

İSTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**ANALYSIS OF THE AVAILABILITY AND APPLICABILITY OF FUEL CELL
AS A MAIN POWER UNIT FOR A COMMERCIAL SHIP**



M.Sc. THESIS

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Department of Maritime Transportation Engineering

Maritime Transportation Engineering Programme

DECEMBER 2018

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**BİR TİCARİ GEMİ İÇİN YAKIT PİLİNİN ANA GÜÇ ÜRETİCİSİ OLARAK
KULLANILABİLİRLİĞİ VE UYGULANABİLİRLİĞİNİN ANALİZİ**

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Second step,



FOREWORD

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ABBREVIATIONS

AFC	: Alkaline Fuel Cell
BV	: Bureau Veritas
DNVGL	: Det Norske Veritas Germanischer Lloyd
DWT	: Dead Weight Tonnage
EEDI	: Energy Efficiency Design Index
EEOI	: Energy Efficiency Operational Index
FCM	: Fuel Cell Module
FPM	: Fuel Processing Module
GHG	: Greenhouse Gases
GT	: Gross Tonnage
HFO	: Heavy Fuel Oil
hP	: Horse Power
IACS	: International Association of Classification Societies
IAPH	: International Association of Ports and Harbors
IGF	: International Code of Safety for Ships Using Gases or Other Low-Flashpoint Fuels
IMO	: International Maritime Organisation
ISO	: International Standardisation Organisation
LNG	: Liquefied Natural Gas
LO	: Lubricating Oil
LPG	: Liquefied Petroleum Gas
MARPOL	: Marine Pollution Regulation
MDO	: Marine Diesel Oil
MT	: Motor Tanker
MCFC	: Molten Carbonate Fuel Cell
MS	: Motor Ship
PAFC	: Phosphoric Acid Fuel Cell
PEMFC	: Proton Exchange Membrane Fuel Cell
RoRo	: Roll on-Roll off Ship
SGMF	: The Society for Gas as a Marine Fuel
SMR	: Steam Reforming
SOFC	: Solid Oxide Fuel Cell
TES	: Thermo Economic System
USD	: United States Dollar
WGS	: Water Gas Shift Reaction
WHR	: Waste Heat Recovery



SYMBOLS

ΔE	: Energy difference
ΔG	: Gibbs free energy difference
ΔH	: Enthalpy difference
ΔS	: Entropy difference
η_t	: Thermal efficiency
ρ	: Density





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ANALYSIS OF THE AVAILABILITY AND APPLICABILITY OF FUEL CELL AS A MAIN POWER UNIT FOR A COMMERCIAL SHIP

SUMMARY

Today, one of the most important problems of humanity is clean energy production and environmental pollution. After the industrial revolution, the production of power from fossil sources that existed in the world was continued with internal combustion engines. However, the atmosphere penetrating gases from the burning of such fuels prevents the earth from providing favourable conditions for human life. For this reason, the countries have signed the Kyoto Protocol as the United Nations to end this process and to inherit a more liveable world.

A significant portion of the greenhouse gas emissions on the world are caused by commercial vessels, and the maritime industry-leading organization IMO is bringing more and more restrictive and effective rules on reducing these emissions. As part of Annex VI of the International Convention for the Prevention of Pollution from Ships, restrictions have been legislated for ship-based CO₂, NO_x and SO_x gases as a result of studies on air pollution. Emission control areas have been created in various regions of the world for ship-based SO_x emissions and it has become mandatory to use low sulphur fuel for the vessels operating in these regions. In the same way, limits for NO_x emission have been determined and the production and use of the machines which are below these limits has become mandatory. CO₂ emissions have been limited with the EEDI to determine the carbon dioxide emissions per load and mile, even under control, for ships under construction. Currently, there are various technologies used to reduce the greenhouse gas emissions from ships that are using diesel engines. However, the difficulties and costs in the use of these technologies are disadvantageous. Moreover, fossil fuel sources that are decreasing in the world also direct the sector to renewable energy sources.

In today's technology, renewable resources such as solar energy, wind energy and hydrogen energy are used in power generation. As an alternative energy sources, fuel cells can also play a role in converting such energy sources into electrical energy. Conceptually, fuel cells are a completely environmental-friendly technology that produces electricity only through chemical withdrawal of electrons from the hydrogen and then re-reacting them in the presence of oxygen. These reaction cycles of fuel cells are also called cold combustion in the literature. The operating principles of fuel cells are generally similar to each other, but are named according to the name of the carrier electrolyte. In addition, the operating characteristics of the electrolyte determine the operating conditions of the fuel cell. Accordingly, the operating conditions of the batteries in a wide perspective, ranging from operating temperatures to efficiency vary. In general, fuel cells are grouped as high and low temperature working types. The main advantages of high temperature fuel cells are their fuel flexibility, high efficiency and high exhaust temperatures combined with turbine systems to achieve higher thermal efficiency. However, the low power density of this type of fuel cells can be considered as a disadvantage of their slower speed due to high temperatures and cause them to be

used in stationary power generation facilities instead of transportation vehicles. Low-temperature fuel cells need high purity hydrogen, expensive and difficult production of hydrogen, as well as limited storage quality make this type of cells difficult to spread. Despite such obstacles, fuel cells have made a serious leap forward in the automotive industry in recent years and the cars that use hydrogen as the primary fuel have taken the road. One of the main reason for this, that is the diesel engine emission rates are not enough to be reduced and fossil fuel sources are being shortened.

As the technology, maritime follows the automotive sector, the reduction in emissions rates makes the diesel engines that use fuel oil and diesel oil more difficult to keep under these limits. Therefore, the use of renewable energy sources or relatively low-emission power supplies becomes a necessity and fuel cells, one of these sources, are the subject of my thesis. Fuel cells can be a powerful alternative with low emissions in the search for a renewable and clean power supply for the maritime industry.

In this thesis, if a chemical tanker ship operated by a 4-stroke diesel engine is operated with a fuel cell that produces the same power, the necessary changes are examined and the results are explained. The rules and regulations of international organizations for the use of fuel cells in ships are examined and clearly stated in the thesis. All of the voyages of the selected vessel since the beginning of 2018 were collected and the fuel produced and the amount of CO₂ it produced were taken from the company data and then NO_x and SO_x emissions were calculated according to the data of the engine manufacturer. The type of fuel cell that is most compatible with ship and sea conditions is selected as the main power unit which is a commercially used model of the same power output. The new fuel consumption, emissions, operation and maintenance behaviour changes of the new system are discussed. The new circuit design of the selected fuel cell has been prepared and the tank types used on the ships have been examined and the most suitable tank conversion for the existing vessel has been proposed for the purpose of making these tanks suitable for LNG storage due to the loss of the need for HFO and MDO tanks on board. Heat transfer in the proposed tank type and volume is calculated and it is seen that fuel consumption is more than the amount of vaporized fuel and it is understood that there is no need for a separate cooling system. As a result of the changing fuel system, it has been seen that the fuel cell which uses LNG is provided financial gain on an annual basis. The decrease of auxiliary equipment such as separators, pumps, injector etc. reduces the need for maintenance and failure of these components. In addition, it is seen that the new system requires a much lower maintenance operation than the diesel engine and consequently may decrease the number of machinery personnel in the ship. As a result of the number of personnel is falling, it is predicted that the annual gain will increase with the decreasing in the accident, cost and maintenance operation. Furthermore, the fuel cell system is structurally modular and the amount of power received can be altered, thus allowing the engine room layout and volume to be flexible.

As a result of the study, it has been understood that the change in the system can take place commercially in the maritime sector with its positive effect on the EEDI concept and its compliance with the emission limits issued by IMO.

BİR TİCARİ GEMİ İÇİN YAKIT PİLİNİN ANA GÜÇ ÜRETİCİSİ OLARAK KULLANILABİLİRLİĞİ VE UYGULANABİLİRLİĞİNİN ANALİZİ

ÖZET

Günümüzde insanlığın en önemli sorunlarından biri temiz enerji üretimi ve çevre kirliliğidir. Sanayi devriminden sonra makineleşmenin başlamasıyla dünya üzerinden var olan fosil kaynaklardan güç üretimi içten yanmalı motorlarla sürdürülmüştür. Fakat bu tip yakıtların yanmasıyla ortaya çıkan atmosfer delici gazlar yerkürenin insan yaşamına elverişli şartlarını sağlamasına engel olmaktadır. Bu sebepten, ülkeler daha yaşanılabilir bir dünya miras bırakmak ve bu gidişatı sonlandırmak için Birleşmiş Milletler olarak Kyoto Protokolünü imzalamıştır.

Dünya üzerindeki sera gazı emisyonlarının önemli bir kısmı ticari gemilerden kaynaklanmaktadır ve denizcilik sektörüne yön veren kuruluş olan IMO da bu emisyonların azaltılması konusunda her geçen gün daha da kısıtlayıcı ve etkili kurallar getirmektedir. Gemilerden Kaynaklanan Kirliliğin Önlenmesi Uluslararası Sözleşmesi Ek VI kısmında hava kirliliği ile ilgili çalışmalar neticesinde gemi kaynaklı CO₂, NO_x ve SO_x gazları için sınırlamalar oluşturulmuştur. Gemi kaynaklı SO_x emisyonları için dünyanın çeşitli bölgelerinde emisyon kontrol alanları oluşturulmuş ve bu bölgelerde seyir yapan gemiler için düşük kükürtlü yakıt kullanmak zorunlu hale gelmiştir. Aynı şekilde NO_x emisyonu için de bazı limitler belirlenmiş ve bu limitlerin altında kalabilen makinelerin üretimi ve kullanımı zorunlu hale getirilmiştir. CO₂ emisyonları ise EEDI ile inşaa aşamasındaki gemiler için bile kontrol altına alınarak taşınan yük ve mil başına düşen karbondioksit emisyonunu belirlemek için oluşturulmuştur. Mevcut durumda dizel ana makine kullanmakta olan bu gemilerin sera gazı etkisi yaratan emisyonlarını azaltmak için çeşitli teknolojiler bulunmakta ve kullanılmaktadır. Fakat bu teknolojilerin kullanımındaki zorluk ve maliyetler dezavantaj olarak karşımıza çıkmaktadır. Ayrıca, dünya üzerindeki azalmakta olan fosil yakıt kaynakları da sektörü yenilenebilir enerji kaynaklarına yönlendirmektedir.

Günümüz teknolojisinde güneş enerjisi, rüzgâr enerjisi, hidrojen enerjisi gibi yenilenebilir kaynaklar güç üretiminde kullanılmaktadır. Bu tip enerji kaynaklarının elektrik enerjisine döndürülmesinde yakıt pilleri de rol alabilmektedir. Kavramsal olarak yakıt pilleri hidrojenden kimyasal yolla elektron koparılması ve ardından da oksijen varlığında tekrar reaksiyona sokulması yoluyla elektrik üreten ve yalnızca su emisyonu yapan tamamen çevreci bir teknolojidir. Yakıt pillerinin bu reaksiyon çevrimlerine literatürde soğuk yanma ismi de verilmektedir. Yakıt pillerinin çalışma prensipleri genel anlamda birbirlerine benzemekle beraber taşıyıcı elektrolitin ismine göre adlandırılmaktadır. Ayrıca elektrolitin çalışma karakteristiği yakıt pilinin çalışma şartlarını da belirlemektedir. Buna göre pillerin çalışma sıcaklıklarından verimlerine kadar geniş bir perspektifte çalışma şartları değişmektedir. Genel olarak yakıt pilleri yüksek ve düşük sıcaklıkta çalışanlar olarak gruplandırılmaktadır. Yüksek sıcaklık yakıt pillerinin en büyük avantajları yakıt esnekliği sağlamaları, yüksek verimde çalışmaları ve yüksek egzoz sıcaklıkları sayesinde türbin sistemleriyle kombinlenerek daha yüksek termal verimlere ulaşabilmeleridir. Fakat bu tip yakıt pillerinin düşük güç

yoğunluğuna sahip olmaları, devreye girme hızlarının yüksek sıcaklıktan ötürü daha yavaş olması dezavantajları arasında sayılabilmekte ve ulaşım araçları yerine sabit güç üretim tesislerinde kullanılmalarına neden olmaktadır. Düşük sıcaklıkta çalışan yakıt pillerinin ise yüksek saflıkta hidrojene ihtiyaç duymaları ve hidrojenin pahalı ve zor üretimi ayrıca kısıtlı depolama niteliği bu tip pillerin yaygınlaşmasını zorlaştırmaktadır. Bu tip engellere rağmen yakıt pilleri otomotiv endüstrisinde son yıllarda ciddi bir atılım yapmış ve hidrojenin birincil yakıt olarak kullanıldığı otomobiller yollara çıkmıştır. Bunun en büyük sebeplerinden biri dizel motor emisyon oranlarının düşürülmesinde yeterli yol kat edilmemesi ve fosil yakıt kaynaklarının tükenmekte olmasıdır.

Teknoloji olarak otomotiv sektörünü takip eden denizcilikte de emisyon oranlarının gittikçe düşürülmesi fuel oil ve dizel yakıtını kullanan gemi dizel motorlarının bu sınırlar altında kalmasını zorlaştırmaktadır. Dolayısıyla yenilenebilir enerji kaynaklarının veya oldukça düşük emisyonu sahip güç kaynaklarının kullanılması zorunlu hale dönüşmektedir ve bu kaynaklardan biri olan yakıt pilleri de tezinin konusunu oluşturmaktadır. Denizcilik sektörü için yenilenebilir ve temiz bir güç kaynağı arayışlarında düşük emisyon oranları ile yakıt pilleri de güçlü bir alternatif olabilir.

Bu tezde 4 stroklu bir dizel motor ile çalıştırılan bir kimyasal tanker gemisinin aynı gücü üreten bir yakıt piliyle çalıştırılması durumunda ortaya çıkan gerekli değişiklikler incelenmiş ve sonuçlar açıklanmıştır. Yakıt pillerinin gemilerde kullanımı için uluslararası kuruluşların kural ve yönetmelikleri incelenmiş ve tezde açıkça belirtilmiştir. Seçilen geminin 2018 yılı başından itibaren yaptığı tüm seferler toplanmış ve bu seferler sonucunda tükettiği yakıt ve ürettiği CO₂ miktarı şirket verilerinden alınmış ardından NO_x, SO_x emisyonları makine üreticisi firmanın verilerine göre hesaplanmıştır. Gemi ve deniz şartlarıyla en uyumlu yakıt pili türü seçilerek aynı güç çıkışı veren büyüklükte hali hazırda ticari olarak kullanılan bir modeli ana güç ünitesi olarak belirlenmiştir. Yeni durumdaki yakıt tüketimi, emisyonları, operasyon ve bakım tutum değişiklikleri irdelenmiştir. Seçilen yakıt pilinin yeni devre tasarımı hazırlanmış, gemide HFO ve MDO tanklarına olan ihtiyacın kaybolmasından ötürü bu tankların LNG depolamaya uygun hale getirilmesi için gemilerde kullanılan tank türleri incelenip mevcut gemi için en uygun tank dönüşümü önerilmiştir. Önerilen tank tipinde ve hacimdeki ısı transferleri hesaplanmış ve yakıt tüketiminin buharlaşan yakıt miktarından fazla olduğu görüldüğünden ayrı bir soğutma sistemine ihtiyaç olmadığı anlaşılmıştır. Yapılan çalışma sonucunda NO_x, SO_x (>%99) ve CO₂ (%17) emisyonlarında ciddi düşüşler olduğu bulunmuştur. Değişen yakıt sistemi sonucunda LNG kullanan pilden yıllık bazda maddi kazanç sağlandığı görülmüştür. Ayrıca, yeni sistemin dizel motora göre çok daha düşük bakım tutum operasyonu gerektirdiği ve buna bağlı olarak gemideki makine personeli sayısında düşüş sağlayabileceği görülmüştür. Düşen personel sayısı sonucunda insan hatasına bağlı kaza olasılığı, maliyeti ve bakım operasyonundan elde edilen kazançla birlikte yıllık kazanç miktarının artacağı öngörülmektedir. Sistemin dizel motorlarda olduğu gibi separatör, pompa, enjektör vb. yardımcı ekipmanlara ihtiyacının az oluşu bu parçalardan ortaya çıkan bakım ihtiyacı ve arıza ihtimallerini de azaltmaktadır. Bunlara ek olarak yakıt pili sisteminin yapısal olarak modüler olması ve alınan güç miktarının değiştirilebilir olması makine dairesi yerleşiminde ve hacminde de esnek olunabilmesini sağlamaktadır.

Yapılan çalışma sonucunda sistem deęişiklięinin EEDI kavramına olan pozitif etkisi ve IMO tarafından yayınlanan emisyon limitlerine olan uygunluęu ile denizcilik sektöründe ticari olarak yer alabileceęi anlaşılmıştır.



1. INTRODUCTION

Today, one of the most common ways of supplying the energy needs of the world is the using fossil fuels. Mechanical energy is produced by combustion of fossil fuels in an internal combustion engine, then, the mechanical energy is converted into the energy form needed. However, this cycle emitting of greenhouse gases, which are causing to global warming and climate change. Increasing energy consumption induces atmospheric pollution, which has become an important social and environmental concern (Shirazi et al., 2012)

Emissions from ships have an important negative aspect on the atmosphere. The ship welded emissions are 3%, 15% and 13% of the global emissions of CO₂, NO_x and SO_x, respectively (Singh et al., 2016).

