0.2 bar) and two different conditions of relative humidity (RH) (100% and 25%). At low RH and middle current density, the results showed that higher pressure improves the water saturation in membrane. At high current density range and high RH, both side and cathode pressurized conditions showed better performance. The results also showed that rise in partial pressure and change of water distribution should be considered together to analyze the effect of operating pressure on PEM fuel cell.

Qin et. al. (2017) investigated 20 kW vehicular PEM fuel cell numarically and incorporating an air compressor are matched. The results show that the performance of the fuel cell stack is increased with the system operating pressure. The optimum operating pressure of the system is found to be 1.2 atm. Also, the optimum operating pressure of the system is affected by compressor efficiency. If compressor efficiency is increased, the fuel cell performance is improved.

Kim and Hong (2008) represent a study that investigate a 10 cell PEM fuel cell stack and active cell area of 100 $cm^2$. The experiments are made different operating conditions such as stack temperature (60˚C and 70˚C) and oxidant and fuel humidity (dry and 100%). The stack performance is directly affected by cathode humidification changes. The mean cell performances at 200 $mA/cm^2$ are measured as; 0.740, 0.738, 0.722 and 0.711 V for 100, 80, 60 and 40% of cathode relative humidity, respectively. This performance comparison shows the cathode humidification effect under 70˚C of stack temperature and full humidification of

anode on PEMFC stack performance. The humidification of anode also affects the performance of fuel cell. The comparison of stack temperature, 70˚C and 60 ˚C, shows less influence on fuel cell performance.

Ozen et. al. (2016) observed the effects of operating temperature and humidity conditions on a single cell PEM fuel cell with 25 $cm^2$ active cell area. The PEM fuel cell stack is experimentally tested for different inlet gas humidification levels (for anode side 66% and 100% RH, for cathode side 26%, 66% and 100% RH)and inlet temperatures, operating temperatures (50, 70 and 80˚C) and oxidant type (air or oxygen). Improvement of cell performance is more remarkable when operating temperature or inlet gas temperature is increased. The cell shows 0.59 W $cm^2$ peak power at an operating temperature of 80 °C.

Wang et. al. (2003) investigated that how different operating parameters affects the performance of a single cell PEM fuel cell with 7.2 cm x 7.2 cm active cell area and Nafion®115 membrane. The fuel cell operating temperature varies from 50 to 90˚C and pressure values of it are 1, 1.34, 1.68, 2, 2.36, 2.70, 3, 3.38, 3.74 atm. The performance of the fuel cell increases with the increase of pressure due to the increase of the ex- change current density and the reactant gas partial pressures. Also, when enough humidification is provided, the performance of the PEM fuel cell improves with the increase of operation temperature. When the gas stream humidification temperatures is higher than fuel cell operating temperature, the performance of the fuel cell can increase. This is particularly true in the low current density region.

Esfeh and Hamid (2014) parametrically investigated of the temperature effect on a PEM fuel cell performance. The test temperature was up to 120˚C and results showed that increment of temperature decreases the concentration losses but decrasing the activation losses over potential up to 80˚C.

**2.2. Energy and Exergy Review**

Energy has a significant role to enhance the contemporary economy for transportation, industry, agriculture and household uses for all over the world. Today, most of the power generation system uses petroleum-based fuels to produce electricity or power. The sources of these fuels will be diminished soon or later. Besides, the detrimental effects of emissions of petroleum-based fuels cause lots of undesired situations such as global warming, depletion of ozone layer etc. Finally, an awakening start, and new alternative energy conversion systems arise. It is important to identify the performance of a system. First law analysis is the first foundation of the conventional thermodynamic analysis and states the principle of conservation of energy. An energy analysis of an energy conversion system is fundamentally an accounting of the inlet and outlet of energies. Efficiencies are frequently assessed as the ratios of quantities of energy (Boettner and Moran, 2004).

Energy efficiency have been often misleading on the evaluating the performance of the system and how it is close to its ideal efficiency. Moreover, the energy analyses may not give the accurate results which are spoiled by the thermodynamic losses within the system and cause to deviate from ideality. The exergy analysis gives precise results considering those thermodynamic losses. It is useful in identifying the magnitudes, locations, and causes of process inefficiencies thanks to the second law (Dincer and Rosen, 2007).

During the recent years, energy and exergy analyses methods have been commonly used in the simulation, design and performance determination of various power generation systems. In this respect, either energy method or exergy method may be performed to various types of PEM fuel cell for identifying losses and efficiencies.

Taner (2018) made an investigation experimentally of a single cell air breathing PEM fuel cell. The experiment parameters are the voltage and the operating pressure. The current, temperature and voltage was controlled via a

software with computer. The modified parameters are voltage and pressure vary between 1-5 V and 1-2 bar which has 0.5 interval, respectively. A manual valve was used to empty the remaining air in fuel cell and it was opened 5-10 s. Then, the data was recorded within 15 minutes after the currents and voltages were obtained. It was concluded that water production was vital for fuel cell. If the water production can be decreased with the optimization, energy and exergy efficiency of PEM fuel cell will improve. The results also showed that the efficiency of energy and exergy was about 47.6% and 50.4% respectively.

Hanapi et. al. (2015) conducted a parametric study which was the exergy efficiency of an open cathode 1 kW vehicular proton exchange membrane fuel cell. The effects of operating pressure and temperature variations was investigated at different pressure ratio ($P/P_0$) and temperature ratio ($T/T_0$) ranging from 1 to 4 and 1 to 1.15, respectively. The results showed that the whole efficiency of exergy of the PEM fuel cell was 61.3%. Also, the increase of operating temperature and pressure increase the fuel cell exergy efficiency. The exergy efficiency difference between the lowest and highest pressure was 4.8%.

Sevjidsuren et. al. (2012) mathematically investigated the energy and exergy efficiency of a 1.2 kW Nexa™ power module at different operating pressure, temperature and air stoichiometry. The analyses were conducted on PEM fuel cell voltages from 0.0001 to 0.84 V at air stoichiometries from 13 to 2.1 to determine their effects on efficiency. Then, the calculations of exergies of reactants and products of the PEM fuel cell are implemented at pressure ratio ($P/P_0$) and temperature ratio ($T/T_0$) ranging from 7.44 to 4.91 and 0.93 to 1.13, respectively. Energy efficiencies change between 41-55%, exergy efficiencies vary from 33% to 42% at the current density of 0.02-0.36 A/cm$^2$. Also, the results showed that exergy efficiency of the system can be enhanced thanks to increment in operating pressure and temperature. It was recommended that air stoichiometry should be lower than 4 to adjust the relative humidity level in the fuel cell to provide membrane from drying out.

Miansari et. al. (2009) made two steps investigation of performance of a PEM fuel cell. The first step was an experimentally study which consists of the effects of different operating parameters such as anode and cathode channel depth, temperature and pressure. The second step was creating a semi-empirical model of the PEM fuel cell and studying the effects of pressure (1, 2 and 3 atm), temperature (55°C, 70°C and 80°C) and air stoichiometry (2 to 4) of performance of fuel cell. In the first part of this study, the single-serpentine flow field geometry with the depth of anode and cathode channel of 1.5 mm and 1mm, respectively were specified. The good arrangement of channels depth high performance was observed at fuel cell and higher temperature and pressure was enhanced the cell performance and exergy efficiency and reduced irreversibilities of the cell. Besides, a parametric study was conducted and resulted that increase of operating pressure and temperature improved the fuel cell efficiency, but no notable increment was found with the raising the air stoichiometry.

Yilanci et. al. (2008) undertaken Nexa PEM fuel cell unit that has maximum 1.2 kW power output in a solar-based hydrogen production system in order to analyze the thermodynamically. In the study both experimental setup and thermodynamic model were used. The exergy and energy efficiencies increase with pressure by 15% and 23%, respectively. No remarkable changes are observed in exergy and energy efficiencies with rise in temperature. The exergy and energy efficiencies decrease with rise in anode stoichiometry by 14% and 17%, respectively. These observations are reported for the given range of current density as 0.047–0.4 A/cm$^2$. The results and analyses show that the PEM fuel cell system has higher energy efficiencies than corresponding exergy efficiencies due to the irreversibilities that are not considered by energy analysis. It was observed that there is decrement in exergy and energy efficiencies (about 14%) with increment in current density from the model results.

Ay et. al (2006) investigated the effects of irreversibilities on the exergy efficiency of a PEMFC at different operating pressure, pressure of cathode and

anode, current density and membrane thickness. The experiments were conducted on various operating temperature and pressure that ranges from 323 K to 353 K with 10 intervals and 3-5 atm with 1 intervals, respectively based on different current density varies from 0.01 $Acm^{-2}$ to 2.0 $Acm^{-2}$ with 0.05 $Acm^{-2}$ intervals and membrane thickness values were 0.02, 0.018 and 0.016 cm. Then the results showed that thermodynamic irreversibilities increased with raising of membrane thickness at invariable operating temperature and pressure range. The exergy efficiencies are found as 0.357, 0.324, 0.293 and 0.263 for 323 K operating temperature and 0.016 cm of membrane thickness and current density varies from 0.5 to 2.0 $Acm^{-2}$ with 0.5 $Acm^{-2}$ intervals at operating pressure of 3 atm. But, for 0.016 cm of membrane thickness, 353 K and 3 atm and current density equal to 0.5–2.0 $Acm^{-2}$ with 0.5 $Acm^{-2}$ intervals, they were calculated as 0.377, 0.352, 0.329 and 0.307, respectively. Thus, the lower membrane thickness and current density, and the higher temperature should be selected to operate a PEM fuel cell at constant pressure to enhance the performance of fuel cell and alike exergy efficiency. Like rise in temperature at constant temperature, increment in pressure at constant temperature could be used to enhance fuel cell exergy efficiency as common membrane thickness and current density range.

Mert et. al. (2012) parametrically investigated a transportation system powered by a PEM fuel cell engine and conducted thermodynamic approach to energy and exergy. The system consists of five main parts such as PEM fuel cell stack, pressure regulator, cooling system, humidifiers and a compressor. The performance of the system was studied in terms of energy and exergy efficiency by changing the operating parameters that were operating temperature and pressure, membrane thickness, anode and cathode stoichiometry, humidity and reference temperature and pressure. The results showed that the exergy efficiency increased with increase of pressure from 2.5 to 4 atm by about 5%, temperature from 323 to 353 K by about 8%, and reference state temperature from 253 to 323 K by about 3%, respectively. In addition, the exergy efficiency increases with decrease of

membrane thickness from 0.02 to 0.005 mm by about 9%, anode stoichiometry from 3 to 1.1 by about 1%, and cathode stoichiometry from 3 to 1.1 by about 35% and humidity from 97% to 80% by about 10%, respectively.