1.1 History of Fuel Cells

The principle of fuel cell operation was discovered by Christian Friedrich Schönbein in 1838 according to the Department of Energy of the United States and the first working hydrogen fuel cell was realized by William Robert Grove in 1839 (Bossell, 2000). Grove carried on a series of experiments which proved that electric current could be produced from an electrochemical reaction between hydrogen and oxygen over a platinum catalyst. He put liquid acid in a container as an electrolyte with two electrodes. He supplied hydrogen to the anode side and air to the cathode and he transferred the free electrons from an external circuit. He termed it as a gas voltaic battery. However, Charles Langer and Ludwig Mond, who researched fuel cells using coal gas as a fuel, firstly used the term fuel cell in 1889. Further attempts to convert coal directly into electricity were made in the early twentieth century. In 1896, William Jacques developed practically the first working fuel cell utilizing of principles of the Grove's gas battery.

Francis T. Bacon developed the first practical alkaline fuel cell in 1932 using of the experiences of Langer and Mond (Andujar and Segura, 2009). During World War 2, Bacon designed a fuel cell for using in submarines of the Royal Navy (Andujar and

Segura, 2009). However, his study have focused on to use common (non-precious) materials in fuel cells and in 1959, Bacon presented a fuel cell of 5 kW and 60% efficiency with financial support of Marshall Aerospace.

Thomas Grubb, a chemist who worked for General Electric in 1955, built the first proton exchange membrane fuel cell. Few years later, another chemist from General Electric Leonard Niedrach switched membranes with platinum catalyst. He developed this new fuel technology for NASA and used during the Gemini program.

Solid oxide fuel cell was first designed by J. Weisbart et al. at Siemens-Westinghouse Electric Corporation in 1958 (Inal and Deniz, 2018). Solid oxide fuel cells were firstly designed in tubular form differently from traditional designs.

In 1961, G.V. Elmore and H.A. Tanner developed the first phosphoric acid fuel cell. They used an acidic electrolyte with 35% of acid and 65% silicon dust (Andujar and Segura, 2009). This type of fuel cell has a slower operating speed due to lower conductivity of acidic electrolyte.

After the 1990's and the beginning of 21st century, fuel cell technology particularly focused on transportation and backup power units. Ballard, a pioneer fuel cell company, developed a fuel cell bus in 1993 and Perry Energy Systems, another fuel cell technology company, manufactured a fuel cell car. The years, since 2000's to now, were the key period for the reducing the dependence on fossil fuels due to increasing environmental pollution and energy production reliability. As regarding to stationary applications, more than 2500 fuel cell systems have been installed in worldwide in hospitals, shelters etc. (Andujar and Segura, 2009).

In our century, fuel cells are the one of the most important energy production ways with their fewer emissions in contrast with the conventional internal combustion engines. Alternative energy sources and alternative energy production methods are in great demand in today's technology since the negative effects of the greenhouse gases were acknowledged. The historical review of the fuel cell development for years is mentioned in figure 1.1.

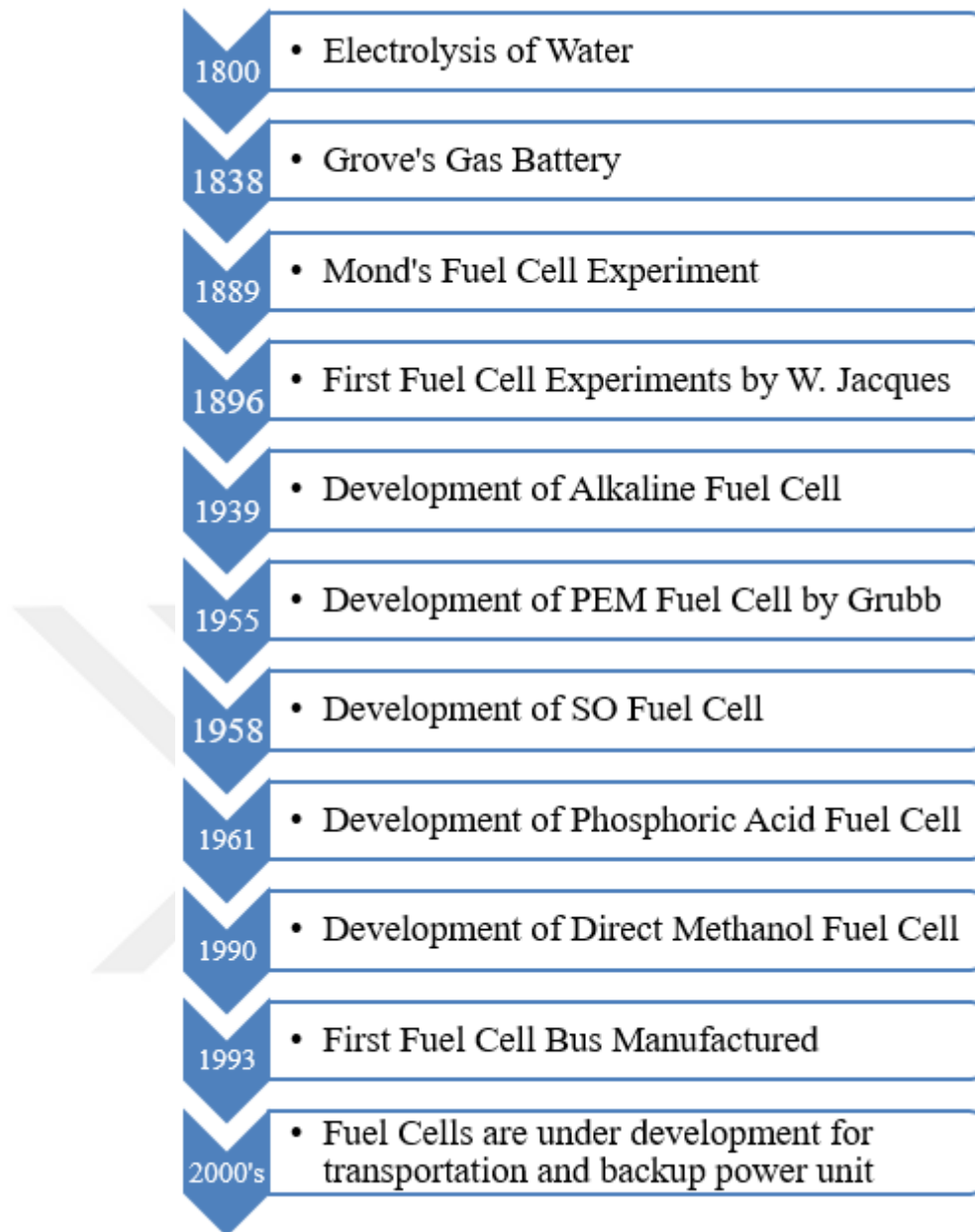


Figure 1.1 : Historical review of fuel cell.

1.2 Fuel Cell Working Principles

Fuel cells are electrochemical mechanisms that convert the chemical energy of a fuel directly into electrical energy without any combustion process. Every fuel cell has two electrodes, one positive and one negative, called, the cathode and anode, respectively. The reactions that produce electricity occur at the electrodes. Every fuel cell also has an electrolyte, which transports electrically charged atoms from one electrode to the other, and a catalyst, which speeds up the reactions at the electrodes. The physical structure of a fuel cell comprises of an electrolyte layer in contact with anode and

cathode on either side. A schematic representation of a fuel cell with the reactant gases and the ion flow directions through the cell is shown in figure 1.2.

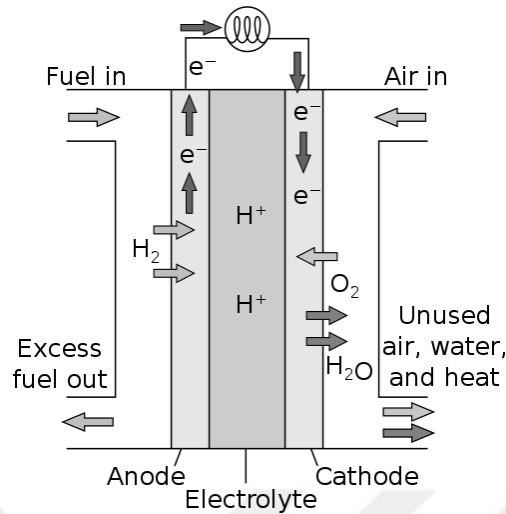


Figure 1.2 : Schematic representation of a fuel cell.

For a typical fuel cell, hydrogen is the basic fuel, which is fed continuously to the anode, and an oxidant, typically oxygen, is fed to the cathode. The electrochemical reactions take place at the electrodes to produce an electric current (EG&G Services, Parsons INC, Science Applications International Corporation, 2000). As a product, pure water is the only emission for this electricity generation by fuel cells.

More detailed, at the anode side, the catalyst forces the hydrogen atom to set free electron and it becomes to proton. The electrons traverse in the form of an electric current that can be used before they return to the fuel cell. At the same time, the protons pass through the membrane and the electrolyte to the cathode side of fuel cell, where the hydrogen atom is reacted with electrons from the external circuit in presence of oxygen and produce pure water.

In the overall process, the electrolyte plays a key role because it has to permit only the ions to traverse between the anode and cathode. If hydrogen ions and oxygen react at anode and cathode, they produce water. During the fuel cell works, it produces water and electricity.

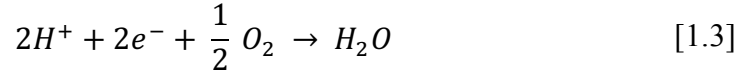
The basic total reaction for the hydrogen - oxygen fuel cell (Barbir, 2005):



At the anode side, where the hydrogen is fed, the reaction is (Barbir, 2005):



At the cathode side, the electrons coming from external circuit and the protons coming from anode react in presence of oxygen; the reaction is (Barbir, 2005):



As a result of this process, the only output is the pure water and heat. As seen in the Figure 1, electrons produced at the anode side must pass through an external circuit to the cathode. In addition, hydrogen ions, namely protons, pass through the electrolyte to reach the cathode side of fuel cell.

A fuel cell generates electricity in direct current form and low voltage. To reach the aimed voltage or current amount, cells can be connected in parallel or series form as batteries. Due to a fuel cell produce direct current, it requires an inverter to convert the output to alternating current.

At the other hand, as the characteristics, fuel cells have no moving parts in the energy conversion, they have a great fuel flexibility, quiet, size flexibility and available for remote operation.

Fuel cell working characteristics is a typical exothermic chemical reaction. The molecule must have enough energy for starting to reaction. It is called as the activation energy and it can be raised with several methods. The three main ways are the use of catalyst, raising the temperature or increasing the electrode area (EG&G Services, Parsons INC, Science Applications International Corporation, 2000).

For better understanding the working principles, chemical and thermodynamics characteristics of a fuel cell there is some notions to explain, which are Gibbs free energy, enthalpy, Nernst energy and fuel cell efficiency formulas.

The useful work obtained from a system as a thermodynamic potential is Gibbs free energy. The Gibbs free energy equals the work exchanged by the system with its surroundings. So, for a reversible transformation the initial state and the final state are the same in energy based. For the fuel cells specifically, Gibbs free energy (ΔG) is equal to the released heat energy (ΔE) of the reaction.

Another important term is the enthalpy. Enthalpy is the total heat and so, the internal energy for a system (Çengel and Boles, 2008, Chapter 2). For an exothermic reaction

at constant pressure, the change of the enthalpy of the system is negative which is equal to energy released by the reaction. By the way, for an endothermic reaction, the system's change in enthalpy is equal to the energy imbibed. After all, to determine a reaction is endothermic or exothermic the sign of enthalpy is important. Whether the sign is positive, the reaction is endothermic, that means heat is absorbed by the system. In contrast, if the sign is negative, the reaction is exothermic, that means the reaction generate heat and it releases.

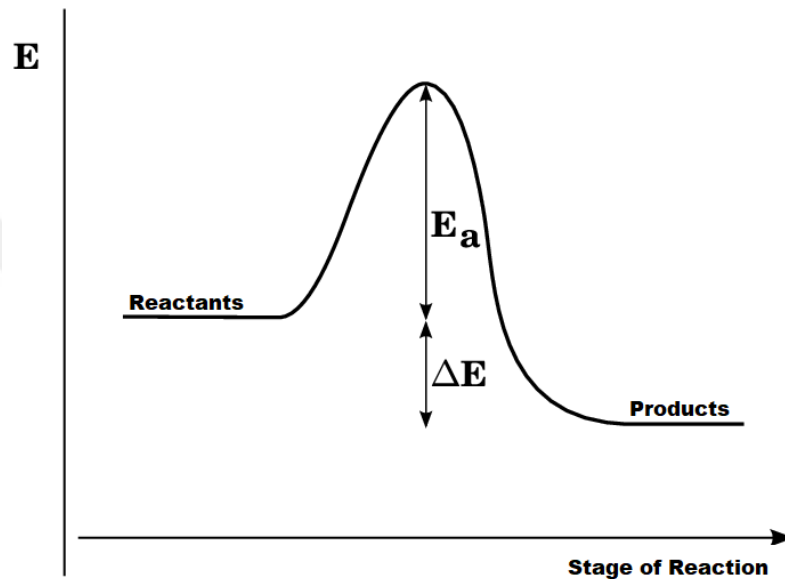


Figure 1.3 : Energy diagram for an exothermic chemical reaction.

General enthalpy expression (Mench, 2008) is showed in equation 1.4.

$$H = U + \frac{P}{\rho} = U + P v \quad [1.4]$$

Nernst potential is an expression of the maximum possible open-circuit voltage as a function of temperature and pressure (Mench, 2008). So, Nernst equation is the theoretical maximum voltage for a fuel cell. As seen in the figure 2, the real cell voltage becomes after the drops from the Nernst potential related to activation, ohmic and concentration losses. Activation losses is the potential required to exceed the activation energy so that the electrode reactions occur at the desired rate and speed. Ohmic losses is caused by the resistance to the transport of ions through the electrolyte and current collectors. Concentration losses are the voltage loss in regards to resistance of electrodes to transportations of mass and diffusion during the replacement of ions in the electrodes.

The thermodynamic efficiency of a fuel cell can be expressed with maximum electrical work ratio to maximum available work, showed in equation 1.5.

$$\eta_{t, \max} = \frac{\text{maximum electrical work}}{\text{maximum available work}} = \frac{\Delta H - T\Delta S}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H} \quad [1.5]$$

In the expression of the efficiency;

ΔH : difference of the enthalpy between the products and the reactants.

ΔS : difference of the entropy between the products and the reactants.

T: Temperature in Kelvin.

1.3 Fuel Cell Types

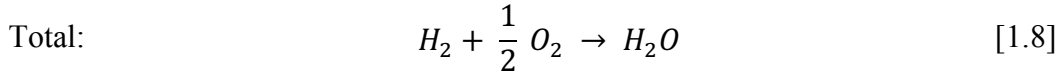
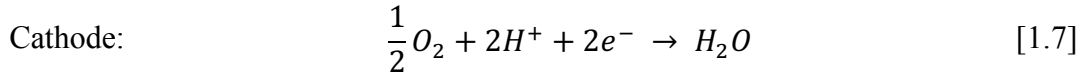
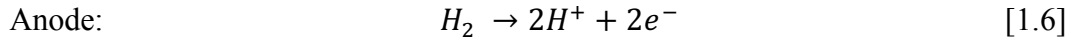
Fuel cells can be classified according to their electrolyte types, working temperatures, fuel types or their working areas, stationary or mobile. However, most common classifying method is related to electrolyte types (de Troya et al., 2016). In this thesis also same route is followed:

- Proton Exchange Membrane Fuel Cell (PEMFC)
- Alkaline Fuel Cell (AFC)
- Phosphoric Acid Fuel Cell (PAFC)
- Molten Carbonate Fuel Cell (MCFC)
- Solid Oxide Fuel Cell (SOFC)

1.3.1 Proton exchange membrane fuel cell (PEMFC)

Proton exchange membrane fuel cells are the most flexible fuel cell type and they have the largest range of application, so, they become the most promising cell to spread in applications (Sharaf and Orhan, 2014). The PEM type fuel cell has platinum-based electrodes and the electrolyte is an ion exchange membrane, which perfectly transfer protons but an electric insulator (EMSA, 2017). The operating temperature is between 50-100 °C and the fuel cell must work under 100 °C because of the water, which is produced in cathode side. To provide the porosity for protons, the membrane needs to stay humid.

The PEM uses hydrogen as a fuel and in presence of oxygen it produces water, moreover, electricity and heat due to an exothermic reaction. The electrochemical reactions that occurs in a proton exchange membrane fuel cells respectively shown below (Mench, 2008):



The proton exchange membrane fuel cell relatively has a low working temperature and that allows for flexible operation and less stringent material requirements that makes research and development focus on. The efficiency of the PEMFC system is around 50-60% (EMSA, 2017). For the efficient working of PEMFC pure hydrogen must be fed into the cell because of the platinum catalyst can be poisoned by carbon monoxide (CO). Hydrocarbons can be used as a fuel but, as stated before, due to low tolerance to carbon, fuels must pass from steam reforming and subsequent water-gas-shift system to ensure the purity of fuel. The working principle and illustration of PEMFC is shown in figure 1.4.

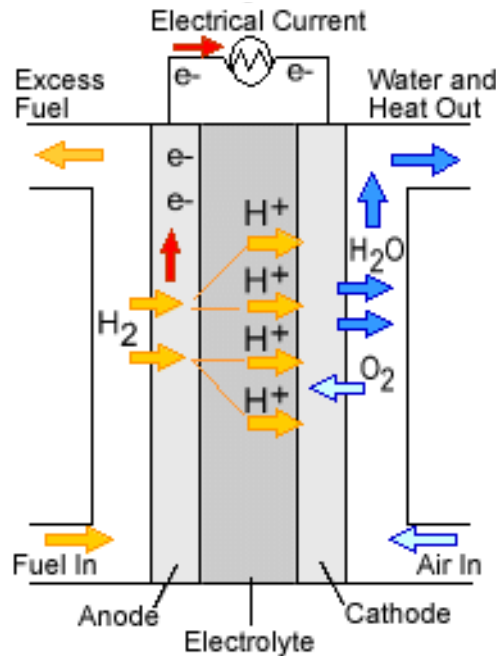


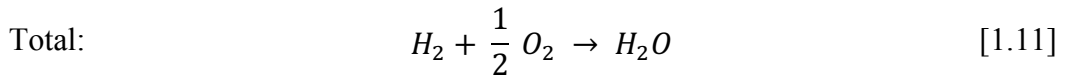
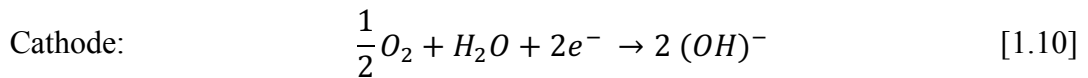
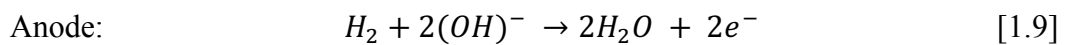
Figure 1.4 : Working principle of PEMFC. (Url-10)

The disadvantages of PEM fuel cells are the need to platinum as a catalyst, water management in cell and use of pure hydrogen as fuel. PEM fuel cells are generally used in automotive and portable applications. A further application of this type of fuel cells is to generate electricity and heat water in residential settings (Sastre et al., 2004).

1.3.2 Alkaline fuel cell (AFC)

Alkaline fuel cell is the first fuel cell developed in 1939 by Bacon. In general power output is 1-5 kW, however recently some test reports of stationary AFCs can reach to 200 kW (EMSA, 2017). AFC's electrolyte is alkaline and as electrode it uses nickel for anode and silver for cathode. As the fuel cell name implies the electrolyte is an alkaline solution generally potassium hydroxide (KOH), hydroxyl ions (OH⁻) are transported through the electrolyte from the cathode to anode and its working temperature is generally below 100 °C (de Troya et al., 2016). The AFC tolerance is nearly zero for carbon dioxide (CO₂) due to the reaction with electrolyte so, the hydrogen and oxygen must be pure before entering to cell unit. Because of the basic characteristic of the electrolyte and acidic carbon dioxide can react and produces solid potassium carbonate particles, as a result, this reaction reduces the concentration of the electrolyte and reduces the efficiency of the cell. This can be considered as a disadvantage. The working principle and illustration of AFC is shown in figure 1.5.

The electrochemical reactions, which occurs in an alkaline fuel cell, is shown with equations 1.9, 1.10, 1.11. (Mench, 2008):



The alkaline fuel cells are mostly used in NASA space shuttles related to their pure water and heat production. This type of fuel cell is relatively low cost with low-cost catalyst (EMSA, 2017). Moreover, low temperature working, low weight and volume and simple operation principles can be seen as advantages (Andujar and Segura, 2009).

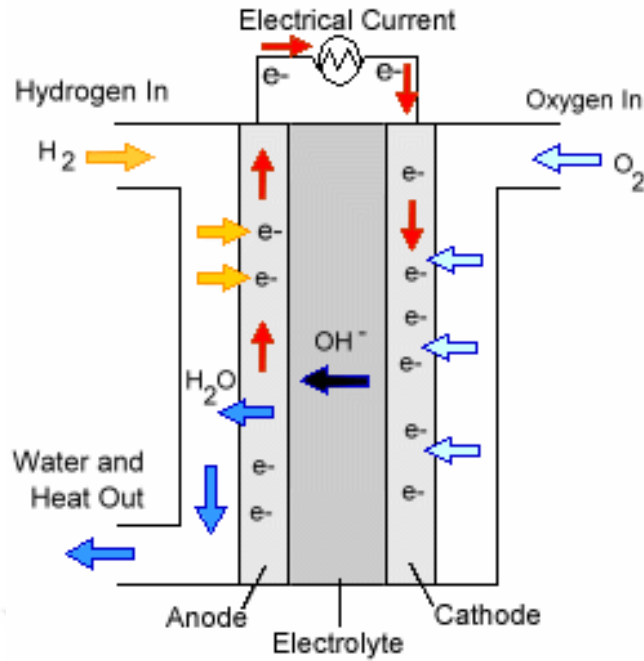
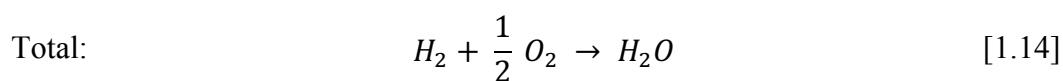
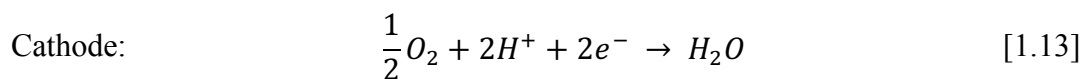
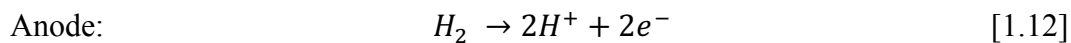


Figure 1.5 : Working Principle of AFC. (Url-10)

1.3.3 Phosphoric acid fuel cell (PAFC)

Phosphoric acid fuel cell operates at high temperatures between 150 to 220 °C (Shilpa and Anurag, 2015). PAFC uses phosphoric acid in liquid form as electrolyte. In this fuel cell type again, the fuel which enters from the anode side, ionizes via catalyst. The protons (H^+) move to cathode side through liquid phosphoric acid electrolyte. In presence of oxygen and with the electrons coming from external circuit they produce water at the cathode. Related to data were collected from experiments, the electrical performance is about 38 - 40% and thermal performance is around 40 - 45%. Therefore, total performance can reach to 85% in combined systems (de Troya et al., 2015). The working principle and illustration of PAFC is shown in figure 1.6.

The electrochemical reactions in PAFC are same with PEMFC, showed in equations 1.12, 1.13, 1.14 (Mench, 2008):



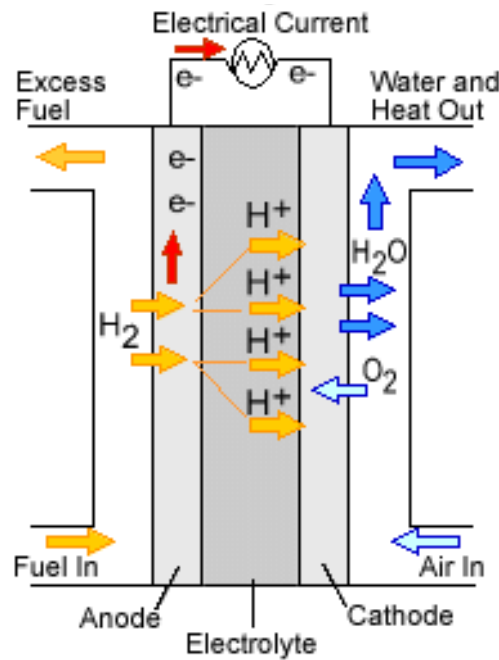


Figure 1.6 : Working Principle of PAFC. (Url-10)

Due to higher working temperatures, hydrogen is not only the fuel source for PAFC, hydrocarbons such as LNG and methanol can be used (EMSA, 2017). The hydrocarbons need to be reformed before entering the cell. However, after reforming unit some carbon dioxide and NO_x will occur.

The efficiency of PAFC is not limited just with electrically, with heat recovery combined system its efficiency is relatively higher than PEMFC and AFC. Besides, the higher temperature makes it less sensitive to carbon monoxide. In spite of these advantages, PAFC has low power density so for the same power generation, the system will be larger and heavier (Mench, 2008). Moreover, because of high operation temperature PAFC start up is slower. (Shilpa and Anurag, 2015).

1.3.4 Molten carbonate fuel cell (MCFC)

The molten carbonate fuel cell is another high temperature working fuel cell and it operates approximately between $600 - 700^\circ\text{C}$ (Sastre et al., 2004). This high temperature provide an effective ion conductivity, furthermore minimize the needs for high cost catalyst such as platinum. The electrolyte is a mixture of a molten alkali metals carbonates (Mench, 2008). The carbonate ions (CO_3^{2-}) consumed in the anode follow out the transportation (de Troya et al., 2015). Nickel at the anode and nickel oxide at the cathode can be used as electrodes. Thanks to high working temperature

MCFC can reach to high total efficiencies. The flue gases can be used after cell exit via gas turbines or steam turbines. The electrical efficiency is around 50 – 60% however with a cogeneration systems, as mentioned before for PAFC, the total efficiency can reach to 85% (EMSA, 2017). The working principle and illustration of MCFC is shown in figure 1.7.

The electrochemical reactions in MCFC are showed in equations 1.15, 1.16, 1.17. (Mench, 2008):

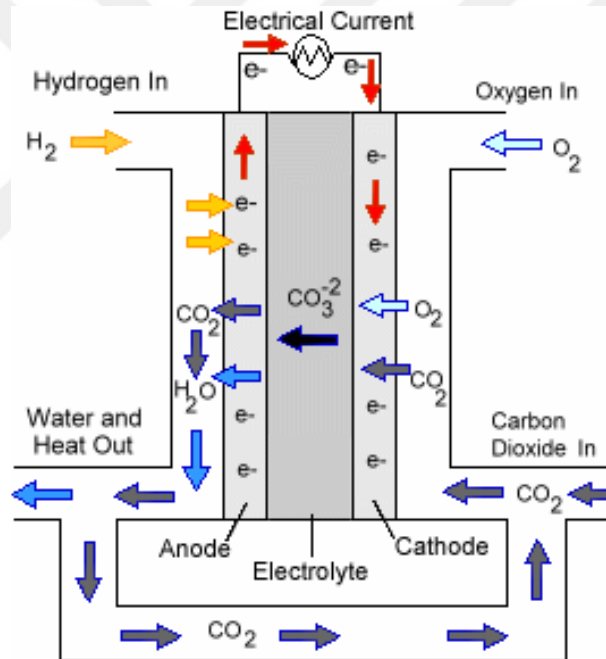
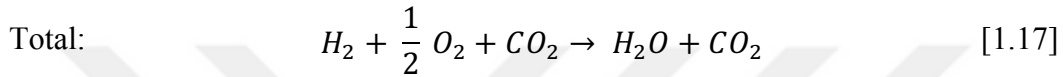
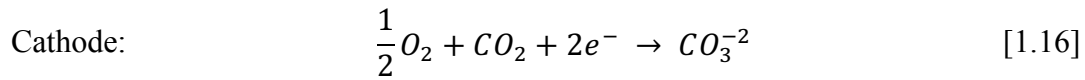
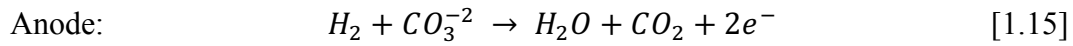


Figure 1.7 : Working Principle of MCFC. (Url-10)

The high temperature makes the MCFC more flexible from fuel perspective. Differently from the PAFC, molten carbonate fuel cell does not need a reforming unit for hydrocarbons fuels because the reforming occurs in the fuel cell.

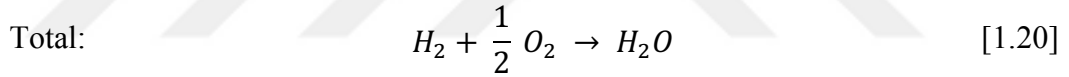
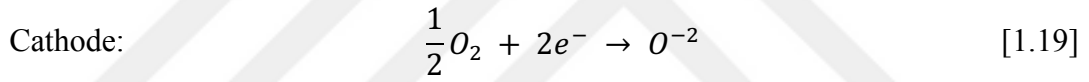
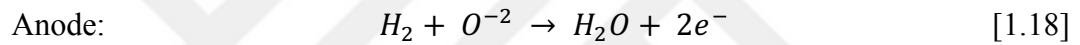
As disadvantages for MCFC, slow start-up, low power density, and related to high temperature high corrosion and cracking of components can be said.

The MCFC type fuel cell using area is generally focused on the high energy demanding areas.

1.3.5 Solid oxide fuel cell (SOFC)

Solid oxide fuel cell is one the high temperature working fuel cells. Its working temperature is between 800 – 1000 °C (Mench, 2008). Solid oxide fuel cells use solid state yttrium stabilized zirconia as electrolyte. As the same with molten carbonate fuel cells, solid oxide fuel cells use a nickel alloy as the anode, however the cathode is made of lanthanum strontium manganite (EMSA, 2017). Electrical efficiency of SOFC is changing between 50 – 60%, but as MCFC due to high temperature SOFC can be used in the heat combined systems and the total efficiency can reach to 80 – 85%. As a result of this high temperature, SOFC does not need expensive catalysts as PEMFC.

The electrochemical reactions in SOFC are mentioned in equations 1.18, 1.19, 1.20 (Mench, 2008):



As difference from the others, the SOFC has two possible geometries; planar and tubular (de Troya et al., 2015). The planar SOFC is the same with other types; an electrolyte between two electrodes. But, in a tubular SOFC the inner and outer tube are the electrodes and between them there is an electrolyte. Air flow is the inside and fuel is fed from the outer side of the cell. The planar SOFC has a higher energy density and it is easier to produce (EMSA, 2017). Most important advantage of SOFC is the highly efficient electric generation and during this operation it produces waste heat at high quality. Also, the SOFC has a multiple options of fuel such as LNG, methanol, hydrogen and hydrocarbons as diesel. The reforming of the fuel occurs in the cell unit (EMSA, 2017). The SOFCs are generally used in high capacity power generation facilities and for alternative power sources. The working principle and illustration of SOFC is shown in figure 1.8.

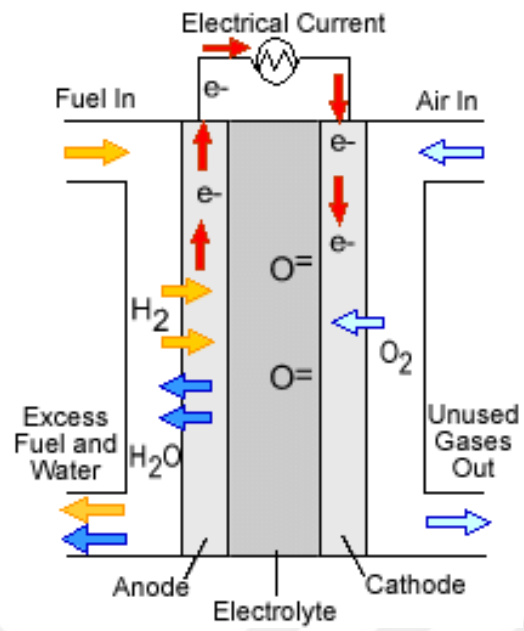


Figure 1.8 : Working Principle of SOFC (Url-10).

2. FUEL CELLS IN SHIPPING

Regarding to IMO emission limitations for ships, maritime industry have to find an alternative way to improve the main engine efficiency or have to try new alternative energy sources. Fuel cells are one of this alternative energy production ways and there is several research and development projects are realized all over the world for using in shipping. Specifically, for the hydrogen using fuel cells, the only emission becomes the pure water in contrast, for the hydrocarbon using fuel cell types, in addition to the water, carbon dioxide production occurs. In this chapter, parameters for the selection of fuel cell type, fuel cell powered ship projects and hybrid using of fuel cell systems with the comparison with the diesel engines are stated.

2.1 Fuel Cell Selection Parameters

For choosing the most promising fuel cell type to use in a merchant ships, power output, working temperature, efficiency, emissions, size, and safety are selected to analyze as criteria.

2.1.1 Power output

Power output for fuel cells is generally around kW levels, but there are some examples also in MW levels especially for high temperature working fuel cells. The most promising fuel cell types are MCFC, SOFC or AFC for on board application in the meaning of power output. Related to latest research up to 500 kW, AFC can perform (EMSA, 2017). However, need of pure hydrogen as a fuel for AFC is a disadvantage in vessel conditions because of the storage difficulty on board. So, with their capability of MW level power production MCFC and SOFC are coming firstly. On the other hand, high market value and technological maturity make the PEMFC an important alternative. In Pa-X-ell project 3 pack of 30 kW PEM is tried and successfully operated (EMSA, 2017). Because of the limited power output, using PEMFC as a main propulsion power generator seems hard but for electric generation it can be feasible.

2.1.2 Temperature

Working temperature is another important criteria to find the optimum fuel cell. Due to the temperature, degradation rate of the fuel cell membrane and electrolyte increases. So, higher temperature means lower operation cycle and lesser life time. But as an advantage, high temperature working fuel cells show less sensitivity to fuel impurities. Due to high temperature carbon monoxide and hydrocarbons can be utilized directly before reformation because it converts to hydrogen in the stack. So, this kind of fuel cells have a significant advantage for marine use. Also, waste heat can be utilized with cogeneration units like gas turbines. However, for high temperature operating fuel cells, start-up time is much longer than the other types and corrosion of the metal stack components are the main disadvantages (Han J et al., 2012).