Kazim (2004) investigated the effects of variable operating temperatures, pressures, cell voltage and air stoichiometries on exergy analysis of a PEM fuel cell which has maximum power output of 10 kW. The estimations of the mass flow rates of reactants and products, the chemical and physical exergies, and exergy efficiency were executed at pressure ratios ($P/P_0$) and temperature ratios ($T/T_0$) changing from 1 to 3 with 1 intervals and 1 to 1.25 with 0.5 intervals. Then, two different cell voltages 0.6 and 0.5 and three different air stoichiometry 4, 3 and 2 were used in order to evaluate the effects on performance of the PEM fuel cell. The results indicated that switching air stoichiometry from 2 to 4 improved system efficiencies about 7%. Secondly, 2.5% and 2% improvement in exergy efficiency of the system could be obtained if the temperature ratio changes from 1 to 1.25 and the pressure ratio enhances from 1 to 3, respectively. As a result, switching of cell voltage 0.5 to 0.6 V improved to system exergy efficiency about 7%.

# 3. MATERIAL AND METHOD

## 3.1. Material

### 3.1.1. PEM Fuel Cell Test Rig

Fuel cell performance experiments were conducted on a 1 kW self-humidified PEM fuel cell which was produced by Horizon Fuel Cell Technologies. Technical specifications of the fuel cell were given in Table 3.1. PEM fuel cell test rig and its schematic representation were shown in Figure 3.1 and Figure 3.2.

Table 3.1. Technical specifications of the fuel cell

| | | |
|---|---|---|
| | Brand | Horizon H-1000XP |
| | Type | PEM |
| Physical | Number of cells | 50 |
| | Dimensions | 264 x 203 x 104mm |
| | Weight | Stack < 4.9 kg<br>System < 6.8 kg |
| Performance | Peak power | 1100W |
| | Rated current | 0 – 33.5A @ 30V |
| | DC voltage | 25-48V |
| Fuel | Reactants | Hydrogen and oxygen |
| | Composition | 99.99% dry $H_2$ |
| | $H_2$ pressure | 7.2 - 9.4 psi (0.5 – 0.7 bar) |
| | Hydrogen consumption @1000W or flowrate | 12.5 SLPM |
| Operation | Ambient temperature | 5 – 35℃ |
| | Max. temperature of stack | 65℃ |
| | Humidification | Self-humidified |
| | Cooling | Air |
| | Relative humidity | non-condensing(10%-95% RH) |
| | Start-up battery | 12V |
| Monitoring | RS232 | System status / historical data |

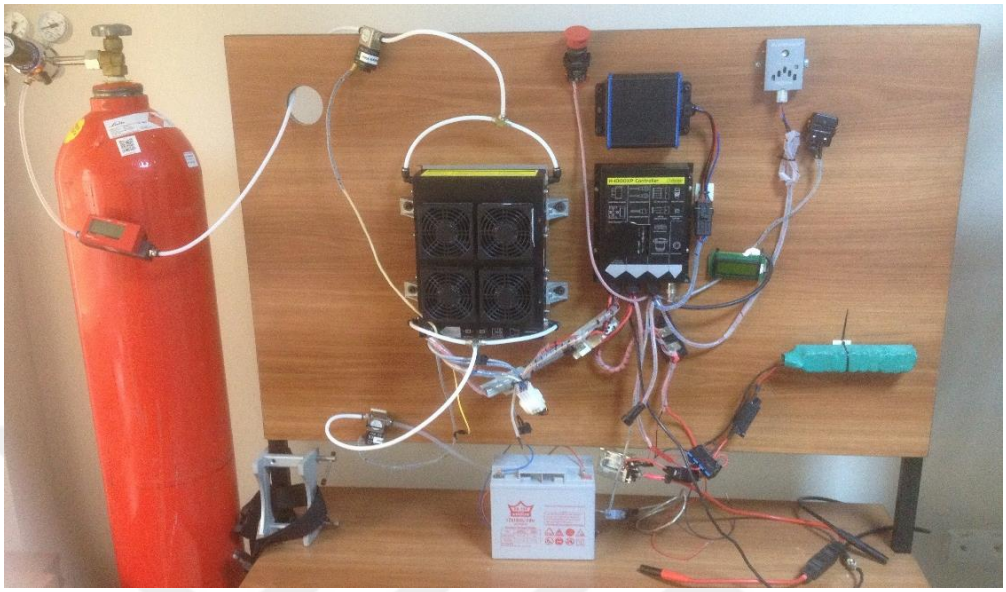

Figure 3.1. PEM fuel cell test rig

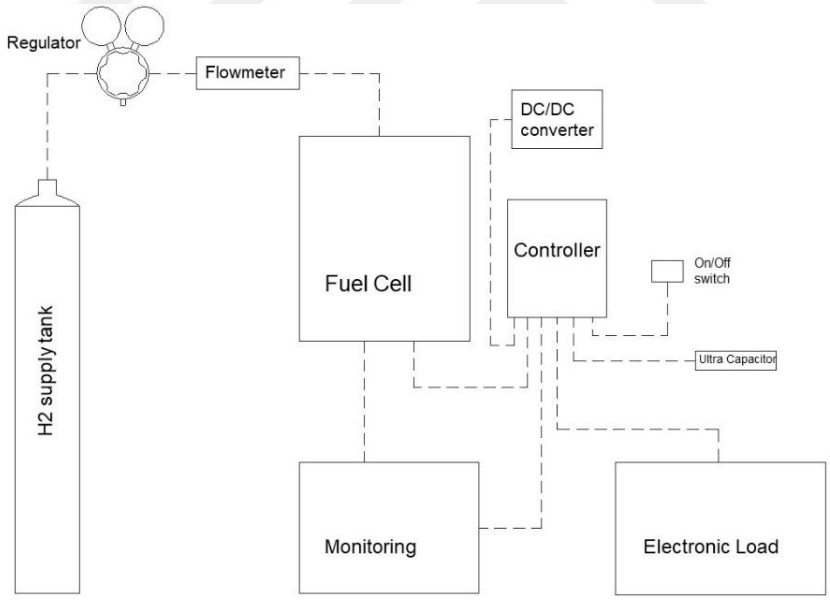


Figure 3.2. Schematic representation of the fuel cell test rig

### 3.1.2. Fuel Cell Components

#### 3.1.2.1. Stack

The stack of H-1000XP fuel cell (Figure 3.3) is an open cathode air cooled proton exchange membrane (PEM) fuel cell stack designed to ensure stable electrical power while operating on dry hydrogen and air. The H-1000XP can achieve 1000W power output with innovative materials.

Figure 3.3. Horizon Fuel Cell Technologies H-1000XP PEM fuel cell

#### 3.1.2.2. Supply Valve

Supply valve (Figure 3.4) controls the $H_2$ input. The supply valve will open when the system is operational. When triggered by the hydrogen sensor (in the case of leakage more than 1% hydrogen in air), the valve acts as emergency shut down valve.


Figure 3.4. Hydrogen supply valve

### 3.1.2.3. Purge Valve

Purge valve (Figure 3.5) is used to purge the gas redundant and water in the fuel cell and the controller will control the purging time.


Figure 3.5. Hydrogen purge valve

### 3.1.2.4. Hydrogen Sensor

Sensor (Figure 3.6) triggers when the concentration of hydrogen is above 1% which is 25% of LFL (lower flammability level).


Figure 3.6. Hydroknowz hydrogen sensor

### 3.1.2.5. DC/DC Converter

The DC/DC converter regulates the output voltage for the controller. The DC/DC converter (Figure 3.7.) can step down the stack voltage (48V to 27.5V) to 12V for the fuel cell controller and other peripheral parts.


Figure 3.7. VOLRAD DC/DC converter

### 3.1.2.6. Ultra-capacitor Bank

The used capacitor is shown in Figure 3.8. It can supply power output during system short-circuiting which could enable system continuous operation without external power supply. Rated voltage and capacitance of ultra-capacitor are 50V and 1.25F.

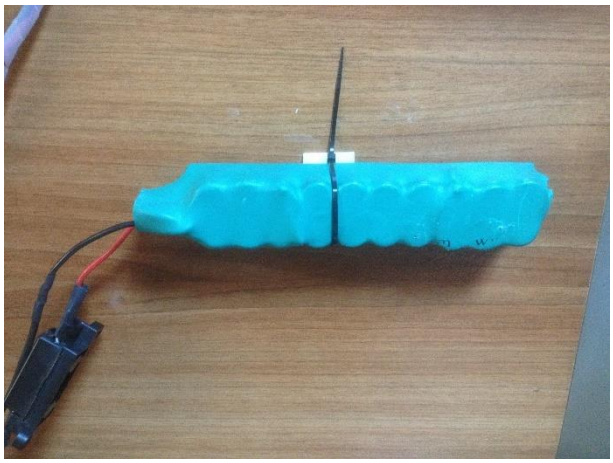

Figure 3.8. Ultra-capacitor

### 3.1.2.7. Blower Controller

When no load is connected, it can be turned off to reduce the power consumption of the stack.


Figure 3.9. Blower controller

### 3.1.2.8. System Controller

It controls the all peripheral parts and stack in order to operate the system at its optimal condition. It has the following features

- Control hydrogen supply and shut down
- Monitoring $H_2$ concentration
- Monitoring stack current and voltage
- Protect stack from possible failures, like stack low voltage, over current, over temperature
- RS232 communication with computer
- Control stack purge rate
- Control stack temperature

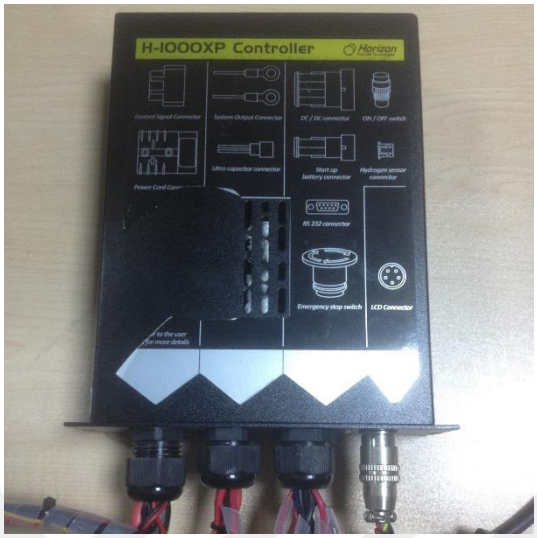


Figure 3.10. H-1000XP controller

### 3.1.2.9. Gas Regulator

It regulates the pressure of the input $H_2$ to prevent the system from damages. It operates between 0-1.5 bar pressure ranges. It is not recommended that operating pressure of the stack is above 0.5 bar.