PEMFC, AFC and PAFC can be classified as low temperature working fuel cells. Major disadvantage is the need of pure hydrogen as a fuel and the need of using platinum and electrocatalyst make them expensive. Especially PEMFC has a significant commercial applications because of its high power density and quick startup.

Related to working temperature MCFC and SOFC are suitable for marine applications with their fuel usage flexibility. Besides, PEMFC also seems very applicable with a large number of projects and its commercial basis.

2.1.3 Efficiency

General fuel cell efficiency is greater than conventional internal combustion engines. Fuel cells have a total electrical efficiency between 50-65% (Barbir, 2005). In contrast for marine diesel engines generally it is between 42-50% (Url-11). The efficiency advantage can be greater for high temperature working fuel cells such as SOFC and MCFC with cogeneration units. The produced hot air by fuel cell can be utilized with gas turbines for an additional electric generation. In this case the total efficiency of the system can reach to 70-80% for MCFC or SOFC (de-Troya et al., 2016). Specifically high temperature fuel cells like MCFC and SOFC are eligible for this combined system.

2.1.4 Emissions

Emission is the key concept for the utilization of fuel cells in maritime. All fuel cell types which use hydrogen as a fuel have only water as emission. However, fuel cells like SOFC, PAFC or MCFC can also put into operation carbon included fuels like diesel, methanol or LNG. Using hydrocarbons gives a flexibility for fuel usage and it is cost effective. Also, storage on board is easier than hydrogen. In this case CO, CO₂ and NO_x occur as emission in addition to water and heat (Choudhury et al, 2012). Especially for alkaline fuel cells and proton exchange membrane fuel cells pureness of hydrogen and air is very important. In any case of using carbon dioxide included fuel, electrolyte reacts and it reduces the effectiveness of fuel cell (Inal and Deniz, 2018). As a reason of hydrogen storage difficulties on board, fuel flexibility becomes more attractive. So, for maritime application SOFC, MCFC or PAFC seems more advantageous than other types of fuel cells.

2.1.5 Size

There are two option to compare size of fuel cells, either specific power or power density. Equation 2.1 shows the specific power and equation 2.2 shows the power density.

$$\text{Specific Power:} \quad \frac{kW}{kg} = \frac{\text{Output Power}}{\text{Mass}} \quad [2.1]$$

$$\text{Power Density:} \quad \frac{kW}{m^3} = \frac{\text{Output Power}}{\text{Volume}} \quad [2.2]$$

The objective is the reach to maximum value for both, meaning the fuel cell has relatively less mass with small volume with maximum power output. Fuel cells require auxiliary equipment such as pumps, blowers, power conditioning equipment etc. and this is called as a system by manufacturers. So, calculations for system will be more accurate to determine the correct specific power and power density for onboard applications. Some examples of fuel cells are mentioned in table 2.1.

Table 2.1 : Power – size relation for several commercial types of fuel cell system (Minnehan and Pratt, 2017; Url-3).

Fuel Cell	Power (kW)	Volume (m ³)	Mass	Specific Power (kW/kg)
SureSource 3000 (MCFC)	2800	252	48 tons	0,058
SureSource 1500 (MCFC)	1400	162	48 tons	0,029
FCe 150 (PEM)	150	0,660	474 kg	0,316
Powercell MS-100 (PEM)	100	0,293	98 kg	1,02
Fce 80 (PEM)	80	0,494	248 kg	0,323

2.1.6 Safety

The major fuel cell safety issue is related to the high temperature exhaust gases and electricity production. Especially for SOFC and MCFC the exhaust gas temperature is relatively higher than the other types. During the discharge of the exhaust from fuel cell, pipes must have double layer and effectively insulated to prevent from any leakage. Additionally, internal equipment like membrane, electrolyte and electrodes must be maintained in good condition to reach the maximum efficiency and safer operation. In any case of leakage of electrolyte from the cell unit, it can be a hazardous to human life. As an additional precaution for the pure hydrogen using fuel cell units, the storage tank and delivering pipes have to be insulated. Due to the physical properties of hydrogen, volatile and highly explosive, transfer between storage tank and anode side of fuel cell must comply with the two barrier principle and it is either achieved by ventilation and gas tight enclosure (Vogler and Vursig). Related to safety aspect, low temperature fuel cells have an advantage due to their safe operability but need of hydrogen as a fuel or hydrogen production units cause it needs more regulations and standards.

2.2 Fuel Cell Ship Projects

There is several projects on the use of fuel cells in ships. Most substantial projects are summarized in table 2.2:

Table 2.2 : Summary of fuel cell projects in shipping.

Project	Period	FC Type	Power (Kw)	Fuel
FellowSHIP	2003-2013	MCFC	320	LNG
METHAPU	2006-2009	SOFC	20	Methanol
FELICITAS	2005-2008	SOFC	250	Diesel, LPG
MC-WAP	2005-2010	MCFC	150	Diesel
ZEMSHIP	2006-2010	PEMFC	96	Hydrogen
SchIBZ	2009-2016	SOFC	100	Diesel
SF-BREEZE	2015-	PEMFC	4920	Hydrogen
Pa-X-ell	2009-2016	PEMFC	60	Methanol

2.2.1 FellowSHIP

In FellowShip project, a 6100 DWT gas powered offshore supply vessel, “Viking Lady”, has been chosen, figure 2.1. This project aimed to survey the use of both battery and fuel cell system in a vessel. In this project LNG fueled molten carbonate is used as a fuel cell system of 320 kW (McConnell, 2010). At full load of fuel cell, the electrical efficiency of 52.1% was measured and 44.1% after internal power losses (EMSA, 2017). The big drop of efficiency is related to being a R&D project and extra safety measures, in case of commercial installment the total efficiency will be higher. This fuel cell worked for 18,500 h at constant load and any emissions of NO_x, SO_x or PM was found (Inal and Deniz, 2018). In conclusion, the project was very exciting and very promising for the future of fully electric green ship concepts.



Figure 2.1 : Viking Lady supply vessel. (Url-14; EMSA, 2017)

2.2.2 METHAPU

The METHAPU (Methanol Auxiliary Power Unit) aims to research the feasibility of fuel cell technology for marine application as an auxiliary power production unit for a RoRo ship. The project was funded by European Commission to determine the maturity of methanol for marine applications by using solid oxide fuel cell and to assess in short term and long term environmental impact of this new technology. This project was important to settle the fuel cell future for maritime availability.

The project was firstly designed for 250 kW solid oxide fuel cell but only 20 kW was practiced on board with a methanol reformer. The project was under study from 2006 until 2010. The concept study with 20 kW SOFC on methanol was successfully worked over 700 hours (EMSA, 2017).

2.2.3 FELICITAS

The goal of FELICITAS project was the maximum efficiency with minimum hazardous emissions and minimum change of classical ship design, which is led by Rolls-Royce Marine Electrical Systems. The project focused on the environmental impacts such as salt, humidified air and sea conditions on the electrochemical operations of fuel cells. Also, to determine the fuel options to use in fuel cells and system response for the changeable ship power demands. The concept study with 250 kW SOFC achieved some outcomes like high efficiency greater than 60% with simulations, partly by experiments, and the alternative fuels other than LNG are needed to pass from a pre-reformer to use in SOFC. At the other hand, physical constraints of the ships and available fuel processing technologies are founded as challenges (FELICITAS, 2009).



Figure 2.2 : Stationary 1 MW fuel cell unit with 250 kW generator module by Rolls-Royce. (FELICITAS, 2009)

2.2.4 MC-WAP

The MC-WAP (Molten Carbonate Waterborne Application) project was under study from 2005 to 2010 and organized by CETENA (Italian Ship Research Center). The project covers a concept design of 500 kW MCFC onshore and 150 kW MCFC onboard testing.

The 150 kW MCFC is using diesel as the fuel with fuel processing module. The module converts diesel to syngas, working as a fuel reformer, for using in the fuel cell. As a direct consequence of MCFC being an high temperature working fuel cell, the hot exhaust gases is used for energy production in order to utilize an extra power unit. The total flow chart of the project is mentioned in figure 2.3.

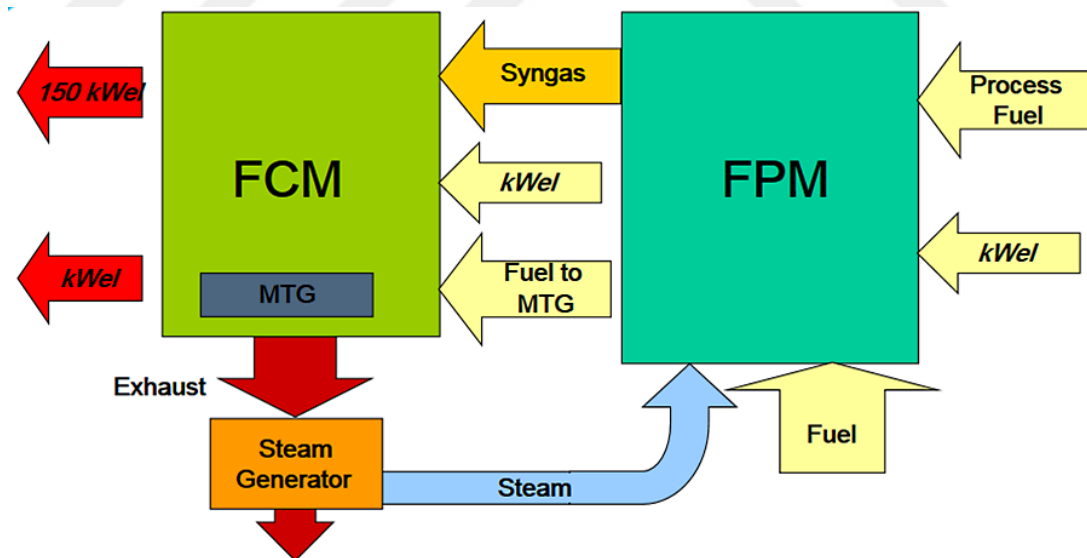


Figure 2.3 : Flow Chart of the MC-WAP Project. (EMSA, 2017)

2.2.5 ZEMSHIP

The ZEMSHIP (Zero Emission Ship) project aims to build an emission free passenger ship to use in Hamburg, Germany. The concept design of the ship is settled on the use

of hybridized fuel cell with battery instead of diesel engine. The project was started in 2006 and ended in 2010. The prototype fuel cell ship Alsterwasser started to operate in 2008 in Hamburg. Until the termination of hydrogen supply, the ship transported more than 43,000 passengers and fuel cell system worked over than 2,500 hours. Regarding to carbon footprints, local emissions of this ship were zero and compared to diesel electric ship, 47,000 kg of carbon dioxide emission is less per year based on 3,000 hours of operation (ZEMSHIP, 2010). Technically, the project had two PEM type fuel cells of 48 kW each and seven battery pack with a total capacity of 560V and 360Ah (EMSA, 2017). The power delivering from fuel cells were stored in batteries and then, transferred to electric motors for propulsion and maneuvering. The prototype ship, Alsterwasser, hydrogen fueling operation is designed of 50 kg compressed hydrogen in twelve 350 bar pressure tanks. This amount of hydrogen is enough to operate for three days (EMSA, 2017). As a result of the project, it is demonstrated that a passenger ship can be operated with zero emission and particularly, silent and vibration free.

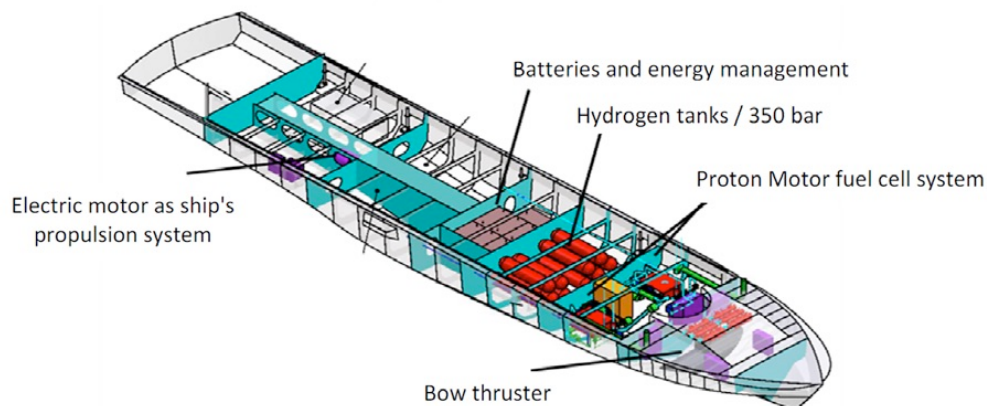


Figure 2.4 : Fuel cell system of Alsterwasser. (EMSA, 2017)

2.2.6 SchIBZ

SchIBZ project focused on the development of modular and efficient fuel cell for merchant vessel. The solid oxide fuel cell system is combined with a battery pack and produces a power from 50 to 500 kW with low sulphur diesel and reaches to an electrical efficiency of 50%. The system is put on the MS Forester for 12 months and the project is prolonged to December 2018 (EMSA, 2017). The project is managed by several company with the leadership of ThyssenKrupp Marine Systems (Url-11). As a result of the project, fuel cells can be a good option for the commercial ships in long-

term perspective if the cost reduction of the system and improvement of exhaust gas recovery can be achieved. Moreover, a battery system can compensate the power demand of the ship with the fuel cell combination.

2.2.7 SF-BREEZE

SF-BREEZE (San Francisco Bay Renewable Energy Electric vessel with Zero Emission) is consortium project between Sandia National Laboratories, the Red and White Fleet, the American Bureau of Shipping, the U.S. Coast Guard and Elliott Bay Design Group and started in 2015 (EMSA, 2017). The concept is to build an aluminum ferry with two electric motors of 2.5 MW driven by 41 fuel cell units of 120 kW each (Pratt and Klebanoff, 2016). The project also include a hydrogen supply station on shore in San Francisco Bay and it still under development.



Figure 2.5 : 3D Drawing of the SF-BREEZE (Url-13).

2.2.8 Pa-X-ell

The Pa-X-ell project was started in April 2009 and terminated in December 2016 (EMSA, 2017). The project is managed by the National Innovation Program for Hydrogen and Fuel Cell Technology (NIP). The purpose is to diminish emissions on ships via using fuel cells for propulsion systems. The system uses eight of 5 kW of high temperature PEM fuel cells and hydrogen as a fuel with internal reforming of methanol (EMSA, 2017). The system onboard is used for electrical power production and heat systems with substantially lower noise, vibration and exhaust emission than diesel generators. The prototype system is experienced on two different ships with different power capacities; first is a German research vessel “Sonne” and the second is a ferry of Viking Lines “MS Mariella”, figure 2.6. Due to the system was used as an

electric power production unit, it provides further development and new regulations for fuel cell use onboard by SOLAS (EMSA, 2017).



Figure 2.6 : MS Mariella (Url-12).

2.3 Comparison of Fuel Cell with Marine Diesel Engine

In this section fuel cell emission, safety, cost, maintenance, vibration, sound and power and energy limits will be compared with conventional marine diesel engines. After the results, the meaning for the adaptation fuel cells to merchant ships will be evaluated.

2.3.1 Emissions

The major advantage of fuel cells is the emissions. For a hydrogen using fuel cell type, only pure water is formed as the product. Other gas emissions like SO_x , NO_x , CO or PM from diesel engines cannot be found during cold combustion process. Also, for carbon included fuels like diesel oil, methanol, natural gas or naphtha using fuel cell types, the CO_2 emission is substantially reduced than conventional internal combustion engines (EMSA, 2017). However LNG fueled engines have an important lower emissions rate of NO_x and PM than diesel engines but fuel cells are again have a significant advantage in total. The formation of NO_x is related to the internal combustion temperature and duration with respect to intake air. NO_x emission from fuel cells will be lower than diesel engines because of the lower working temperature (Bourne et al., 2001).

Otherwise, fuel cell generators can offer an alternative for cold ironing operations under green port perspective, where ships can buy electricity from ports during their berthing period and this system could be technically and commercially feasible (L. van Biert et al., 2016).

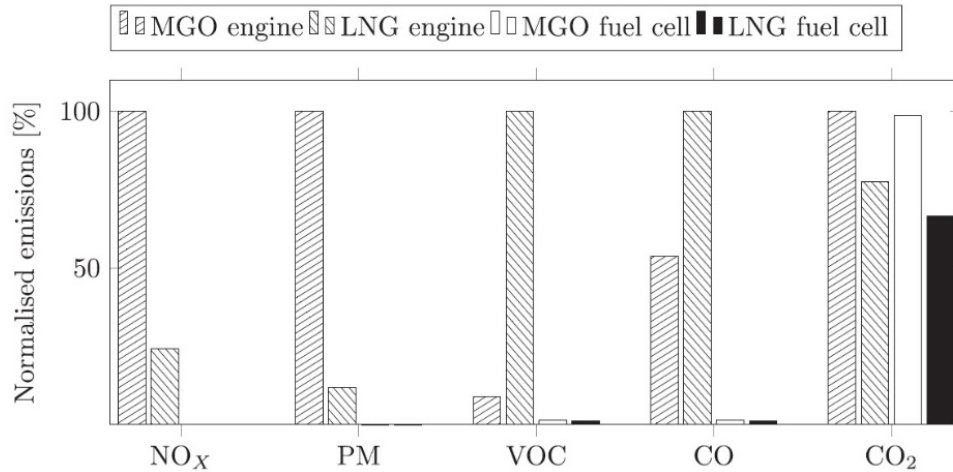


Figure 2.7 : Emission comparison for internal combustion engine types and fuel cell (L. van Biert et al., 2016).

2.3.2 Safety

Safety is one of the most important issues in shipping industry. As the nature of the working place, vessels are considered as high risk areas (Arslan and Kececi, 2017). However, fuel cells are not dangerous power production units. Without any moving part in the cell unit and the procedure of cold combustion during of working of fuel cells are the main superiorities against internal combustion engines. At the other hand, the main problem is about the storage of hydrogen. Hydrogen can be stored in two based phenomena; physical based and material based. The compressed gas, cold compressed and liquid hydrogen storage are the physical based, and, adsorbent, liquid organic, interstitial and complex hydride and chemical hydrogen are the material based storage options. Generally, compressed gas storage, using fiber reinforced composites are capable of reaching 700 bar pressure and it is the most common near-term pathway for storage hydrogen (Url-10). However, for using on board, this high pressurized tanks may be a source of risk for maintenance and management of hydrogen and fuel cell. Other critical events are related to; leakage of hydrogen rich gases and during bunkering operation, failure of pressure reduction, failure of electrical power conditioning system and fracture of compressed hydrogen tank system.

In contrast, major diesel engine operational risk is the fire due to high temperature. For decreasing the possibility and human based errors several types of sensors and emergency procedures have been installed to main engine and engine room. However,

just these type precautions or emergency drills are not sufficient for a safer maritime future.

2.3.3 Cost

The main obstacle against the widespread usage of fuel cells is the cost and lack of refueling infrastructure. Fuel cell system are in development state and for now they are significantly more expensive than diesel generators, however many researchers and companies see probability for reducing the cost of fuel cell technology. To be more specific, PEM type fuel cell usage in automotive sector is spreading and the cost of the technology has been decreasing in recent years. A price level around 50 \$/kW will put the fuel cells direct competition with diesel engines (L. van Biert et al., 2016), but for today's production volume it seems difficult. Fuel cell prices are in downward trend as indicated in figure 2.8 and related to production volume the cost for kW is decreasing. Between 2003 and 2008 relative cost for kW is diminished around 60% (see figure 2.2). For instance, at annual production between 20,000 and 500,000 units cost vary from 280 \$/kW and to 50 \$/kW (L. van Biert et al., 2016).

Another important point which affects the cost is the lifetime. Marine diesel engines are generally used for more than 20 years in a ship. But, the stack lifetime for fuel cells is specified maximum 5 years and stack efficiency shows decreasing in performance and at the end of lifetime it cannot reach to first years' efficiencies. In conclusion, for today's technology marine diesel engines have cost advantage against fuel cells.

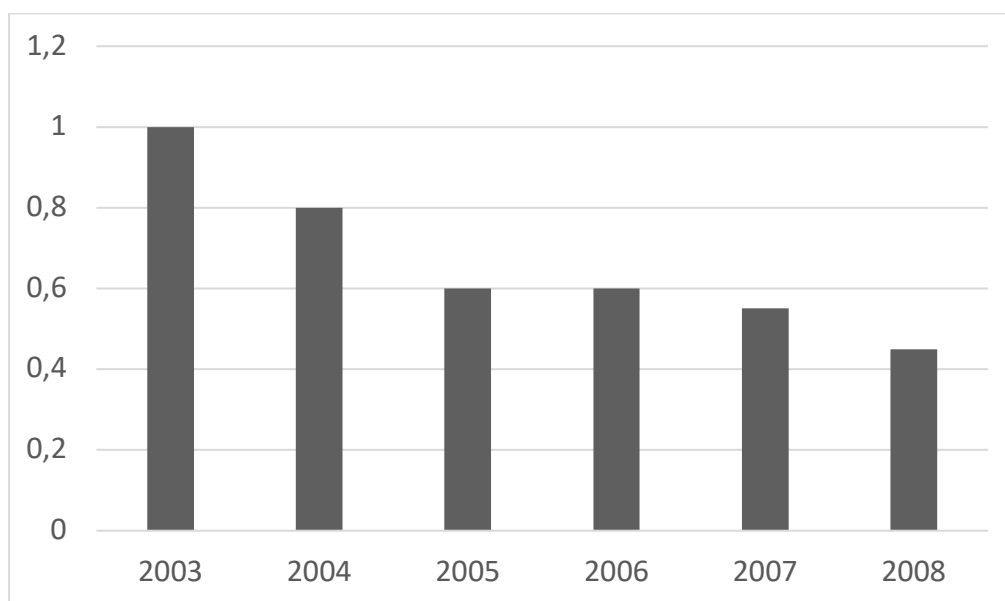


Figure 2.8 : Relative cost decrease trend for the FC (de Troya et al., 2016).

Table 2.3 : A comparison of fuel cells and other conventional systems (Sharaf and Orhan, 2014).

System	Power level (kW)	Efficiency (%)	Power density (kW/L)	Capital cost (\$/kW)
PEMFC (on-board fuel processing)	10 – 300	40 – 45	600 – 2000	100
PEMFC (off-board hydrogen)	10 – 300	50 – 55	600 – 2000	100
Gasoline engine	10 – 300	15 – 25	> 1000	20 – 50
Diesel engine	10 – 300	30 – 35	> 1000	20 – 50
Diesel engine/battery hybrid	50 – 100	45	> 1000	50 – 80

2.3.4 Maintenance

Fuel cells have less moving parts than conventional diesel engines. This is the direct cause for the longer maintenance periods and reduces maintenance cost. Moving parts and corrosion related to the mechanical frictions are the main reason for the shortened maintenance periods and cost for marine diesel engines. However, in a ship, there are several different equipment except the main engine such as fuel oil tanks and separators, lubricating oil tanks and separators, pumps, air compressors, water cooling system or electrical systems which need also periodic maintenance. About the durability of PEM type fuel cells, major failure modes may be the membrane, electrocatalyst and catalyst layer, gas diffusion layer and bipolar plates (Wu et al., 2008). Fuel cell maintenance is limited with the cleaning of air intake filters, hydrogen or fuel delivering systems, pumps, compressors and electronic equipment. Furthermore, as a direct consequence of less maintenance requirements, less spare part cost and reduced manpower requirement will be advantages (Bourne et al., 2001)

2.3.5 Vibration and noise

For maritime vessels limits of vibration and sound have been regulated in 1984 in the ISO 6954: Guidelines for permissible mechanical vibrations on board seagoing vessels

(Carlton and Vlastic, 2005). The origin for noise and vibration on board are almost same in all types of ships. The main noise and vibration producer is the main diesel engine and diesel electric generators. The other sources are air conditioning systems, cargo handling and mooring machinery, maneuvering devices, shaft dynamics, propeller radiated pressures and bearing forces and turbines (Carlton and Vlastic, 2005). Regulations related exposure limits for noise is determined by IMO MSC (Maritime Safety Committee) in the code on noise levels on board ships in 2012. In contrast with the diesel engines, vibration and sound levels of fuel cells are substantially lesser because of the fewer mechanical part, for instance, 72 dB at 10 feet distance is mentioned by FuelCellEnergy Company for SureSource 3000, table 3.5. This lower noise and vibration of fuel cell increases the comfort level on board and directly effect of crew health and working motivation. The related noise levels which are defined by IMO is given and summarized in table 2.4.

Table 2.4 : Noise levels for bigger than 10,000 GT ships (IMO, 1991).

Area	IMO Limit (dB)
Machinery Space	110
Messroom	60
Galley	75
Machinery Control Room	75

2.3.6 Power and energy limits

Generally for middle and big size merchant ships require an engine power between 5 – 40 MW. Diesel engines are more flexible than fuel cells in power production range. The most powerful marine diesel engine can reach to 108,920 hP which is produced by Wärtsilä - Sulzer (Url-7) at the other hand, it can be also in kW levels. However, fuel cells are usually produced at lower power scale. So, as a main power production unit fuel cells can be used in small size ships, but also they can be electric generators for any type of ships. The most promising fuel cell types for marine use are SOFC and MCFC with their high range of power and PEMFC with being most commercialized type. As stated before and shown in the previous projects, MCFC and SOFC can be used as a main propulsion unit for small type ships like river boats, passenger ships, mega yachts and small bulk carriers. However, PEMFC generally can be used for electric production instead of diesel generators, but, need of pure hydrogen as a fuel

for PEMFC is another challenge and a negative aspect for spreading on board use. As a solution, the usage of fuel cells in parallel or series connection could raise the total power output. Another important point which differentiate fuel cells from diesel engines is the long term power output. Due to fuel cell membrane and electrolyte degradation in years, the efficiency is decreasing. In contrast, diesel engine life time is much longer and thanks to periodic correct maintenance, it can keep the efficiency stable for years.





3. REGULATIONS AND EMISSION STANDARDS FOR FUEL CELLS

The main purpose for the research of fuel cell use in shipping is the zero emission perspective. The ship sourced GHG emission limitations are forcing ship owners to use conventional propulsion systems, based on internal combustion engines, by integrating costly exhaust cleaning technologies. In that respect fuel cell technology represents a promising option. The biggest advantage of fuel cells is the significantly lower GHG emissions than conventional internal combustion engines. In this chapter, regulations and standards to adopt fuel cells on board ship and emission reduction systems for marine diesel engine are investigated. Specifically NO_x , SO_x , and CO_2 emissions reduction ways for marine diesel engines are stated with respect to energy management system of marine industry. Then, currently important applicable standards for fuel cells on board are summarized from the perspective of IMO and classes. Terminally, design and operational characteristics for fuel cell application is given.

3.1 Emission Reduction Procedures and Energy Management Standards

MARPOL Annex VI deals with restricting the amounts of harmful emissions from ships' main propulsion system for substances such as SO_x , NO_x or CO_2 . Several technologies have been introduced to reduce harmful emissions level.

Exhaust gas recirculation, water injection or selective catalytic reduction are introduced methods to reduce NO_x emissions from ships. In the exhaust gas recirculation system some amount of engine exhaust gases are send back to the scavenge to mix up with the fresh air and it reduces the oxygen amount in the air so, reduces formation of NO_x (Hansen et., 2013). In the water injection method, water is added to reduce the temperature of combustion, however this method increases the specific fuel oil consumption with NO_x reduction (Zhang et al., 2017). The other type, selective catalytic reduction, it is considered the most promising way the exhaust is mixed water solution by urea and then passed through catalytic reactor, but this system installation and operating is very expensive (Guo et al., 2015).

The ways for reducing SO_x and PM emissions from marine diesel engines are specifically, using low sulphur fuel or exhaust gas scrubber system. The exhaust gas scrubber system is an already proven technology but the system needs additional equipment. The exhaust gas from the engine is gone through the scrubber pinnacle where a fluid is showered over it. Water mixed with soda (NaOH) is utilized as a scrubbing fluid which lessens the SO_x to 95% (Di Natale and Carotenuto, 2015). The cleaning water is then sent to a water treatment effluent emulsion breaking plant after which it very well may be released overboard.

The increasing interest in energy efficiency and as a direct consequence, emission reduction in shipping forcing ship owners to ensure optimal using of marine engines. To stay under limits of MARPOL Annex VI and to maintain most efficient engine management, shipping industry has some rules, such as EEDI (Energy Efficiency Design Index), EEOI (Energy Efficiency Operational Indicator) and SEEMP (Ship energy efficiency plan). The EEDI was became mandatory for all new ships and the SEEMP for all ships at MEPC 62 (Marine Environment Protection Committee with the adoption of amendments to MARPOL Annex VI (Url-6).

The EEDI is the most important technical criteria to assess the engine and auxiliary equipment working efficiency. The EEDI expresses in grams of CO₂ emission per ships capacity-mile (Url-8). So, the smallest amount of emission shows the most efficient ship design. The EEDI is calculated by a formula based on the technical design parameters of the ships. The EEDI level will be incrementally tightened in every five years, so it is expected to encourage all innovation and technical development from the design stage of all components that affect the fuel efficiency of a ship. After 2014 the EEDI starts to cover tankers, bulk carriers, gas carriers, general cargo ships, container ships, refrigerated cargo carriers, combination carriers, LNG carriers, ro-ro cargo ships (vehicle carriers), ro-ro cargo ships; ro-ro passenger ships and cruise passenger ships. These changes mean that ship types responsible for approximately 85% of CO₂ emissions from international transport (Url-6)

The SEEMP and the EEOI are interconnected concepts while planning and determining of the ship energy efficiency. The SEEMP is an operational measure to set up a system to evolve most cost effective in the energy efficiency manner (Url-6). The SEEMP is a notion which provides to shipping companies to manage their fleet energy efficiently using the EEOI as a tracking tool. The EEOI enables operators to

measure the fuel efficiency of a ship in operation and to measure the effect of any changes in operation, such as improved voyage planning or more frequent propeller cleaning, or introduction of technical measures such as waste heat recovery systems or a new propeller, as well as this kind of operational data are playing the key role to establish the SEEMP (Url-6). The SEEMP encourages the owner and operator of the ship to take under consideration new technologies and practices at every stage of the plan, while trying to optimize a ship's performance.

Since 2012, Marine Environment Protection Committee (MEPC) adopted important guidelines aimed at assisting the implementation of the mandatory regulations on Energy Efficiency for Ships in MARPOL Annex VI and summarized in figure 3.1.

The energy efficient ship management is roughly equivalent to reduction in fuel consumption and reduction in greenhouse gases emission, thus every preventive actions to reduce hazardous emissions from ships have direct consequences in energy efficiency subject. The latest goal of manufacturers is corresponding to 30% reduction in fuel consumption per voyage of ship in future (MAN, 2014). To reach the maximum emission reduction and, so, maximum total efficiency, manufacturers have designed and applied several methods and systems to ships such as; WHR (Waste Heat Recovery System) and TES (Thermo Efficiency System).

The waste heat recovery (WHR) system aims to reutilize of the heat in the exhaust gases. The primary source of waste heat of a main engine is the exhaust gas which accounts for about half of the total waste heat 25% (MAN, 2014).

The figure 3.2 shows that the engine which combined with WHR system reach to an efficiency of 55%. The WHR system has also an advantageous effect on lowering EEDI, which is a measure of emitted CO₂.

The working principle of the WHR is that part of the exhaust gas flow is bypassed the turbocharger, thus, the amount of exhaust gas and intake air is reduced. This reducing of amount in intake air and exhaust gases results an increase of exhaust gas temperature. This high temperature exhaust gases can be used in exhaust gas boiler for steam production which can be used in steam generator to produce electricity. Also, the bypassed exhaust gas is a part of the total system, can be used to produce electricity in a power turbine. The figure 3.2 shows the system configuration which is designed and applied by MAN B&W.

Resolution / Circular	Title	Status	Relevant regulation in MARPOL Annex VI
MEPC.254(67) and its amendments (MEPC.261(68))	2014 Guidelines on survey and certification of the Energy Efficiency Design Index (EEDI) (Consolidated text: MEPC.1/Circ.855/Rev.1)	Revokes MEPC.214(63) MEPC.234(65)	Regulation 5
MEPC.1/Circ.876	Sample format for the confirmation of compliance pursuant to regulation 5.4.5 of MARPOL Annex VI		Regulation 5.4.5
MEPC.245(66) (MEPC.263(68), MEPC.281(70))	2014 Guidelines on the method of calculation of the attained Energy Efficiency Design Index (EEDI) for new ships (Consolidated text: MEPC.1/Circ.866)	Supersedes MEPC.212(63) MEPC.224(64)	Regulation 20.2
MEPC.1/Circ.815	2013 Guidance on treatment of innovative energy efficiency technologies for calculation and verification of the attained EEDI		Regulation 20
MEPC.1/Circ.796	Interim Guidelines for the calculation of the coefficient f_{wv} for decrease in ship speed in a representative sea condition for trial use		Regulation 20
MEPC.233(65)	2013 guidelines for calculation of reference lines for use with the Energy Efficiency Design Index (EEDI) for cruise passenger ships having non-conventional propulsion		Regulation 21
MEPC.231(65)	2013 Guidelines for calculation of reference lines for use with the Energy Efficiency Design Index (EEDI)	Revokes MEPC.215(63)	Regulation 21
MEPC.232(65) and its amendments, (MEPC.255(67) and MEPC.262(68))	2013 Interim guidelines for determining minimum propulsion power to maintain the manoeuvrability of ships in adverse conditions (Consolidated text: MEPC.1/Circ.850/Rev.2)		Regulation 21.5
MEPC.282(70)	2016 Guidelines for the development of a ship energy efficiency management plan (SEEMP)	Supersedes MEPC.213(63)	Regulation 22
Circular Letter No.3827	Global Integrated Shipping Information System (GISIS) - IMO Ship Fuel Oil Consumption Database Module		Regulation 22A
MEPC.292(71)	2017 Guidelines for Administration verification of ship fuel oil consumption data		Regulation 22A.7
MEPC.293(71)	2017 Guidelines for the development and management of the IMO Ship Fuel Oil Consumption Database		Regulation 22A.12
MEPC.1/Circ.871	Submission of data to the IMO data collection system of fuel oil consumption of ships from a State not party to MARPOL Annex VI		Regulation 22A
MEPC.1/Circ.684	Guidelines for voluntary use of the Ship Energy Efficiency Operational Indicator (EEOI)		---
MEPC.1/Circ.863	Recommendation on exemption of ships not normally engaged on international voyages from the requirements in chapter 4 of MARPOL Annex VI		---

Figure 3.1 : MEPC guidelines for ship sourced emissions (Url-6).