Figure 3.11. LINDE 9521F-5 hydrogen gas regulator

### 3.1.2.10. Flowmeter

The hydrogen consumptions were measured by Voegtlin red-y compact series (Figure 3.12) which shows the both instantaneous (l/min) and total amount of consumption of hydrogen.


Figure 3.12. Voegtlin instruments red-y compact series (hydrogen)

### 3.1.2.11. Start-up Battery

12V start-up voltage is needed for the operation of the fuel cell. Thus, Or-Tec 12V battery was used to start the system.


Figure 3.13. Or-Tec plus Battery

### 3.1.2.12. Electronic Load

Heliocentris EL1500 (Figure 3.14) electronic load was used to generate different power values from the fuel cell. Maximum power, voltage and current values are 1500W, 75V and 100A respectively. It was rather suitable for the using in the system.

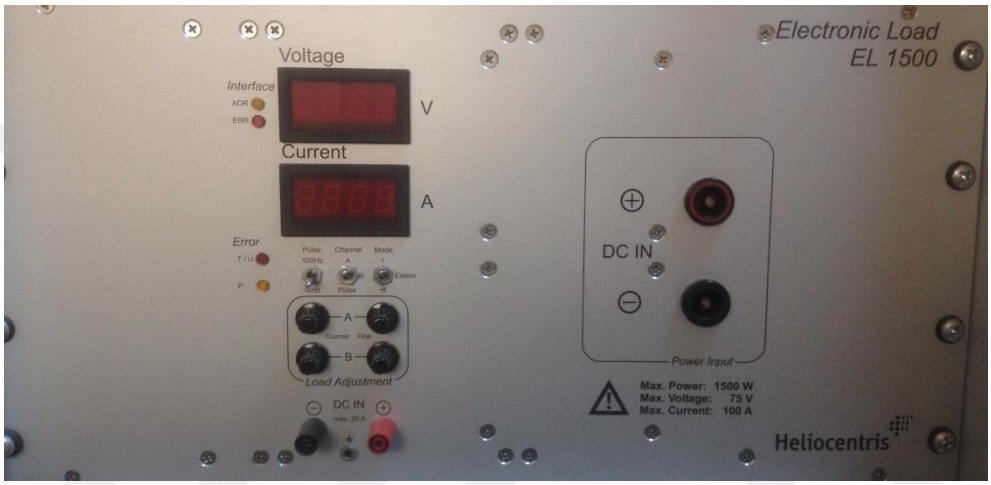


Figure 3.14. Heliocentris EL 1500 electronic load

### 3.1.3. Hydrogen

The PEM fuel cell uses hydrogen as a fuel and the purity of the hydrogen must be 99.99% or above. Table 3.2 shows the technical specifications of the used hydrogen as compressed gas.

Table 3.2. Technical specifications of hydrogen

| | |
|---|---|
| Quality | High purity |
| Purity | >99.99% |
| Oxygen content | < 3 vpm (volumes per million) |
| Humidity | < 3 vpm |
| Nitrogen content | < 50 vpm |

Hydrogen was used as compressed gas formation in the fuel cell. Compressed hydrogen is a storage form where hydrogen gas is kept under pressure to raise the density of storage. Since hydrogen gas has bad energy density by volume, it must be compressed for good energy density by weight. The pressure of hydrogen in gas formation in compressed hydrogen tanks can be reached to 700 bar.

## 3.2. Methods

### 3.2.1. First and Second Law of Thermodynamics

Thermodynamics could be defined as the scientific study of the energy. Even though everyone has an idea in the aspect of energy, it is difficult task to make a completely precise definition for that term. The ability of causing changes can be thought as energy.

The first law of thermodynamics also known as the conservation of energy principle indicates that there are two ways to change the energy of a closed system; which are energy transfer by heat change or by work. Moreover, based on the experiment of Joule and other scientists, a basis of the energy concept is that energy is conversed which is also called first law of thermodynamics (FLT) or just first law (Moran et. al., 2010). The first law indicates that energy can be neither created nor destroyed during a process; it can only change forms.

Figure 3.15. depicts the basic of the first law schematically. A rock has some potential energy due to the elevation. The potential energy of the rock is converted to kinetic energy with neglecting the air resistance while losing elevation.

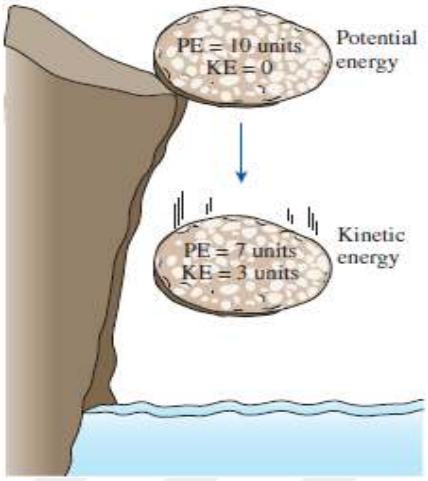


Figure 3.15. Conversation of energy (Adapted from Çengel and Boles, 2015)

In the early part of the 19th century, Joule examined the processes of a closed system whose the equilibrium state altered from one to another. Especially, the adiabatic processes which the work interactions involve but no heat work is involved between the surrounding and the control volume. According to studies of Joule, he figured out that for all adiabatic processes between two equilibrium states the value of the net work is the same. With a different expression, the net work value done by the closed system or on the system in an adiabatic process between two given states are related only on the end states. And it is not on the adiabatic process details. (Moran et. al., 2010).

The conservation principles are not always sufficient, but the second law of thermodynamics (SLT) combines the conservation of energy and mass principles together with property relations. The second law is also considered, including performance limits for thermodynamic cycles. This can also be defined as energy has quality as well as quantity. For general, a balance of energy cannot enable the preferred direction to be predicted and cannot permit the processes that can occur to be allocated from those that cannot. In basic situations, such as the illustrated in Figure 3.16, experience can be utilized to figure out if spontaneous processes occur

and to figure out their directions. In the case of more complexity, where experience is uncertain or lacking, a guiding principle is required. That is ensured by the second law.

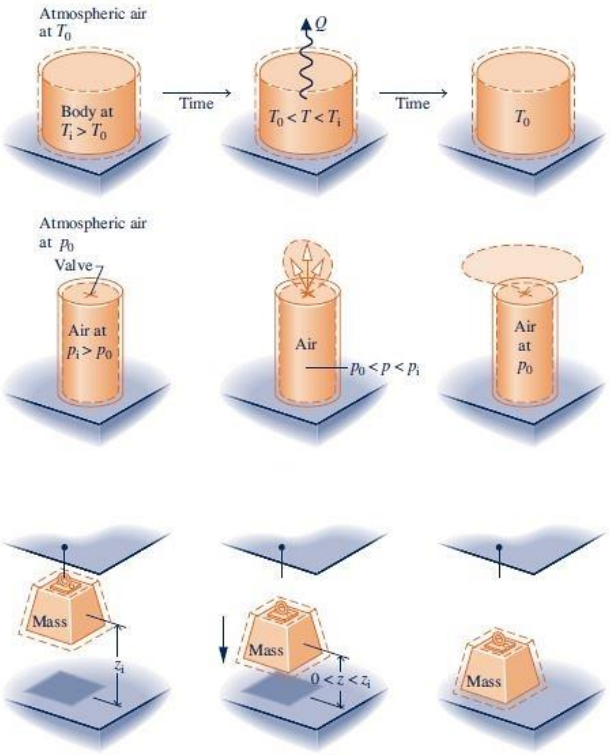


Figure 3.16. Schematic of the spontaneous processes and the final accomplishment of the equilibrium with surroundings

The previous discussion also shows that when systems tend to undergo spontaneous changes until an equilibrium state is accomplished, both with their surroundings and internally. Equilibrium can be reached quickly or slowly. For instance, some particular chemical reactions reach the equilibrium state in seconds; a solid ice cube needs a few minutes to change phase to liquid state; and it may even last for years to rust away of an iron bar. It does not matter the speed of the process, it may be slow or quick, it must satisfy the principle of energy

conservation. However, it may not be sufficient solely to determine the final equilibrium state. Another general principle which is the second law is required (Moran et. al., 2010).

There are several alternative statements of the SLT but in this section three of them are given below (Moran et. al., 2010).

The second law of thermodynamics states that the process occurs in a certain direction and the energy has quality as well as quantity. Also, there are some other statement on second law of thermodynamics;

Clausius statement: This statement argues that it is not possible to transfer energy from a cooler body to hotter one without any other energy interaction. For instance, to cool down the foods in a refrigerator. A thermodynamic cycle is required which the cycle is driven by an electric motor. This cooling cycle requires energy input from the surrounding as electric current. The Clausius statement mentions that it is not possible to construct a refrigeration cycle without an energy input.

Kelvin-Planck statement: This statement imply that it is not possible to construct a device which is delivering net amount of work to its surroundings with a single thermal reservoir.

Also, there is another statement of second law which stands for the entropy destruction. The statement implies that it is not possible for any system operating in a way that the entropy is destroyed.

### 3.2.2. Energy and Exergy Analysis

Energy is the basic term of thermodynamics and it is very important subject for engineering analysis. Thermodynamics studies let to be known of efficiency, behavior and performance characteristics of any system that is in interaction with heat and work. Thermodynamics analyses are generally based on

energy conservation (First Law of Thermodynamics) and the calculations are made on the inlet and outlet quantities of energy and masses (Dincer and Rosen, 2007).