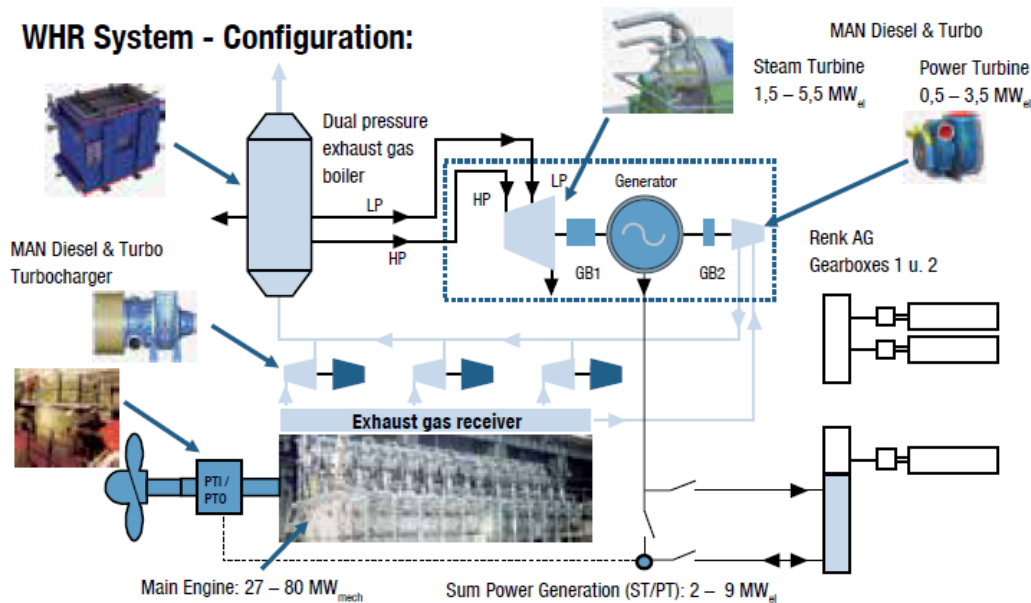


Figure 3.2 : MAN B&W WHR system configuration (MAN, 2014).

The working principle of thermo efficiency system (TES) is the electricity production via passing a part of exhaust gases through an exhaust gas turbine. The power production of the exhaust gas turbine depends on the exhaust gas flow.

The power output from the exhaust gas turbine is transferred to the steam turbine through a reduction gear and then, to the exhaust gas boiler. The total electric power output of the system is a gain with a simple and minimum design changing at the exhaust side of the engine. The calculations of the manufacturer shows a reduction of fuel consumption of 8-10% (MAN, 2014). This is directly effecting on reducing of the hazardous emission from ship.

3.2 Standards and Regulations for Fuel Cells in Shipping

In this chapter, current applicable standards and regulations for on-board use and fuel cell installation in shipping is given.

The lack of internationally-accepted standards for using of hydrogen and particularly fuel cell systems is related to intensity of usage. Since several years regulatory basement for alternative fuel usage in shipping is increasing due to the limitation of hazardous emissions from ships. More specifically, expanding global hydrogen trade will provide a higher demand and wider utilization of fuel cells in shipping. This market expanding is directly related to emissions from ships. So, supply, transportation and distribution chain is a key element for the commercialization and wider usage of fuel cell as a power source in shipping. To enhance the global quality and sustainability of this chain, maritime industry must have a series of standards and regulations.

Maritime applications of fuel cells must satisfy firstly the requirements for on board energy generation systems and fuel-specific requirements regarding the design of the fuel management like the piping, materials or storage (EMSA, 2017). To accomplish this purpose, one of the primary document to use hydrogen on board is the “IGF Code” or 2015 International Code of Safety for Ships using Gases or other Low-flashpoint Fuels, published by IMO.

The IGF Code is a subtopic of SOLAS (International Convention for the Safety of Life at Sea) and aims to minimize the risk for the ship, its crew and the environment, taking into account the nature of the respective fuels. IGF Code is primarily focused on the usage of liquefied natural gas for vessel and then the hydrogen and it includes

mandatory provisions for the regulation, installation, monitoring, and control of machinery, equipment and systems using low flash point fuel, initially focusing on LNG (Url-8). In respect of the goal of the Code is to satisfy a criteria for the arrangement and installation for main propulsion power or auxiliary purposes using LNG or hydrogen in terms of safety and reliability (Url-9). In addition to IGF Code, IMO has developed some requirements under SOLAS II-2 reg.20.1 for vessels carrying motor vehicles with compressed hydrogen or natural gas in their tanks which is pertinent part to fuel cells. Under the perspective of class rules, the five relevant class guidelines about the fuel cell applications, their release dates and interested fuel types are investigated.

Table 3.1 : Overview of relevant class rules (EMSA, 2017).

Class Name	Document	Release Date	Fuel Type
American Bureau of Shipping (ABS)	Fuel Cell Powered Ships Guide	In Development	Not specified
Bureau Veritas (BV)	Guidelines for Fuel Cell Systems on-board Commercial Ships	2009	Natural gas and Hydrogen
Det Norske Veritas Germanischer Lloyd (DNV GL)	DNVGL Rules for Classification of Ships Pt.6 Ch.2	2016	All fuels with flashpoint <60 °C
Korean Register of Shipping (KR)	Guidance for Fuel Cell Systems on-board of Ships	2014	All fuels with flashpoint <60 °C
Lloyd Register (LR)	Requirements for Fuel Cells in the Marine Environment Performance and Prescription	2006	Not specified

The most current document published by DNVGL and covers aspect such as design principles, material requirements, arrangement, fire safety, electrical system etc. in part 6 chapter 2 section 3 (DNVGL, 2017). Notwithstanding prescriptive plan necessities, DNVGL rules require a Failure Mode and Effect Analysis (FMEA) and a test program "Stationary energy unit control frameworks Safety" for the fuel cells.

The current DNVGL fuel cell rules are produced in light of hydrogen fuel, without anyway containing explicit arrangements for high weight hydrogen stockpiling advances. The other relevant class rules are listed in table 3.1.

3.3 Fuel Cell Powered Ship Design and Operation

During the design period of a fuel cell powered new ship, some rules and recommendation must be applied. The German class DNVGL has published a series of guidelines for the use of fuel cell on board ships and boats. The main source of this chapter is not only this mentioned guideline but also with the IGF code, some articles and fuel cell ship projects feasibility reports, the recommendations are supported.

Fire and explosion are the major references to the design a fuel cell-driven ship. To prevent the ship and its crew from any risky situation, the fuel cell room must be separated and ventilation of the room to the atmosphere must be kept clean and effective for any leakage of hydrogen. Hydrogen storage tank must contain a pressure relief valve outlet and its minimum distance is specified in IGF Code (GL, 2003). The piping systems and its components should be tested 1,5 times the maximum working pressure (GL, 2003). The two barrier principle, using double wall piping, will ensure the safe supply and transfer of the gas (Vogler and Wursig, 2010). Also, due to high explosion risk of pressurized hydrogen, an area classification has to be accomplished according to DIN EN 60079-10 to define explosion protection measures (Vogler and Wursig, 2010). Spaces where fuel cell and its equipment are located shall be monitored by gas detection systems and crew must pay attention to low rate of air circulation (GL FC, 2003). The ship should have the backup power for any emergency case like passing a channel, bay or heavy traffic areas (Pratt and Klebanoff, 2016).

The three basic explosion protection ways are specifically focused on the preventive actions. The first is the prevention of explosive atmosphere using double wall piping or preventing from gas accumulation. The second is the eliminating the ignition

sources from risky area. Avoiding from electrostatic electricity and/or only using of certified ex-proof and non-flammable equipment can be some options. The third is the actions for reduction the explosion effect like separating of fuel cell room and fuel storage tanks (Vogler and Wursig, 2010).

Regarding to operational aspects of a fuel cell-driven ship, there is much lesser maintenance operation need against conventional diesel engines. In any case of malfunction or cell power cut-off, waiting for the manufacturer service is recommended (Pratt and Klebanoff, 2016). However, for general bunkering operation of liquefied hydrogen or other fuel types the sector offers some observations like testing the bunkering system like lines, valves etc. with liquefied nitrogen before the hydrogen is used. The fueling station may be manned for security and safe operation.

4. CASE STUDY

The purpose of the case study is to determine the availability and the applicability of the chosen type fuel cell to a real merchant vessel. A chemical tanker under management of Chemfleet Ship Management Company is selected for the case study.

4.1 Ship Properties and Courses

M/T YM Neptune is chosen for the case study. The reason is the main engine's output power. Due to the limited power capacity of the fuel cells, as mentioned before, they can be used just as the main power producer for small size ships or electric generators for big size ships. However, the main source of emissions from ships is the main engine, not diesel generators. Therefore, a small size chemical tanker with 3 MW output power of main engine is well suited for the case study of this thesis. Technical details of the ship are given in table 4.1.



Figure 4.1 : M/T YM Neptune. (Url-2)

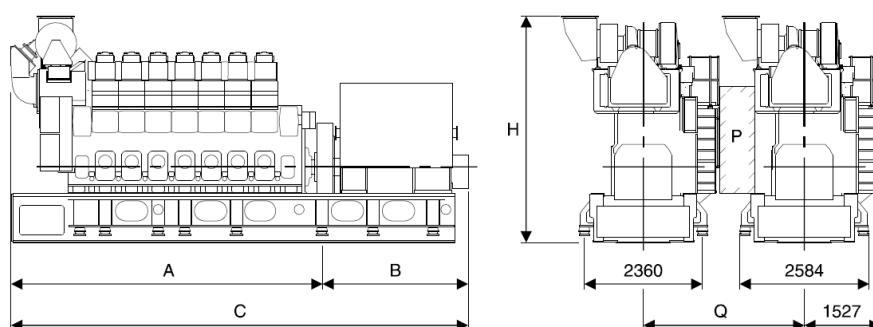
M/T YM Neptune has MAN STX 6L32/40 as a main engine. This engine has 6 cylinder in-line form with 320 mm bore and 400 mm stroke length. This medium speed four-stroke diesel engine has 2880 kW output power at constant 750 RPM. Main engine sizes and weight are given in figure 4.2 (MAN, 2009).

Table 4.1 : Technical information of M/T YM NEPTUNE.

Title	Properties
Ship Name	YM Neptune
Ship Type	Oil / Chemical Tanker
IMO No	9464106
Call Sign	9HA2017
Flag	Malta
Home Port	Valletta
Gross Tonnage	4829
Deadweight	6970 t
Length	119,1 m
Breadth	16.9 m
Year Built	2009
Main Engine	MAN STX 6L32/40
Main Engine Power	2880 kW

M/T YM Neptune has MAN STX 6L32/40 as a main engine. This engine has 6 cylinder in-line form with 320 mm bore and 400 mm stroke length. This medium speed four-stroke diesel engine has 2880 kW output power at constant 750 RPM. Main engine sizes and weight are given in figure 4.2 (MAN, 2009).

As seen in the figure 4.2, total length and the height of the engine (alternator included) are respectively denoted with “C” and “H”. The “A” shows engine length and “B” is the alternator.

**Figure 4.2 :** MAN STX 6L32/40 dimensions (MAN, 2009).

The numerical equivalents of letters are given in table 4.1.

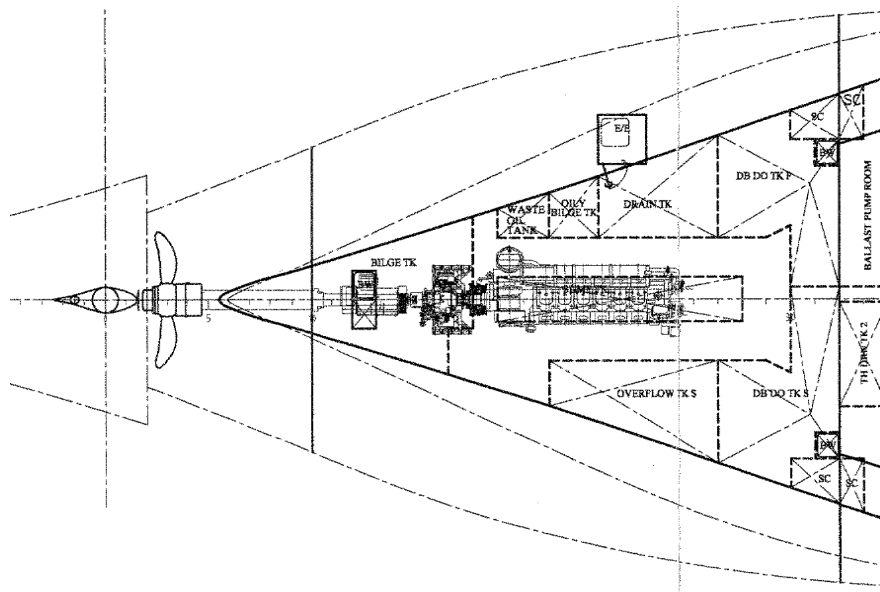
Table 4.1 : Engine dimensions (MAN, 2009).

Dry Weight (t)	A (mm)	B (mm)	C (mm)	H(mm)
75	6340	3415	9755	4622

Table 4.2 : Exhaust gas constituent for MAN STX 6L32/40 (MAN, 2009).

Main exhaust gas constituent	Emission factor (g/kWh)
N ₂	5,09
Steam H ₂ O	305
SO _x	10
NO _x	12
CO	0,6
HC	0,8

The exhaust gas composition for different fuel types and their effects on emissions are given as seen in the table 4.2 (MAN, 2009). The engine manufacturer with respect to fuel type gives all the exhaust gas constituent. SO_x, NO_x, CO and HC are calculated according to ISO-8178 and specifically SO_x is determined in conformity with a sulphur content in the fuel oil of 2,5% by weight (MAN, 2009). The vessel engine room consists of three floors. The main engine, shaft, several tanks and pumps are located at the bottom floor. The plan of the floor is in the figure 4.3. Generators, fuel oil, diesel oil and lubricating oil separators and other tanks are in the second floor, figure 4.4. The third floor consists engine control room, workshop and boiler room, figure 4.5.

**Figure 4.3** : Bottom floor of the engine room.

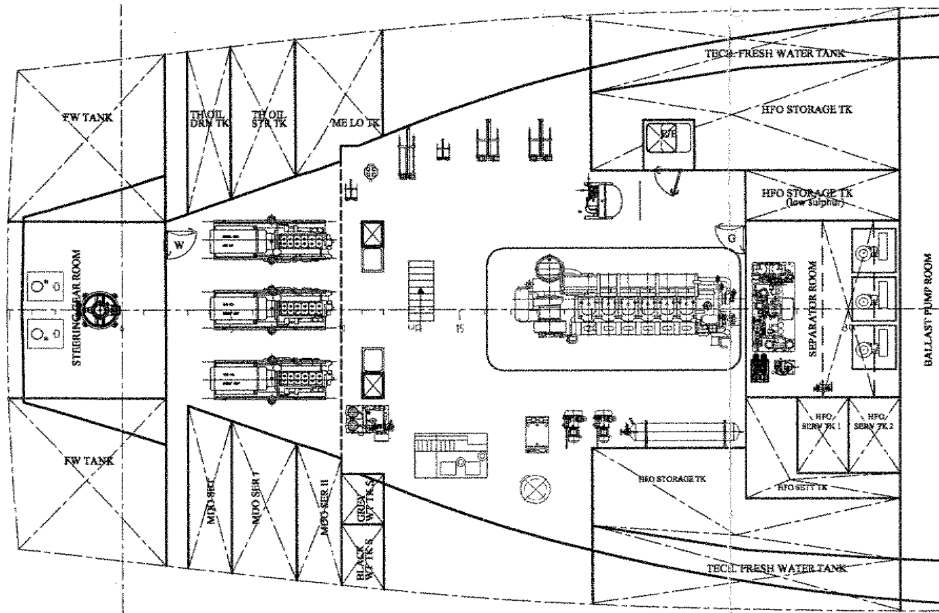


Figure 4.4 : Second floor of the engine room.

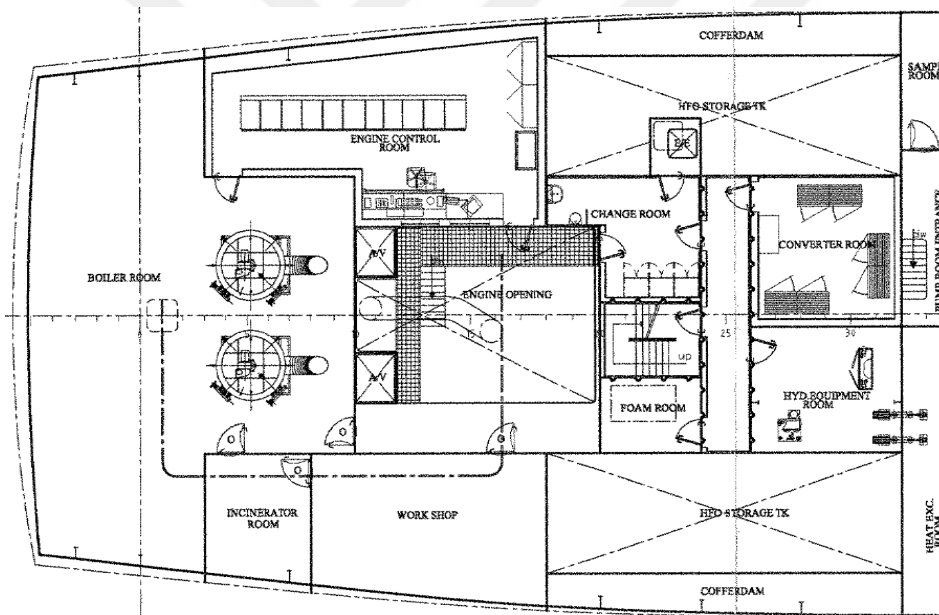


Figure 4.5 : Third floor of the engine room.