Exergy is the useful work potential that can be achieved by bringing a system into equilibrium with its surroundings. It is also called available energy or availability. Every system has a quantity of exergy, in the case of no equilibrium with its environment, and oppositely, in the case of the equilibrium with its environment it has zero exergy means it has no ability to do work with respect to its environment (Colpan, 2005).

The exergy analysis is an effective method for the study of a system. The exergy analysis differs from the conventional energy analysis by considering the quality of the energy as well as the quantity. The exergy analysis ensures the calculation of the losses, conversion efficiencies and the limitations (Ye et. al, 2015).

Solely energy efficiency can mislead on the evaluating the performance of the system and how it is close to its ideal efficiency. Moreover, the energy analyses may not give the accurate results which are spoiled by the thermodynamic losses within the system and cause to deviate from ideality. The exergy analysis gives precise results considering those thermodynamic losses. The basic inefficiencies can be shown by the energy analysis results within the wrong parts of the system. This means a realistic efficiency definition is required. This can only be conducted by exergy efficiency since exergy analysis allows many of the limitations of energy analysis to get over. It is useful in identifying the magnitudes, locations, and causes of process inefficiencies thanks to the second law (Dincer and Ratlamwala, 2013).

Table 3.3. Differences between energy and exergy

| Energy | Exergy |
|---|---|
| independent of environmental features and dependent on energy flow or properties of a matter | dependent on of both the environment and energy flow or a matter |
| has values does not equal to zero in the case of equilibrium with the environment | equal to zero when in the dead state in consequence of being in exact equilibrium with environment |
| based on FLT and conserved for all processes | based on SLT and not conversed for real processes due to irreversibilities but, conserved for reversible processes |
| can be neither destroyed nor produced | in a reversible process, it can be neither destroyed nor produced, but in an irreversible process it is always destroyed (consumed) |
| emerges in many forms (e.g., potential and kinetic energy, heat, and work) and is evaluated in that form | is measured on the basis of work or ability to produce work and appears in many forms (e.g., potential and kinetic exergy, thermal exergy, and work) |
| is only measure of quantity | is a measure of either quantity or quality |

Some definitions should be given before performing exergy analysis.

- ✓ Dead state: It is defined as if a system in mechanical, thermal, and chemical equilibrium (thermodynamic equilibrium) with a reference surroundings (Dincer and Ratlamwala, 2013).
- ✓ Entropy: It can be described as a measure of molecular randomness or molecular disorder. While a system state becomes more disordered, the

molecules positions become less predictable and the entropy increases. The second law points out that entropy can be created however it cannot be destroyed (Çengel and Boles, 2015).

- ✓ Reversible and irreversible processes: If any system and its surroundings can be gone back to their first states then it is called reversible process. And if any system and surroundings cannot be exactly restored to their respective initial states after the process has occurred then it is called irreversible process (Moran et. al., 2010).
- ✓ Reversible work: It is described as the minimum work that is required to be supplied or maximum amount of useful work that can be produced as a system undergoes a process between the specified first and final states (Çengel and Boles, 2015)
- ✓ Irreversibility (or exergy destruction or lost work): It is stated that any difference between the useful work and the reversible work is owing to irreversibilities present during the process, and the difference is called irreversibility (Çengel and Boles, 2015).

A chemical reaction was considered which occurs theoretically when there was a combustion of hydrogen and oxygen mixture in PEM fuel cell in order to perform energy and exergy analyses. The reaction equation is given as below:

$$2H_2 + O_2 \rightarrow 2H_2O \qquad (0.15.)$$

Some assumptions made in the energy and exergy analysis are listed below:

- Considered control volume (Figure 3.17.) is whole PEM fuel cell and it runs as a steady state open system.

- The potential and kinetic energy effects of all reactant and product gases are neglected.
- The reference environment is represented in Table 3.4, $P_0$=1 and $T_0$=25˚C (Kazim, 2004).
- For the calculation of chemical exergy of reactant and product gases of a PEM fuel cell is taken from literature and listed in Table 3.5 (Hanapi et. al., 2015; Larminie and Dicks, 2001).
- Properties at operating conditions are also taken from literature and listed in Table 3.6 (Hanapi et. al., 2015; Kazim, 2004).


Figure 3.17. Control volume of the system (PEM fuel cell)

Table 3.4. Mole fractions of reference environment

| Component | Mole fraction (%) |
|---|---|
| $N_2$ | 77.48 |
| $O_2$ | 20.59 |
| $CO_2$ | 0.03 |
| $H_2O$ | 1.9 |
| Others | Neglected |

Table 3.5. Chemical exergy of the reactants and products of a PEM fuel cell system

| Chemical exergy, $ex^{ch}$ (kJ/kg) | | | | |
|---|---|---|---|---|
| Reactant/Product | Reactant air | Reactant $H_2$ | Product $H_2O$ | Product Air |
| PEM fuel cell | 0 | 159138 | 2.5 | 8.58 |

Table 3.6. Properties at standard condition

| Property | Value |
|---|---|
| Temperature of standard, $T_0$ | 298 K |
| Pressure of standard, $P_0$ | 1 atm |
| Average specific heat of air, $c_p$ | 1.005 kJ/kg K |
| Average specific heat of hydrogen, $c_p$ | 14.3 kJ/kg K |
| Average specific heat of hydrogen, $c_v$ | 10.16 kJ/kg K |
| Specific heat ratio of air and hydrogen, $k=c_p/c_v$ | 1.4 |
| Water enthalpy at standard condition, $h_0$ | 104.88 kJ/kg |
| Water entropy at standard condition, $s_0$ | 0.3674 kJ/kg K |
| Air stoichiometry, $\lambda$ | 3 |

The mass and energy balances for the control volume, steady state open system can be written as:

$$\sum \dot{m}_{in} = \sum \dot{m}_{out} \tag{0.16.}$$

$$\dot{Q} - \dot{W} = \sum \dot{m}_{out}\, h_{out} - \sum \dot{m}_{in}\, h_{in} \tag{0.17.}$$

where subscript in and out represents inlet and outlet, $\dot{Q}$ (kW) represents heat transfer rate through control volume, $\dot{W}$ (kW) represents work rate, $\dot{m}$ (kg/s) represents mass flow rate, $h$ represents specific enthalpy. Equation (3.2) denotes that total amount of mass entering control volume through system boundary equals to total amount of mass leaving control volume (mass balance). Equation (3.3) denotes that total energy entering control volume through system boundary equals to total energy leaving control volume (energy balance).

Energy input rate ($E_{fuel}$) can be found using mass flow rate of fuel ($\dot{m}_{fuel}$) (kg/s) and lower heating value of the fuel which is hydrogen $LHV_{H_2}$ (kJ/kg) as follows:

$$E_{fuel} = \dot{m}_{H_2} LHV_{H_2} \tag{0.18.}$$

Heat losses are evaluated as the difference between energy input rate ($E_{fuel}$) and work rate ($\dot{W}$) by:

$$\dot{Q}_{loss} = E_{fuel} - \dot{W} \tag{0.19.}$$

Energy efficiency (first law efficiency) is calculated as the ratio of work rate ($\dot{W}$) to energy input rate of fuel ($E_{fuel}$) from:

$$\eta = \frac{\dot{W}}{E_{fuel}} \tag{0.20.}$$

After energy analyses have been estimated, exergy analyses can be defined. Exergy balance for a flow of matter through a control volume of a system is obtained using following relation (Yilanci et. al., 2008).

$$\sum \dot{E}x_{mass,in} - \sum \dot{E}x_{mass,out} + \dot{E}x^{Q} + \dot{E}x^{W} + \dot{E}x_{dest} = 0 \tag{0.21.}$$

where subscript in and out represents inlet and outlet, $\dot{E}x^{Q}$ (kW) represents exergy transfer rate related with heat loss from the PEM fuel cell (control volume) to the

environment, $\dot{E}x^{W}$ (kW) represents exergy work rate, $\dot{E}x_{dest}$ (kW) represents exergy destruction due to irreversibilities, $\varepsilon$ (kJ/kg) represents specific flow exergy.

The exergy efficiency which is described as the second law efficiency, gives the true performance of an energy system from the thermodynamic viewpoint. The exergy efficiency or the exergetic efficiency of a fuel cell is the ratio of the power output $\dot{W}$, over the exergy differences of reactants and products and it can be calculated by the following formula:

$$\psi = \frac{\dot{W}}{\left(\dot{E}x_{air,R} + \dot{E}x_{H_2,R}\right) - \left(\dot{E}x_{air,P} + \dot{E}x_{H_2O,P}\right)} \tag{0.22.}$$

where subscript *R* and *P* represent the reactant and products, respectively.

The total exergy transfer of a stream for any matter can be expressed as the sum of the specific physical ($ex^{ph}$), chemical ($ex^{ch}$), kinetic ($ex^{kn}$) and potential exergies ($ex^{pt}$).

$$\dot{E}x = \dot{m}(ex^{ph} + ex^{ch} + ex^{kn} + ex^{pt}) \tag{0.23.}$$

However, the kinetic and potential exergies are not taken into consideration for the exergy calculation in a PEM fuel cell. Under these circumstances, the specific exergy of each chemical component throughout PEM fuel cell operation consists of only physical and chemical exergies and defined as:

$$ex = ex^{ph} + ex^{ch} \tag{0.24.}$$

Physical exergy associated with the temperature and pressure of the reactants and the products in the fuel cell. The general expression of the specific physical exergies on mass basis can be described as:

$$ex^{ph} = h - h_0 - T_0(s - s_0) \tag{0.25.}$$

where $h$ is the enthalpy (kJ/kg), $s$ is the entropy (kJ/kg K) and the subscript zero indicates properties at the restricted dead state of $P_0$=1 atm and $T_0$=298 K. The physical exergy of an ideal gas with constant specific heat $c_p$ and specific heat constant ratio $k$ can be written as:

$$ex^{ph} = c_p T_0 \left[ \frac{T}{T_0} - 1 - \ln\left(\frac{T}{T_0}\right) + \ln\left(\frac{P}{P_0}\right)^{\left(\frac{k-1}{k}\right)} \right] \tag{0.26.}$$

The chemical exergy is associated with the departure of the chemical composition of a system from that environment. For the simplicity, the chemical exergy considered in the analyses is rather a standard chemical exergy that is based on the standard values of the environment (Kazim, 2004; Rezaee and Houshmand, 2015). The chemical exergy can be determined from:

$$ex^{ch} = x_n ex_n^{ch} + RT_0 x_n \ln x_n \tag{0.27.}$$

where $x_n$ is the mass fraction of the species $n$, $ex^{ch}$ is the standard chemical exergies (kJ/kg) of the species $n$ evaluated at dead state. The values of the chemical exergies of the reactants and products are taken from the literature and listed in Table 3.5.