Ship route is collected from the January to October 2018 on account of company. The port list, time spent at sea, total distance between the ports and ship's average speed are summarized in table 4.3.

Table 4.3 : YM Neptune January – October 2018 routes.

No	Departure	Arrival	Distance (nm)	Time Spent at Sea (h)	Average Speed (kts)
1	Ravenna	Antwerp	3119,6	322	9,69
2	Koper	Ravenna	136,5	13,83	9,87
3	Kulevi	Koper	1815,85	176,17	10,31
4	Constantza	Kulevi	618,9	61,03	10,14
5	Elevsis	Constantza	616,7	69,5	8,87
6	Ravenna	Elevsis	953,7	87,42	10,91
7	Runcorn	Ravenna	3085,9	302,58	10,20
8	Aughinish	Runcorn	576	57,33	10,05
9	Port Said	Aughinish	3177,5	330	9,63
10	Haifa	Port Said	223	25,25	8,83
11	Fos	Haifa	1698,5	166	10,23
12	Aliğa	Fos	1488,9	136,5	10,91
13	Gemlik	Aliğa	324	31,05	10,43
14	İzmit Bay	Gemlik	79	8	9,88
15	Augusta	İzmit Bay	859,2	93,4	9,20
16	Berre	Augusta	736,7	71,4	10,32
17	Augusta	Berre	723	77,23	9,36
18	İzmit Bay	Augusta	904,6	83,55	10,83
19	Aliğa	İzmit Bay	306	35	8,74
20	Algeciras	Aliğa	1673,3	159,4	10,50
21	Leixoes	Algeciras	531,5	63,55	8,36
22	Safi	Leixoes	851,5	122,7	6,94
23	Lavera	Safi	1576,8	285,2	5,53
24	Livorno	Lavera	299	29	10,31
25	Genoa	Livorno	102	11,33	9,00
26	Haifa	Genoa	1534,5	157	9,77
27	Rotterdam	Haifa	3457	352	9,82

4.2 Fuel Cell Selection

The criterions are defined of eight important attributes; relative cost, lifetime, fuel, size, emissions, safety, efficiency and power output. All fuel cell types are pointed 1 to 10 to find the final scores, then, all types are ranked by their scores to detect the most fitted cell type (Sharaf and Orhan, 2014; de-Troya et al., 2016; van Biert et al., 2016; EMSA, 2017; Pratt and Klebanoff, 2016; Barbir, 2005; Miola et al., 2010). Finally, the total evaluation for the selection of the most promising fuel cell type is summarized in table 4.4.

Table 4.4 : Evaluating of fuel cell types for ship usage.

Criteria	MCFC	SOFC	PEMFC	AFC	PAFC
Cost	6	4	9	7	6
Lifetime	8	7	7	6	7
Fuel	10	10	5	5	5
Size	6	6	9	9	9
Emission	9	9	10	10	10
Safety	8	8	9	9	9
Efficiency	9	9	8	7	7
Power	9	9	7	2	5
Total	65	62	64	55	58

As seen in the table 4.4, the molten carbonate fuel cell is chosen as the most promising fuel cell type for marine usage in our study. The second is the proton exchange membrane fuel cell and its biggest advantages are the high market value and the technological maturity. However, need of high purity hydrogen, as a fuel is an important disadvantage for merchant vessels. The fuel flexibility towards LNG, diesel or hydrogen without any need of reforming equipment and the opportunity of hybridization with gas or steam turbines for high efficiency make the MCFC the first choice.

The product SureSource 3000 of Fuel Cell Energy Company is selected for the case study. It is a molten carbonate type fuel cell using LNG as a fuel and produces 2.8 MW output power (Url-3). The fuel cell is comprised of two 1.4 MW modules (Url-3). The total system includes both a mechanical balance of plant and electrical balance of plant. The system is modular, settlement is changeable and power output can be raised with integration of extra cell units, figure 4.6. The technical details of the fuel cell is mentioned in table 4.5.

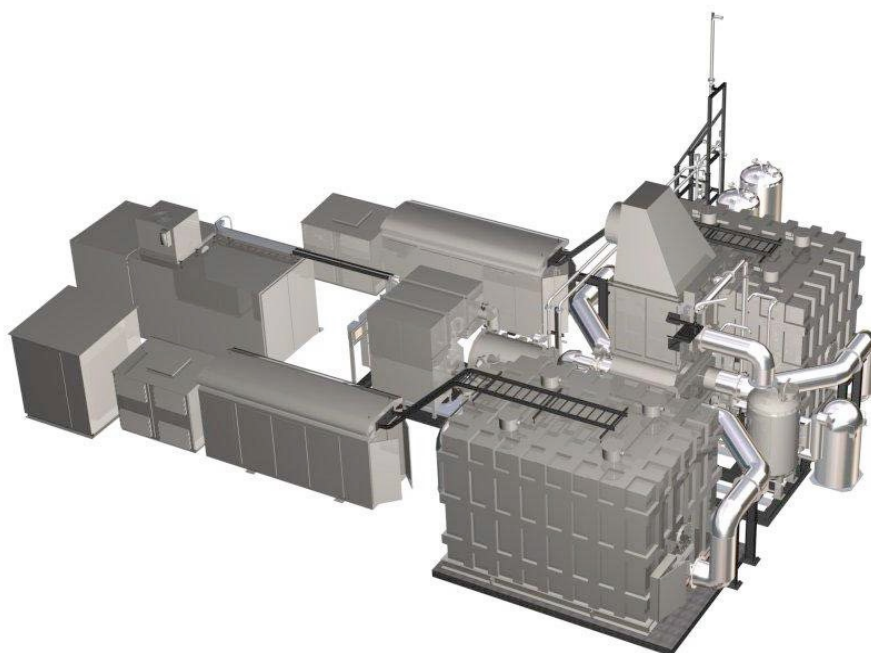


Figure 4.6 : The SureSource 3000 (Url-3).

Table 4.5 : Technical details of SureSource 3000 (Url-3).

Criteria	SureSource 3000 MCFC
Power Output	2,800 kW
Standard output AC Voltage	13,800
Standard Frequency (Optional)	60 Hz (50 Hz)
Exhaust Temperature	370 – 400 °C
NO _x Emission	0,045 g/kWh
SO _x Emission	0,00045 g/kWh
CO ₂ Emission	444,5 g/kWh
CO ₂ Emission (with WHR)	272 g/kWh
PM Emission	9,07.10 ⁻⁶ g/kWh
Efficiency	47 +/- 2%
Weight (total system)	160 tons
Fuel Consumption (NG)	615,12 m ³ /h
Sound Level	72 dB at 3m
Maximum Height	6,6 meters
Cell Unit Length	6,5 meters
Cell Unit Width	13,1 meters

The SureSource 3000 uses LNG as a fuel, so, vessel's fuel tanks should be transform to LNG storage tanks. The tanks, which can be transformed, are the heavy fuel oil, marine diesel oil and lubricating oil tanks. The tanks capacities are listed in table 4.6. Other tanks will be needed during ship operations like fresh water tanks, bilge tank, black water tanks etc. After removing of main engine HFO, MDO and LO tanks will be out of use. To sum up, the total capacity of the tank, which can be switched to LNG tanks, is approximately 530 m³.

Table 4.6 : Ship tank capacities.

Tank	Volume (m ³)
HFO	421,64
MDO	66,78
LO	41,27

4.3 System Design and Components in Ship

The system design is done under the accompanying assumptions (Aminyavari M, et al., 2016; Nami et al., 2017; Ahn et al., 2018):

- All chemical reactions are in equilibrium and the temperature, pressure and system operations are same and at steady state.
- The kinetic and potential energy differences are negligible.
- All system components are adiabatic except fuel cell stack.

As seen in the figure 4.7, LNG is transferred to mixer through a compressor, then, both LNG and water are delivered to internal reformer which is situated in stack. In internal reformer, LNG and water react and produce hydrogen to be fed to the anode side of the cell unit. Before entering to internal reformer, reactants must be heated to be prepared for an effective steam methane reforming and water gas shift reaction (Ahn et al. 2018). These two important reactions which occur to produce hydrogen and carbon monoxide inside of the fuel cell stack (Munoz de Escalona et al., 2011) Since the reforming reaction is a profoundly serious endothermic process, it expels the heat produced by the hydrogen oxidation (Kim et al., 2017) The electrochemical reactions are the followings: (Ovrum and Dimopoulos, 2012)

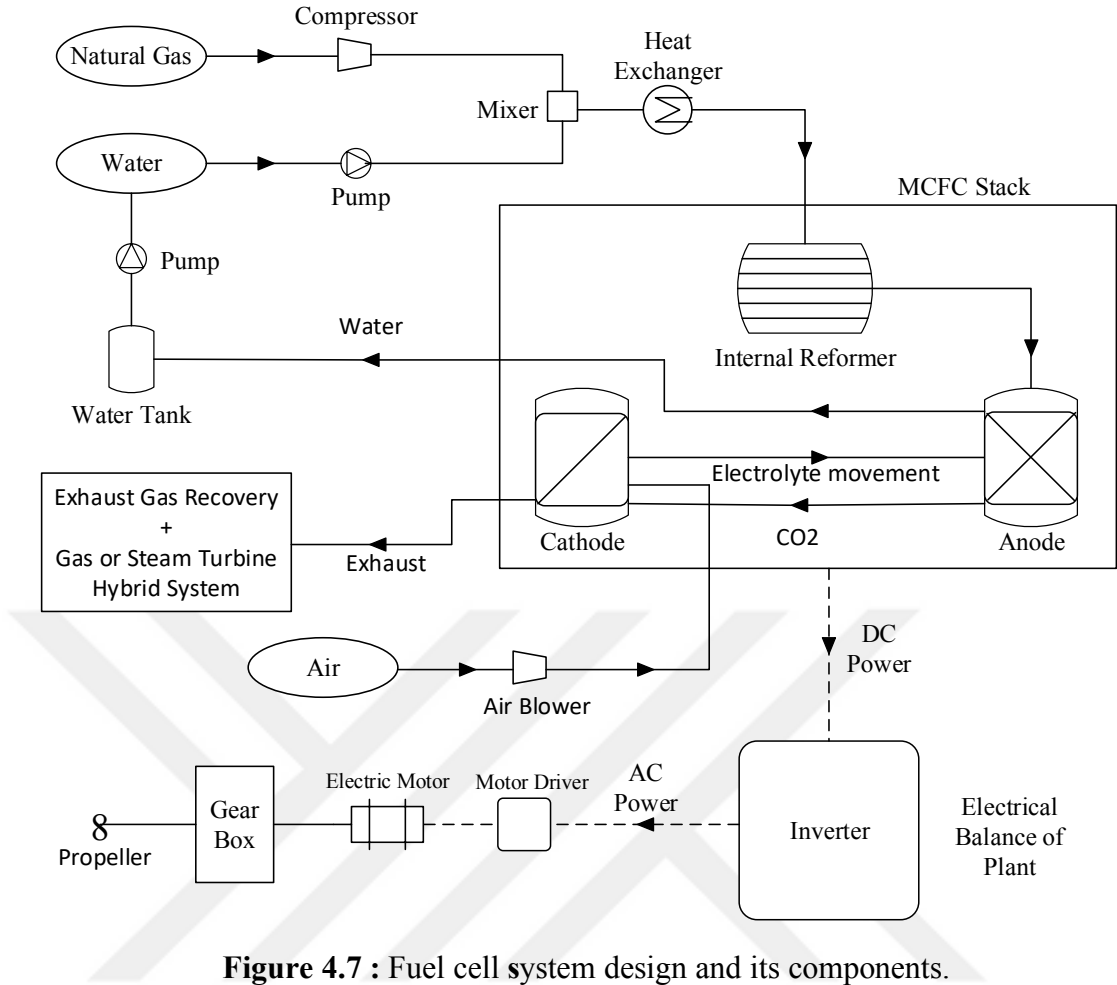
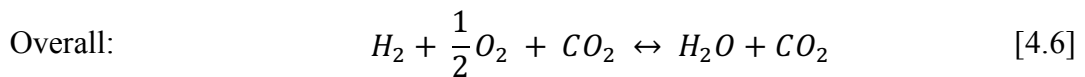
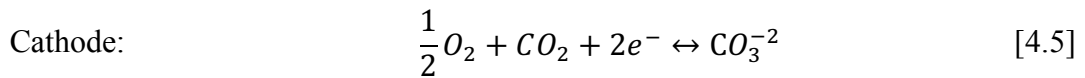
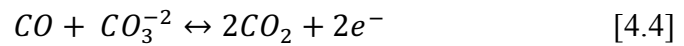
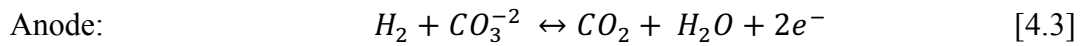
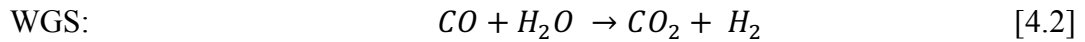
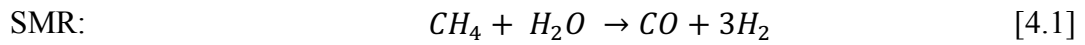


Figure 4.7 : Fuel cell system design and its components.

After several electrochemical reactions the produced DC power is transformed to usable AC power by an inverter system which is included to the total fuel cell system under name of electrical balance of plant (Figure 4.7). The high temperature exhaust gases can be used in a combined gas or steam turbine system as exhaust gas recovery.



The total heat energy available for recovery is given 1300 kW for 121 °C (Url-3). However, recovery energy for the main diesel engine is given 1150 kW in instruction book (MAN, 2009).

4.4 Propulsion Equipment Selection

The fuel cell electrical output properties are 2,8 MW power and 13,800 volt. Electric motor and driver unit should work in coherence with propeller for an efficient propulsion; therefore, electric motor selection is very important. The chosen motor must be suitable for the output power of the fuel cell. The key features are the voltage and power compatibility, as well as the complying with marine standards.

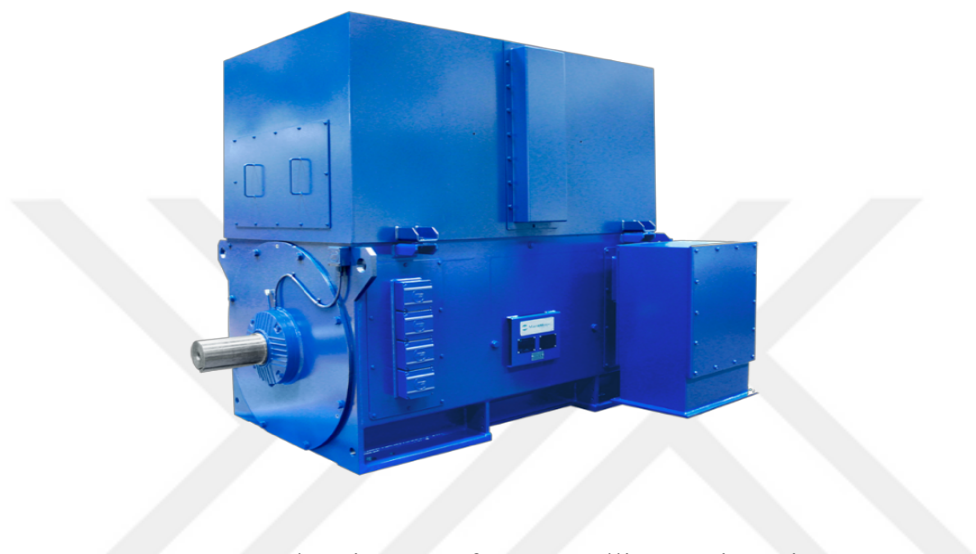


Figure 4.8 : B5V type electric motor from Marelli Motori Marine Company.

Therefore, B5V marine type electric motor chosen from Marelli Motori Marine Company, figure 4.9. The technical details of the motor is given in table 4.7 and power output data in relation with pole number is given in table 4.8.

Table 4.7 : Electric motor technical details (Marelli Motori, 2018).

Criteria	Data
Power	Up to 10.000 kW
Voltages	Up to 15.000 V
Pole	4, 6, and 8
Cooling	IC 81W (IC 86W, IC 611, IC 616, IC 666 on request)
IP	IP 55 (IP 23, IP 44, IP 24W NEMA, IP 56 on request)
Application Areas	Thrusters, Hybrid Machine, Propulsion, PTO-PTI System

Table 4.8 : Power output in relation with pole number (Marelli Motori, 2018).

Poles	4 Poles	6 Poles	8 Poles
kW at 60 Hz	3,100	2,500	2,000

As seen in table 4.8, 4 poles motor is enough to operate ship's propeller with 90% load. However electric motors work with high RPM and if the propeller is connected directly, it will cause cavitation. Therefore, the system needs a reduction gear between the propeller and motor. The motor RPM must be known in order to find the reduction ratio. The motor RPM can be calculated using formula:

$$RPM = \frac{120 \times f(Hz)}{Pole\ Number} \quad [4.7]$$

After calculations, motor's RPM is found 1800 and it has to be reduced to the propeller's RPM with a reduction gear unit, to 133. The electric motor is suitable for marine propulsion and it has IP certificates for marine operating conditions.