Depending on power output $\dot{W}$ and a fuel cell voltage $V_{cell}$, and the stoichiometry of air $\lambda$, the mass flow rates of each reactants and products in the

fuel cell can be easily determined (Larminie and Dicks, 2001). The mass flow rates of the reactants and products can be described as follows:

$$\dot{m}_{air,R} = 3.57x10^{-7}\left(\frac{\lambda \dot{W}}{V_{cell}}\right) \text{ kg/s} \quad (0.28.)$$

$$\dot{m}_{H_2,R} = 1.05x10^{-8}\left(\frac{\dot{W}}{V_{cell}}\right) \text{ kg/s} \quad (0.29.)$$

$$\dot{m}_{air,P} = 3.57x10^{-7}\left(\frac{\lambda \dot{W}}{V_{cell}}\right) - 8.29x10^{-8}\left(\frac{\dot{W}}{V_{cell}}\right) \text{ kg/s} \quad (0.30.)$$

$$\dot{m}_{H_2O,P} = 9.34x10^{-8}\left(\frac{\dot{W}}{V_{cell}}\right) \text{ kg/s} \quad (0.31.)$$

In equation 3.16 the oxygen usage in a fuel cell is shown as $8.29x10^{-8}\left(\frac{\dot{W}}{V_{cell}}\right)$ kg/s.

As a result, the total exergy of the reactants and the products can be calculated through the following equations (Kazim, 2004; Larminie and Dicks, 2001; Sevjidsuren et. al., 2012):

$$\dot{E}x_{air,R} = \dot{m}_{air,R}\, ex_{air,R} = \dot{m}_{air,R}\left(ex^{ph} + ex^{ch}\right)_{air,R} \text{kW} \quad (0.32.)$$

$$\dot{E}x_{H_2,R} = \dot{m}_{H_2,R}\, ex_{H_2,R} = \dot{m}_{H_2,R}\left(ex^{ph} + ex^{ch}\right)_{H_2,R} \text{ kW} \quad (0.33.)$$

$$\dot{E}x_{air,P} = \dot{m}_{air,P}\, ex_{air,P} = \dot{m}_{air,P}\left(ex^{ph} + ex^{ch}\right)_{air,P} \text{ kW} \quad (0.34.)$$

$$\dot{E}x_{H_2O,P} = \dot{m}_{H_2O,P}\, ex_{H_2O,P} = \dot{m}_{H_2O,P}\left(ex^{ph} + ex^{ch}\right)_{H_2O,P} \text{ kW} \quad (0.35.)$$

### 3.2.3. Calculations for Energy and Exergy Efficiency

All equations needed for performing energy and exergy analysis were given in this chapter. Calculations in order to determine energetic and exergetic efficiency were shown for PEM fuel cell in here.

The data obtained from both PEM fuel cell and literature. In the calculations only, full load performance characteristics have been shown but the all determinations at different load have been given a few tables.

Table 3.7. Cell voltage data at different power output

| Power (W) | Stack voltage (V) | Cell voltage (V) |
|---|---|---|
| 100 | 40 | 0,79 |
| 200 | 37 | 0,75 |
| 300 | 36 | 0,73 |
| 400 | 35 | 0,70 |
| 500 | 34 | 0,67 |
| 600 | 32 | 0,64 |
| 700 | 31 | 0,62 |
| 800 | 29 | 0,58 |
| 900 | 28 | 0,55 |
| 1000 | 26 | 0,52 |

Table 3.8. Data obtained from fuel cell

| Fuel ($H_2$) / Power (W) | Heating value (kJ/kg) | Mass flow rate of $H_2$ (kg/s) | Mass flow rate of air (kg/s) | Mass flow rate of water (kg/s) | Mass flow rate of product air (kg/s) |
|---|---|---|---|---|---|
| 100 | 120000 | 1,33E-06 | 1,35E-04 | 1,18E-05 | 1,25E-04 |
| 200 | 120000 | 2,72E-06 | 2,86E-04 | 2,49E-05 | 2,64E-04 |
| 300 | 120000 | 4,08E-06 | 4,42E-04 | 3,86E-05 | 4,08E-04 |
| 400 | 120000 | 5,56E-06 | 6,15E-04 | 5,36E-05 | 5,67E-04 |
| 500 | 120000 | 7,26E-06 | 7,94E-04 | 6,92E-05 | 7,33E-04 |
| 600 | 120000 | 9,14E-06 | 9,99E-04 | 8,71E-05 | 9,21E-04 |
| 700 | 120000 | 1,11E-05 | 1,20E-03 | 1,05E-04 | 1,11E-03 |
| 800 | 120000 | 1,35E-05 | 1,47E-03 | 1,28E-04 | 1,35E-03 |
| 900 | 120000 | 1,62E-05 | 1,75E-03 | 1,53E-04 | 1,61E-03 |
| 1000 | 120000 | 1,83E-05 | 2,06E-03 | 1,80E-04 | 1,90E-03 |

### 3.2.3.1. Energy Input Rate

$E_{fuel}$ = (0.0000183)(120000) = 2.196 kW (Equation 3.4)

### 3.2.3.2. Total Heat Losses

$\dot{Q}_{loss}$ = (2.196)-(1) = 1.196 kW (Equation 3.5)

### 3.2.3.3. Energy Efficiency

$\eta$ = (1) / (2.196) = 0.4504 (45.04%) (Equation 3.6)

### 3.2.3.4. Physical Exergy of Hydrogen

The physical exergy calculations of hydrogen were made at different operating temperature and operating pressure ratio varies from 1 to 1.12 and 1 to 2, respectively and listed in Table 3.8.

$$ex_{H_2}^{ph} = (14.3)(298)\left[1.2 - 1 - \ln(1.2) + \ln(2)^{\left(\frac{1.4-1}{1.4}\right)}\right] = 920.1153\ \text{kg/s}$$ (Equation 3.12)

Table 3.9. Physical exergy of hydrogen

| $ex^{ph}$ (kg/s) | $P/P_0=1$ | $P/P_0=2$ |
|---|---|---|
| $T/T_0=1$ | 0 | 844.7803 |
| $T/T_0=1.05$ | 5.1556 | 849.9359 |
| $T/T_0=1.1$ | 19.9852 | 864.7655 |
| $T/T_0=1.15$ | 43.6285 | 888.4088 |
| $T/T_0=1.2$ | 75.3349 | 920.1153 |

### 3.2.3.5. Physical Exergy of Air

The calculations of physical exergy of air were made at different operating temperature and operating pressure ratio varies from 1 to 1.12 and 1 to 3, respectively and listed in Table 3.9.

$$ex_{air,R}^{ph} = (1.005)(298)\left[1.2 - 1 - \ln(1.2) + \ln(2)^{\left(\frac{1.4-1}{1.4}\right)}\right] = 64.6654 \text{ kg/s (Equation 3.12)}$$

Table 3.10. Physical exergy of air

| $ex^{ph}$ (kg/s) | $P/P_0=1$ | $P/P_0=2$ |
|---|---|---|
| $T/T_0=1$ | 0 | 59.3709 |
| $T/T_0=1.05$ | 0.3623 | 59.7333 |
| $T/T_0=1.1$ | 1.4045 | 60.7755 |
| $T/T_0=1.15$ | 3.0662 | 62.4371 |
| $T/T_0=1.2$ | 5.2945 | 64.6654 |

### 3.2.3.6. Physical Exergy of Water

The general expression of the specific physical exergies on mass basis (Equation 3.11) was used to calculate the physical exergy of water. The results were listed in Table 3.10. In order to determine the physical exergy, the enthalpy and entropy values of the water at related temperature which are operating temperatures and dead state temperature. The operating temperature values can be obtained 313, 328, 343 and 358 K from operating temperature ratios which ranges from 1 to 1.2 with 0.05 intervals.

$$ex_{H_2O}^{ph} = (431.2 - 104.88) - (298)(1.339 - 0.3674) = 34.21 \text{ kJ/kg (Equation 3.11)}$$

Table 3.11. Physical exergy of water

| $ex^{ph}$ (kJ/kg) | $P/P_0=1$ | $P/P_0=2$ |
|---|---|---|
| $T/T_0=1.05$ | 5.92 | 6.11 |
| $T/T_0=1.1$ | 17.1 | 17.416 |
| $T/T_0=1.15$ | 26.21 | 26.85 |
| $T/T_0=1.2$ | 33.41 | 34.21 |

### 3.2.3.7. Physical Exergy of Exit Air

The physical exergy values of the exit air were taken from literature and listed in Table 3.12 (Hanapi et. al., 2015).

Table 3.12. Physical exergy of exit air

| $ex^{ph}$ (kJ/kg) | $P/P_0=1$ | $P/P_0=2$ |
|---|---|---|
| $T/T_0=1$ | 0 | 132.53 |
| $T/T_0=1.05$ | 9.03 | 141.56 |
| $T/T_0=1.1$ | 18.27 | 150.26 |
| $T/T_0=1.15$ | 27.49 | 160.01 |
| $T/T_0=1.2$ | 36.81 | 170.2 |

### 3.2.3.8. Mass Flow Rate of Air

$$\dot{m}_{air,R} = 3.57x10^{-7}\left(\frac{(3)(1000)}{0.52}\right) = 0.00206 \text{ kg/s (Equation 3.14)}$$

### 3.2.3.9. Mass Flow Rate of Hydrogen

The comparison of theoretical and experimental fuel consumptions was shown in Table 3.13.

$$\dot{m}_{H_2,R} = 1.05x10^{-8}\left(\frac{1000}{0.52}\right) = 0.0000202 \text{ kg/s (Equation 3.15)}$$

Table 3.13. Fuel consumption

| $H_2$ Consumption (kg/s) / Power (W) | Theoretical (kg/s) | Experimental (kg/s) |
|---|---|---|
| 100 | 0.0000013 | 0.0000013 |
| 200 | 0.0000028 | 0.0000027 |
| 300 | 0.0000043 | 0.0000041 |
| 400 | 0.0000060 | 0.0000056 |
| 500 | 0.0000078 | 0.0000073 |
| 600 | 0.0000098 | 0.0000091 |
| 700 | 0.0000118 | 0.0000111 |
| 800 | 0.0000144 | 0.0000135 |
| 900 | 0.0000171 | 0.0000162 |
| 1000 | 0.0000202 | 0.0000183 |

**3.2.3.10. Mass Flow Rate of Oxygen Usage**

$$\dot{m}_{o_2} = 8.29x10^{-8}\left(\frac{1000}{0.52}\right) = 0.000159 \text{ kg/s}$$

**3.2.3.11. Mass Flow Rate of Exit Air**

Exit air mass flow rate can be calculated subtraction oxygen usage rate from inlet air flow rate.

$$\dot{m}_{air,P} = 3.57x10^{-7}\left(\frac{(3)(1000)}{0.52}\right) - 8.29x10^{-8}\left(\frac{1000}{0.52}\right) = 0.0019 \quad \text{kg/s}$$

(Equation 3.16)

**3.2.3.12. Mass Flow Rate of Water**

$$\dot{m}_{H_2O,P} = 9.34x10^{-8}\left(\frac{1000}{0.52}\right) = 0.00018 \text{ kg/s (Equation 3.17)}$$

**3.2.3.13. Exergy of Air**

$$\dot{E}x_{air,R} = 0.00206\left(99.3952 + 0\right) = 0.2047 \text{ kW (Equation 3.18)}$$

**3.2.3.14. Exergy of Hydrogen**

$$\dot{E}x_{H_2,R} = 0.0000183\left(1414.2801 + 159138\right) = 2.89 \text{ kW (Equation 3.19)}$$

**3.2.3.15. Exergy of Product Air**

$$\dot{E}x_{air,P} = 0.0019\left(196.1 + 8.58\right) = 0.389 \text{ kW (Equation 3.20)}$$

**3.2.3.16. Exergy of Water**

$$\dot{E}x_{H_2O,P} = 0.0018\left(22.5002 + 2.5\right) = 0.045 \text{ kW (Equation 3.21)}$$

**3.2.3.17. Exergy Efficiency**

$$\psi = \frac{1}{\left(0.2047 + 2.89\right) - \left(0.389 + 0.045\right)} = 0.3635 \ (36.35\%) \quad \text{(Equation 3.8)}$$

# 4. RESULTS AND DISCUSSIONS

Fuel cell performance experiments were conducted on a 1 kW self-humidified PEM fuel cell which takes place in Hydrogen Laboratories the Department of Automotive Engineering in Çukurova University. The specifications of the fuel cell are listed in Table 3.1. The fuel cell gives the maximum 1 kW electrical power and it was operated 900 seconds for each power ranges to implement both exergy and energy analysis.

In the experiments hydrogen was used as a fuel and air was used to feed PEM fuel cell for oxygen need. The results of first law (energy) analysis are given in Table 4.1 and in Figure 4.1 through 4.3.

Table 4.1. Energy analysis results

| First Law | Experimental | | | Theoretical | | |
|---|---|---|---|---|---|---|
| Power (W) | Energy input rate (kW) | Total heat loss (kW) | Energy efficiency (%) | Energy input rate (kW) | Total heat loss (kW) | Energy efficiency (%) |
| 100 | 0.1592 | 0.0592 | 62.81 | 0.1592 | 0.0592 | 62.81 |
| 200 | 0.3259 | 0.1259 | 61.37 | 0.3361 | 0.1361 | 59.50 |
| 300 | 0.4900 | 0.1900 | 61.22 | 0.5202 | 0.2202 | 57.67 |
| 400 | 0.6672 | 0.2672 | 59.96 | 0.7234 | 0.3234 | 55.30 |
| 500 | 0.8713 | 0.3713 | 57.39 | 0.9341 | 0.4341 | 53.53 |
| 600 | 1.0972 | 0.4972 | 54.69 | 1.1750 | 0.5750 | 51.06 |
| 700 | 1.3289 | 0.6289 | 52.67 | 1.4143 | 0.7143 | 49.49 |
| 800 | 1.6250 | 0.8250 | 49.23 | 1.7262 | 0.9262 | 46.35 |
| 900 | 1.9410 | 1.0410 | 46.37 | 2.0579 | 1.1579 | 43.73 |
| 1000 | 2.1960 | 1.1960 | 45.58 | 2.4231 | 1.4231 | 41.27 |

Energy input rate is the energy supplied to the engine which includes work rate, heat losses and it is determined by using lower heating value and mass flow rates of hydrogen. The energy that is supplied to the control volume is directly affected by heating value and mass flow rate of hydrogen. Figure 4.1. shows the energy input rate of both theoretical and experimental calculation at different power output. The difference between energy input rate is caused by different mass flow rates of experimental and theoretical calculations. Energy input rate of the hydrogen increases from 0.1592 kW to 2.1960 kW for experimental test and increases from 0.1592 kW to 2.4231 for theoretical calculation. It is also clearly seen that the energy input rate of theoretical calculation is higher than experimental test data about 10%.

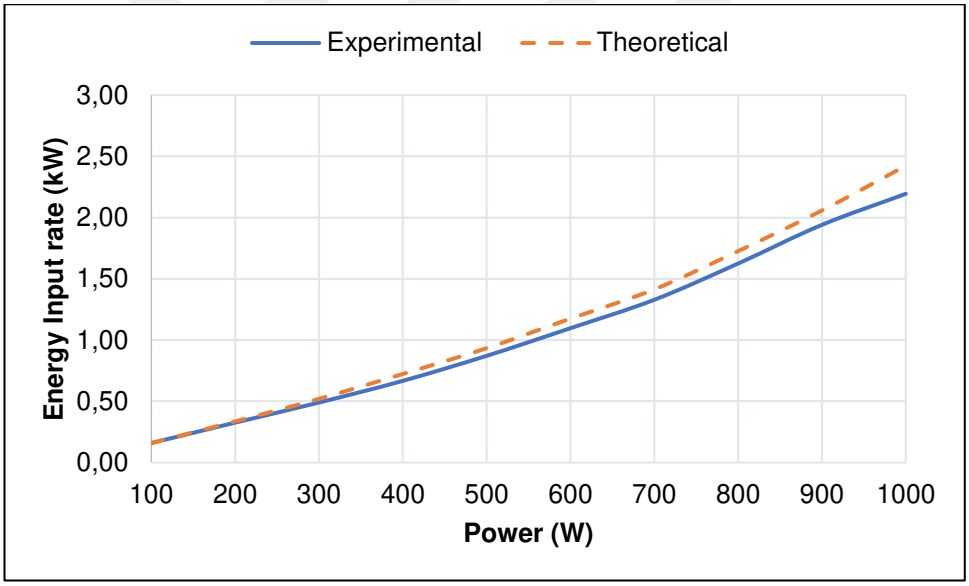


Figure 4.1. Energy input rate at different power output

When the useful work which is the power that is obtained from the PEM fuel cell is subtracted from supplied energy by hydrogen, the remaining can be called as heat losses. Figure 4.2 shows the heat losses of PEM fuel cell for both experimental data and theoretical calculation results at different power output. It can be obviously seen that the heat losses of the fuel cell increase with increment in power demand. The heat losses of the fuel cell are 1.1960 kW for experimental calculation and 1.4231 kW for theoretical calculation.

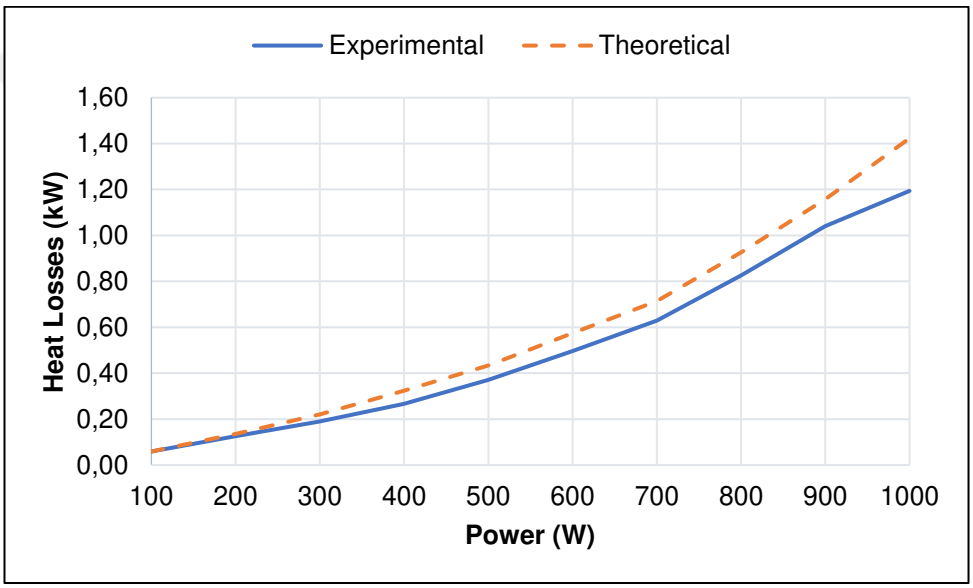


Figure 4.2. Heat losses at different power output

Figure 4.3 shows efficiency of energy of PEM fuel cell at different power (work) output. It can be seen from the figure that both experimental and theoretical energy efficiency of PEM fuel cell decreases with increasing the power demand. The efficiency of first law of PEM fuel cell decreases from 62.81% to 45.58% for experimental calculation and decreases from 62.81% to 41.27% for parametric calculation. The reduction of efficiency can be explained by the losses which raises with increasing the power demand. The energy efficiency of experiment was about 10% higher than the energy efficiency of parametric results at full load condition that was 1000W.

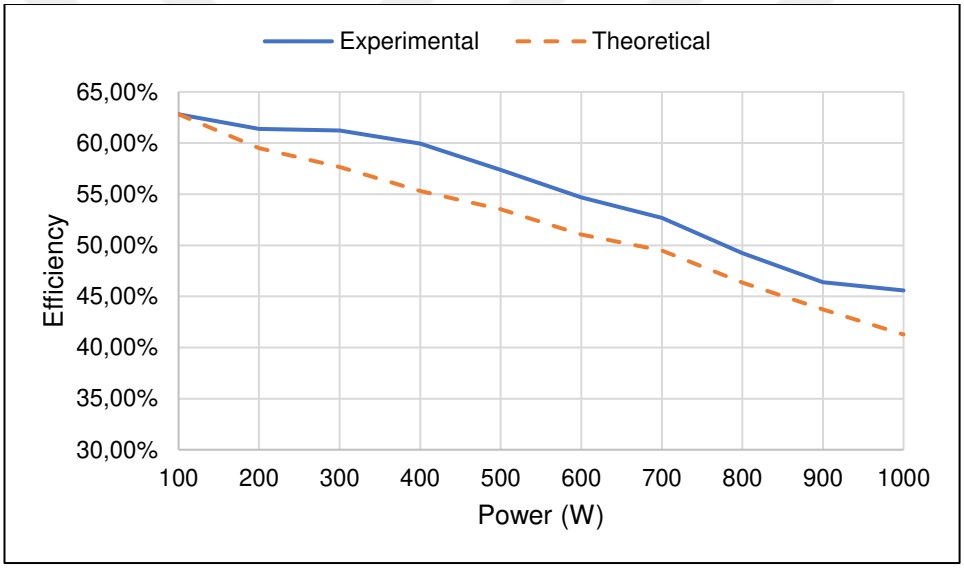


Figure 4.3. Energy efficiency of PEM fuel cell at different power output

Table 4.2. Physical exergy results of PEM fuel cell at variable operating conditions

| Physical exergy | Pressure ratio ($P/P_0$) | Temperature ratio ($T/T_0$) | | | | |
|---|---|---|---|---|---|---|
| | | $T/T_0$=1 | $T/T_0$=1.05 | $T/T_0$=1.1 | $T/T_0$=1.15 | $T/T_0$=1.2 |
| Hydrogen | $P/P_0$=1 | 0 | 5.1556 | 19.9852 | 43.6285 | 75.3349 |
| | $P/P_0$=2 | 844.7803 | 849.9359 | 864.765 | 888.4088 | 920.115 |
| Reactant air | $P/P_0$=1 | 0 | 0.3623 | 1.4045 | 3.0662 | 5.2945 |
| | $P/P_0$=2 | 59.3709 | 59.7333 | 60.7755 | 62.4371 | 64.6645 |
| Water | $P/P_0$=1 | 0 | 5.92 | 17.1 | 26.21 | 33.41 |
| | $P/P_0$=2 | 0.775 | 6.11 | 17.416 | 26.85 | 34.21 |
| Product air | $P/P_0$=1 | 0 | 9.03 | 18.27 | 27.49 | 36.81 |
| | $P/P_0$=2 | 132.53 | 141.56 | 150.26 | 160.01 | 170.2 |

Table 4.3. Efficiency of exergy results of PEM fuel cell at P/P0=1

| Exergy efficiency (%) | Temperature ratio ($T/T_0$) | | | | |
|---|---|---|---|---|---|
| Power (W) | $T/T_0$=1 | $T/T_0$=1.05 | $T/T_0$=1.1 | $T/T_0$=1.15 | $T/T_0$=1.2 |
| 100 | 47.61 | 47.87 | 48.13 | 48.37 | 48.58 |
| 200 | 46.53 | 46.79 | 47.05 | 47.29 | 47.50 |
| 300 | 46.42 | 46.69 | 46.96 | 47.21 | 47.43 |
| 400 | 45.47 | 45.74 | 46.01 | 46.25 | 46.47 |
| 500 | 43.52 | 43.77 | 44.03 | 44.26 | 44.47 |
| 600 | 41.47 | 41.71 | 41.95 | 42.17 | 42.37 |
| 700 | 39.94 | 40.17 | 40.40 | 40.61 | 40.80 |
| 800 | 37.33 | 37.55 | 37.76 | 37.96 | 38.14 |
| 900 | 35.16 | 35.36 | 35.57 | 35.75 | 35.92 |
| 1000 | 34.57 | 34.78 | 34.99 | 35.17 | 35.35 |

Table 4.4. Efficiency of exergy results of PEM fuel cell at P/P0=2

| Exergy efficiency (%) | Temperature ratio ($T/T_0$) | | | | |
|---|---|---|---|---|---|
| Power (W) | $T/T_0$=1 | $T/T_0$=1.05 | $T/T_0$=1.1 | $T/T_0$=1.15 | $T/T_0$=1.2 |
| 100 | 49.35 | 49.63 | 49.89 | 50.16 | 50.42 |
| 200 | 48.29 | 48.57 | 48.84 | 49.11 | 49.37 |
| 300 | 48.25 | 48.53 | 48.81 | 49.09 | 49.36 |
| 400 | 47.30 | 47.59 | 47.86 | 48.14 | 48.41 |
| 500 | 45.24 | 45.52 | 45.78 | 46.04 | 46.30 |
| 600 | 43.11 | 43.37 | 43.62 | 43.87 | 44.11 |
| 700 | 41.51 | 41.76 | 42.00 | 42.24 | 42.47 |
| 800 | 38.79 | 39.03 | 39.25 | 39.47 | 39.69 |
| 900 | 36.54 | 36.76 | 36.96 | 37.17 | 37.38 |
| 1000 | 35.99 | 36.22 | 36.43 | 36.65 | 36.86 |

The results of second law (exergy) analysis are given both in Table 4.2 through 4.4 and in Figure 4.4 through 4.7.

Figure 4.4 shows the physical exergy of hydrogen at different operating pressure and temperature ratios. It is clearly visible that the specific physical exergy of hydrogen can be increased with increasing the operating temperature and operating pressure ratios. Also, it can be said that the effects of operating temperature ratio are lower than the effects of operating pressure ratios. The physical exergy of hydrogen ranges from zero at reference pressure of 1 atm and temperature of 298 K to 75.3349 kJ/kg at 1 atm and 358 K. Moreover, as temperature increase from 298 K to 358 K, the physical exergy of hydrogen ranges from zero at reference pressure of 1 atm to 920.115 kJ/kg at operating pressure of 2 atm.

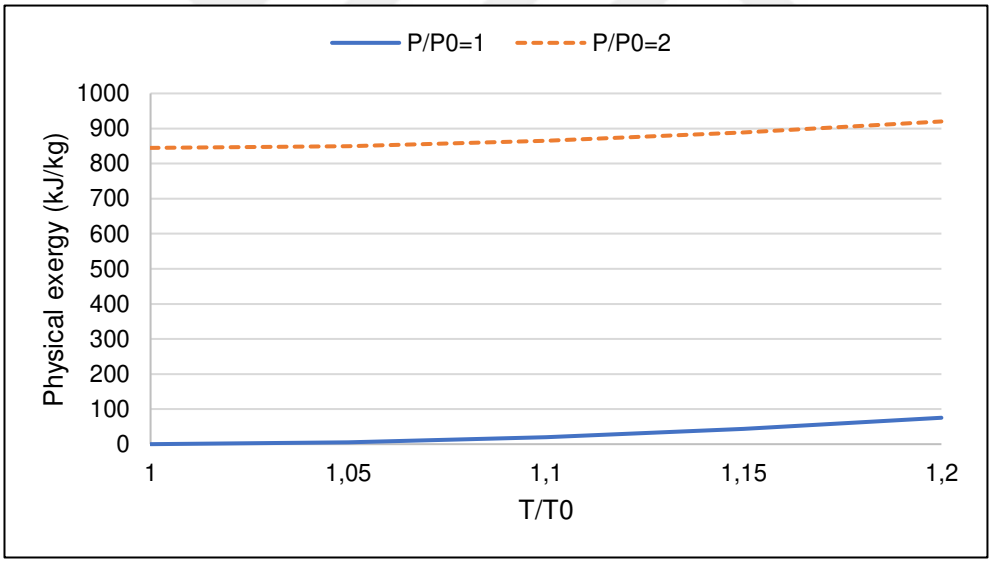


Figure 4.4. Physical exergy of hydrogen

Figure 4.5 shows the physical exergy of air entering the fuel cell at different operating temperature and pressure ratios. Physical exergy of entering air increases from zero at reference pressure and temperature condition (1 atm, 298 K) to 64.6645 kJ/kg at pressure of 2 atm and temperature of 358 K.

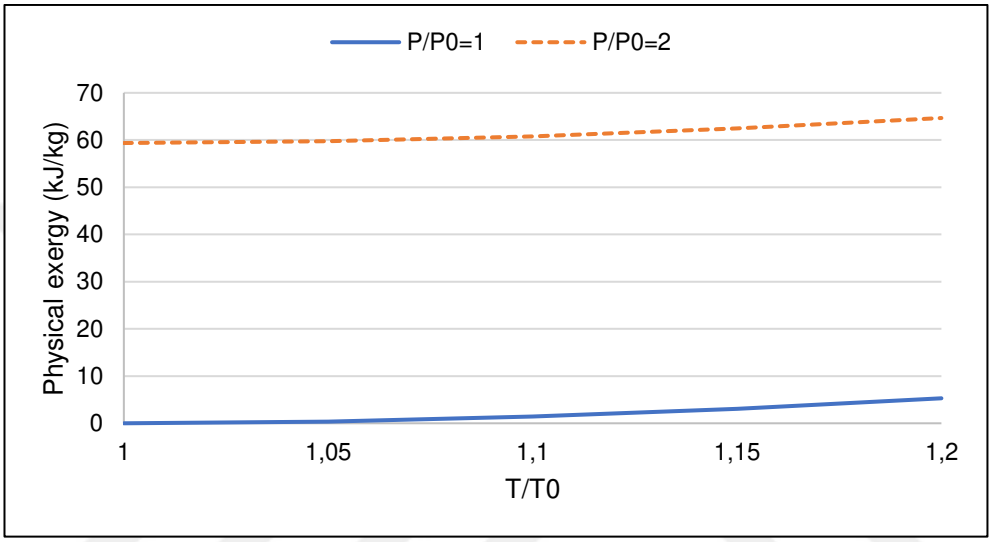


Figure 4.5. Physical exergy of entering air

Figure 4.6 shows the physical exergy of product water for different operating pressure and temperature ratios. It can be said that the increment in pressure ratio does not affects significantly the physical exergy of product water. As contrast to increment in pressure ratio, increment in temperature ratio from 1 to 1.2 increase the physical exergy of product water. It is seen from figure the maximum physical exergy of water is about 35 kJ/kg.

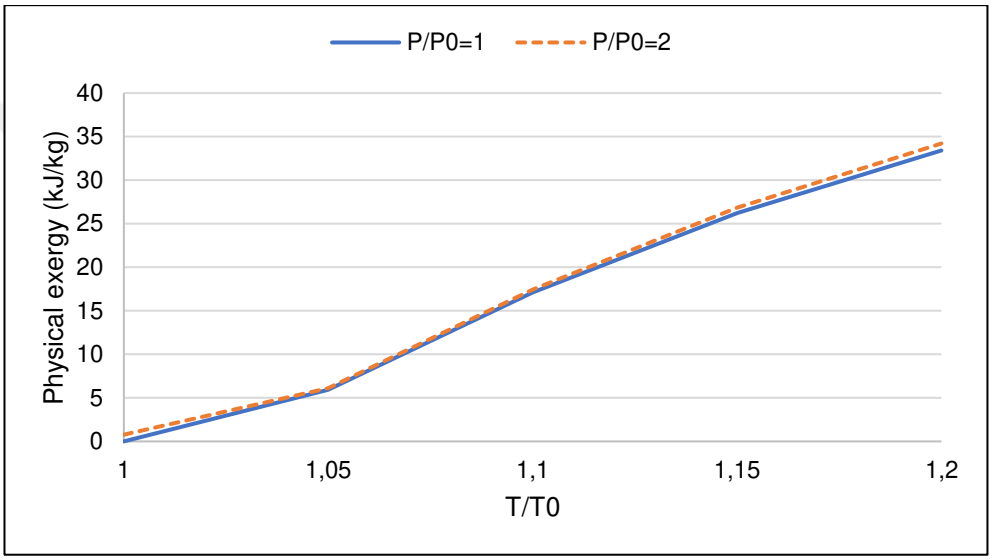


Figure 4.6. Physical exergy of water product

Figure 4.7 shows the physical exergy of exit air for different operating temperature and pressure ratios. The exit air was acted like a waste product of the fuel cell. The physical exergy of the exit air which is not used in the system ranges from zero at the respective temperature and pressure ratios of $T/T_0=1$ and $P/P_0=1$ to 170.2 kJ/kg at $T/T_0=1.2$ and $P/P_0=2$. Additionally, a remarkable increase in the physical exergy of air can be seen from the figure just by raising the operating pressure ratio from 1 to 2.

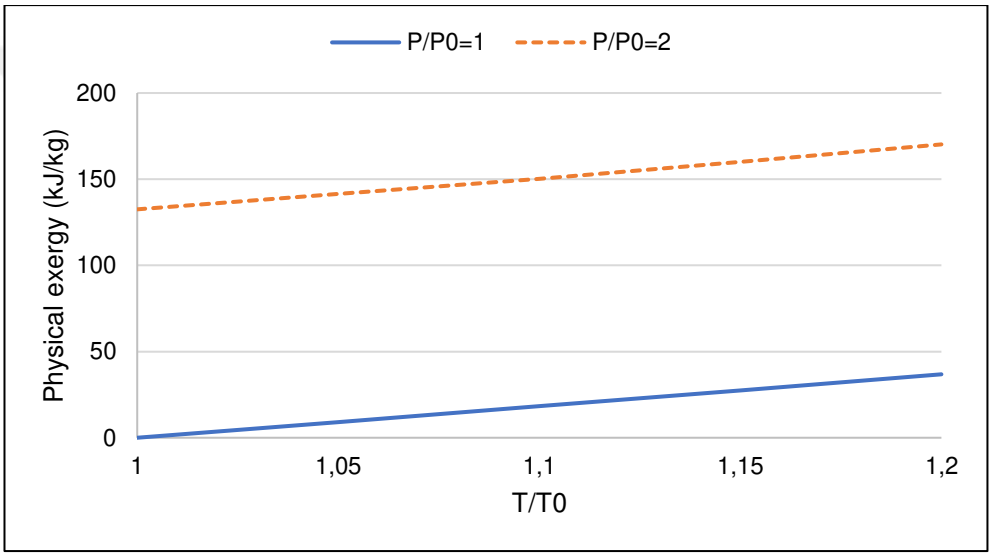


Figure 4.7. Physical exergy of exit air

Figure 4.8 shows the variation of exergy efficiency for different operating conditions at full load. Exergy efficiency can be found by dividing the power output to the exergy differences of reactants and products. The exergy efficiency of PEM fuel cell ranges from 34.57% and 35.99% at respective temperature of 298 K to 35.35% and 36.86% at operating temperature of 358 K for $P/P_0$=1 and $P/P_0$=2, respectively. For generalization, increment in operating pressure and temperature affects the fuel cell performance positively.

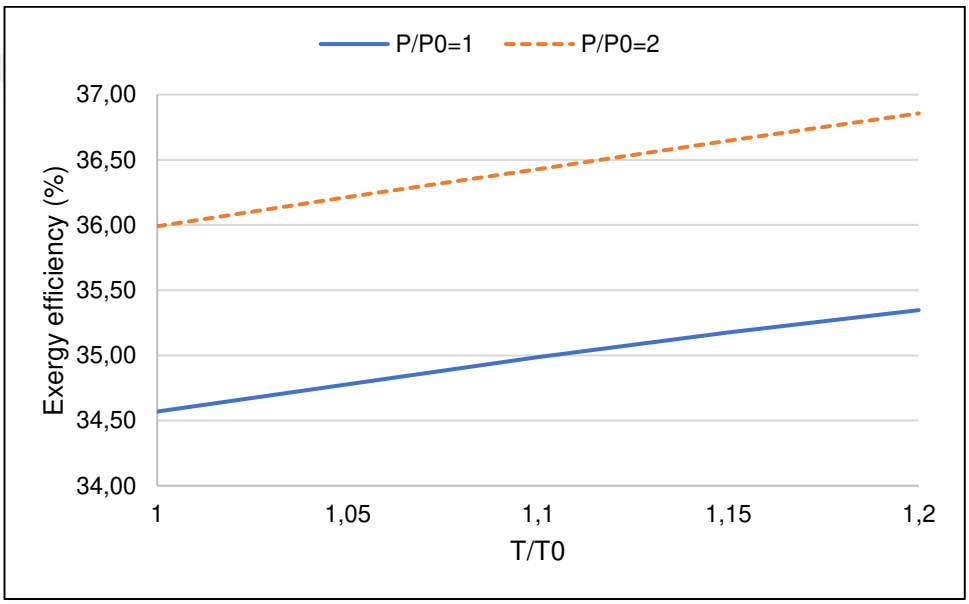


Figure 4.8. Exergy efficiency for different operating conditions at full load

Figure 4.9 shows the exergy efficiency of the PEM fuel cell at respective operating temperature of 298 K and different pressure ratio for different power output. The efficiency of exergy of PEM fuel cell ranges from 47.61% and 49.35% at respective temperature of 298 K to 34.57% and 35.99% at $P/P_0$=1, $P/P_0$=2, respectively for power output variations. It can be seen from the figure exergetic efficiency of PEM fuel cell more efficient at $P/P_0$=2 than $P/P_0$=1 about 4.2%.

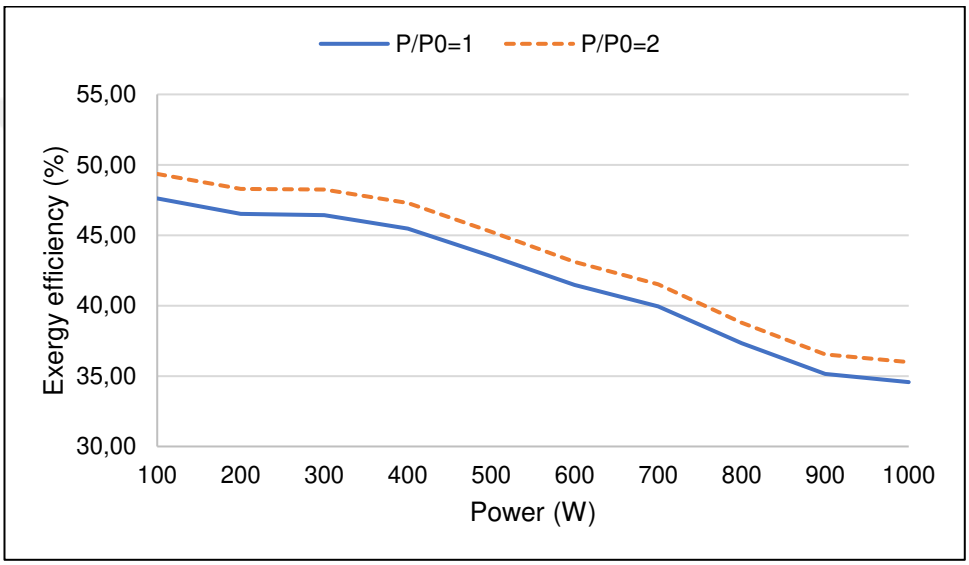


Figure 4.9. Exergy efficiency for different power output at different operating pressure ratio

# 5. CONCLUSIONS

This study was carried out in order to find out the performance of a PEM fuel cell at various operating temperature and operating pressure ratio. During the study the operating temperature ratio ($T/T_0$) is ranged from 1 to 1.2 and operating pressure ratio ($P/P_0$) is ranged from 1 to 2, also, power output is ranged from 100 W to 1000 W. according to test results, the following can be summarized;

- The increment in power output decreased energy efficiency from 62.81% to 45.58% for experimental results.
- The increment in power output decreased energy efficiency from 62.81% to 41.27% for parametric results.
- The energy efficiency of experiment was about 10% higher than the energy efficiency of parametric results at full load condition that was 1000W.
- Increasing operating temperature and operating pressure enhances the specific physical exergy of all reactants and products.
- Also, increment in operating pressure and operating temperature raised the exergy efficiency of the PEM fuel cell.
- Higher temperature means higher reaction rate and high reaction rate means high efficiency.
- Due to increased operating temperature, exergy performance of PEM fuel cell was raised from 34.57% to 35.35% for operating pressure ratio of 1, from 35.99% to 36.86% for operating pressure ratio of 2.
- About 4.2% performance improvement was obtained due to changing the operating pressure ratio from 1 to 2.
- With the increasing of power output, the exergy efficiency of fuel cell decreased due to the irreversibilities of PEM fuel cell such as heat losses.

- More feasible and exact process assessment was obtained from exergy analysis rather than energy analysis.

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