Another important equipment is the motor driving unit. The system need a driving unit before the electricity reach to the motor. The most important data for choosing drive unit is the drive technology and compatibility with maritime conditions. Stadt Lean Propulsion's drivers are suitable for marine application and they can be used together with controllable pitch propellers. Its drive technology is sinus and it provides power losses lesser than <0,2% with lesser than <1% total harmonic distortion. The generated electric from the fuel cell is collected in a main switch board, then without a voltage changing equipment (transformator), with sinus waves the produced electricity comes through motor driver unit. Figure 4.9 shows the working principle (Stadt, 2018).

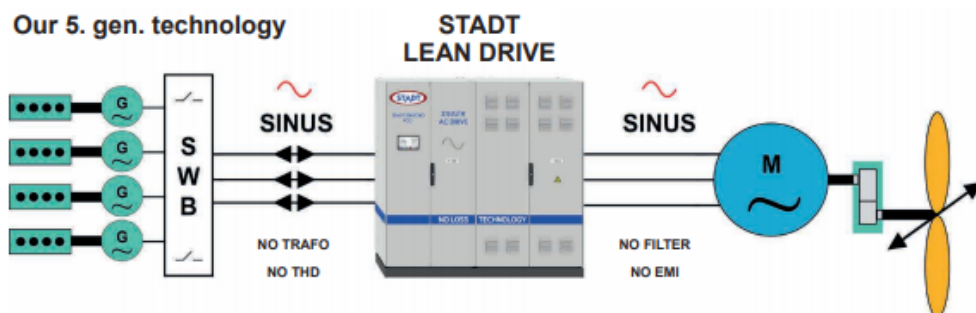


Figure 4.9 : Motor driver working principle (Stadt, 2018).

4.5 LNG Storage in Ship

There are three different types of LNG carriage method in shipping: Moss type, SPB (self-supporting, prismatic shape, IMO type-B) and membrane type (Witherby Seamanship International, 2011). In case study fuel oil and diesel oil tanks would be transformed to LNG tanks. The total fuel oil tank capacity is 421 m³ and total diesel oil tank capacity is 66 m³ as mentioned in table 4.5. The maximum LNG consumption of the fuel cell for its longest route is 360 m³ in 10 months. The membrane type tank is selected for application in order to easier transformation and to be an already self-proving technology. The Moss type tank was the other important alternative, however due to its spherical shape, during the transformation and adaptation of the system it would cause a severe volume loss in tanks. The table 4.9 shows a summary of the membrane system storage tanks and so, combined system shows a great harmony with transformation of the conventional diesel and fuel oil tanks, related to its lower weight and membrane thickness.

The volume reduction because of the insulation is calculated 96 m³ for 487 m³, total of the diesel oil and fuel oil tanks, and this makes almost 20% of volume loss from the total, so the maximum LNG transportation capacity becomes 391 m³. The longest voyage of the chosen ship is determined and it is clearly seen that the new tank volume is satisfying for the vessel's routes, so vessel wouldn't need any LNG bunkering operation during its longest voyage.

The three alternatives of membrane type tank comparison is in the table 4.9.

Table 4.9 : Membrane containment system tank comparison. (Witherby Seamanship International, 2011)

System	Gas Transport 96	Technigaz Mk III	Combined System
Primary Membrane	0.7 mm Invar	T1.2 mm Corrugated Stainless Steel	0.7 mm Invar
Secondary Membrane	0.7 mm Invar	0.6 mm Triplex	0.6 mm Triplex
Insulation Material	Plywood / perlite	Reinforced Polyurethane Foam	Reinforced Polyurethane Foam
Containment System Weight	138 kg / m ³	73 kg / m ³	67 kg / m ³
Welding process	Seamwelding	TIG / Plasma	Seamwelding

4.6 Operational Aspect

The powerplant is separated into four components: fuel cell stacks, electrical balance of plant, mechanical balance of plant and electric motors.

The fuel cell stack, electrical balance of plant and electric motor do not require a specific maintenance or operation periodically. Electrical equipment are very reliable but they need a routine small maintenance such as filters, connectors and other miscellaneous items. The major equipment for maintenance is the mechanical balance of plant and its components. To be more specific; pumps, compressors, valves and filters (Toyota, 2018). This types of auxiliary maintenance are almost same with the conventional diesel engines and their equipment, so any disadvantages or advantages cannot be designated. However, as a main power producer, lack of diesel engine is a great advantage in the operational perspective. This will cause to less personnel requirement and directly affect the human sourced risk and operational cost. The major fuel cell maintenance need is at the end of lifecycle with the changing of electrolyte and electrodes. The results are showing that approximately 50,000 hours of work is reached (Alkaner and Zhou, 2005).

In addition, fuel cell using reduces noise and vibration dramatically. The chosen fuel cell make 72 decibels sound but the main diesel engine 134 decibels (MAN, 2009). Also mechanical parts are the main source of vibration in a vessel, with a fuel cell system lesser mechanical equipment provides more comfortable voyages for seafarers.

For bunkering operation of the gaseous fuels onboard the vessels, several guidelines have been reported especially by shipping classes and societies. LNG is determined as the reference fuel while preparing of guidelines. With difference from hydrogen LNG is a mixture of gases methane, ethane, propane, butane, nitrogen and other trace gases. The percentage of methane can vary from 87% to 96% depending on source (Hajbabaei, et al., 2013). Both hydrogen and methane are lighter than the air so, it cause to pay more attention than the conventional marine fuels during bunkering operations. The operators of the bunkering facility should satisfy the higher standards with regard of safety, reliability and environmental protection (EMSA, 2017). According to ISO/TS 18683, bunkering operations of the vessels shall be conducted under the control of a safety management system (SMS) (Url-1). The most detailed

guidelines is published by DNVGL in October 2015. The other relevant publishing are listed in table 4.10.

Table 4.10 : Relevant LNG bunkering guidelines.

Publisher	Name	Year
IACS	LNG Bunkering Guideline	2016
SGMF	LNG Bunkering Safety Guideline	2015
DNVGL	Development and Operation of LNG	2015
IAPH	Checklist for LNG Bunkering	2014
BV	LNG Bunkering Guideline	2014

The common point of all these guidelines is providing recommendations for the responsibilities and procedures required for LNG bunkering operations of vessels to comply the maximum efficiency with minimum risk.

German Lloyd has listed the clauses for the bunkering and the fuel transfer system in the “Guidelines for the Use of Fuel Cell Systems on Board of Ships and Boats” in 2003. The most important clauses are listed below:

- The bunkering station shall be located on the deck.
- The bunkering station and fuel transfer pipes shall be provided with shut-off valves located directly at the transfer point and directly before the distribution manifold to the fuel tanks.
- A suitable fire-extinguishing device shall be provided in the vicinity of the bunkering station.
- Measures shall be taken to ensure that the fuel transfer pipe can be gas-freed after use.
- Openings of blow-off pipes for gas-freeing shall be arranged at points where no sources of ignition exist.
- Entrances, ventilation openings and openings leading to accommodation and service spaces, machinery spaces, and control rooms shall be located outside hazardous areas. They shall not face the bunkering station.

- Openings to spaces that are located up to 10 meters away from the transfer connection shall be kept closed during fuel transfer. Appropriate warning notices shall be displayed.

4.7 Evaluation of the Fuel Cell Application

The system is evaluated regarding to exhaust emissions, economic feasibility and in operational manner. The main purpose is to evaluate the results of the ship route if the vessel was equipped with the chosen fuel cell. Regarding to figure 4.6, the collected data from the company, verification with emission factors and calculations from the datasheet of the main engine, the total exhaust emission for 10 months is found 5249 tons of CO₂, 115 tons of NO_x and 96 tons of SO_x. If the vessel was made the same way with fuel cell the results would become; 4400 tons of CO₂, 45 kg of NO_x and 0,45 kg of SO_x. The figure 4.10 is for CO₂, figure 4.11 for NO_x, and figure 4.12 for SO_x.

The NO_x, SO_x and CO₂ emissions are calculated for diesel engine using the formula below:

$$Emission (kg) = \frac{emission\ factor \times power\ output \times voyage\ time}{1000} \quad [4.8]$$

The emission factor is taken into account from the datasheets of the engine and the company log book, in terms of g/kWh. The emission results are found in terms of kg, when the power output and time are given in terms of kW and hours, respectively.

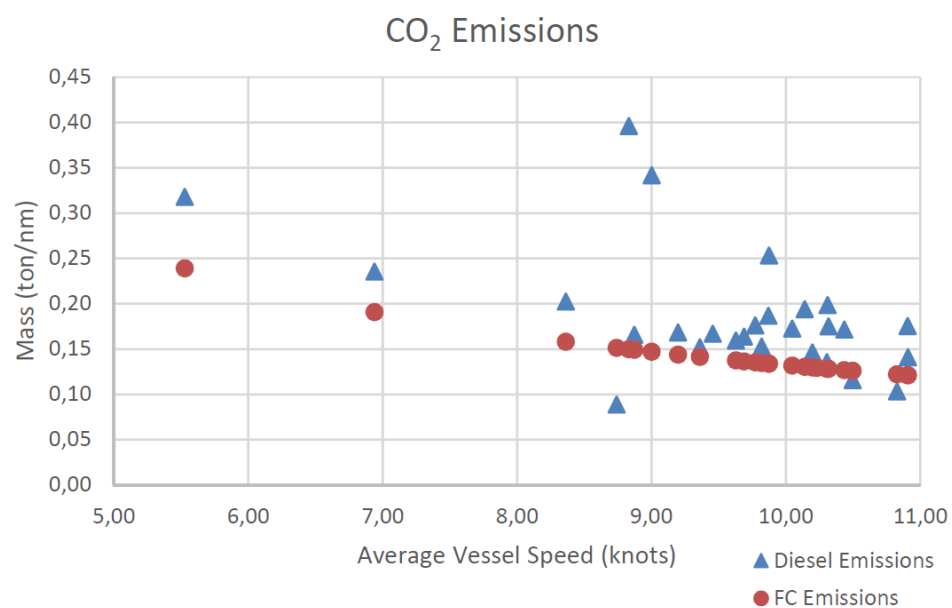


Figure 4.10 : CO₂ emission differences between diesel engine and fuel cell.

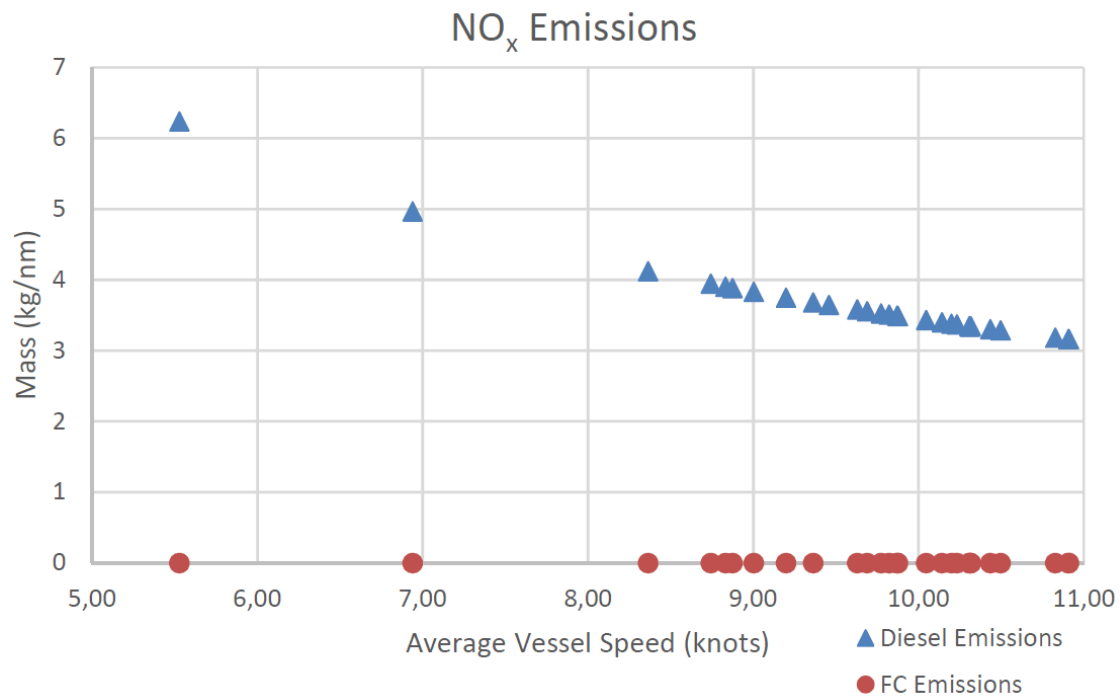


Figure 4.11 : NO_x emission differences between diesel engine and fuel cell.

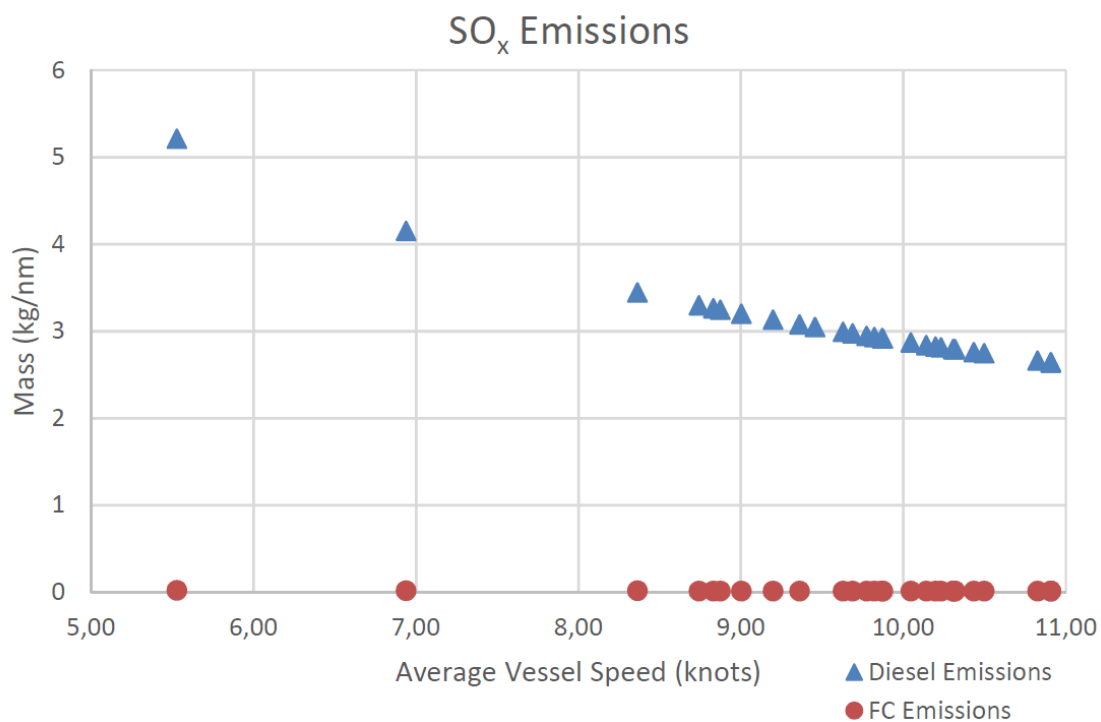


Figure 4.12 : SO_x emission differences between diesel engine and fuel cell.

All emission results are compared in average speed based. The mass of the CO₂ emission is calculated in unit of ton/nm. The general average speed of the ship is around 10 knots. Therefore, the data grouping is accumulated in this area as seen in

figure 4.10. CO₂ emissions are approximately 17% reduced in ten months, and numerically it corresponds to 850 tons.

The emissions of NO_x and SO_x are dramatically reduced in comparison with CO₂. In figure 4.11 difference between NO_x emissions can be noticed. The source of NO_x in conventional diesel engines is the air and the combustion temperature. The emission reduction is more than 99%. Same situation applies also for SO_x. The sulphur content of the fuel causes SO_x emissions in shipping. Due to LNG is a sulphur free fuel type so its emission is negligible against fuel oil based emission of diesel engine (Thomson et al, 2015). As seen in the figure 4.12, SO_x emission unit is kg/nm, but for fuel cell, it is just g/nm and the reduction is more than 99%.

The fuel consumption of the fuel cell is approximately given 615 m³/h in datasheet. The total time of sea passage is 3327 hours and total LNG consumption is calculated 2.10⁶ m³. LNG cost in Europe is 0,32 USD for m³ and the total cost becomes 655.262 dollars (Url-4). Total fuel oil and marine diesel oil consumption is collected from company. In ten months of the sea passage 1500 tons of fuel oil and 190 tons of diesel oil are consumed. Fuel oil cost and diesel oil costs in Europe are consecutively 473 and 680 USD (Url-5). To sum up, total fuel oil cost is calculated 705.238 USD and total marine diesel oil cost is 129.526 USD. The difference between the fuel costs is given in figure 4.13 and summarized in table 4.11. The figure 4.13 shows cost of fuel consumption to make a nautical mile in average speed based.

Table 4.11 : Fuel costs and consumed amounts.

Fuel	Cost (USD)	Consumed	Total (USD)
HFO (IFO 380)	473/ton	1500 tons	705.238
MDO	680/ton	190 tons	129.526
LNG	0,32/m ³	2x10 ⁶ m ³	655.262

For 10 months operation, the vessel's fuel cost reduces approximately 180.000 USD. As a result of calculation, 216.000 USD can be saved annually with LNG using molten carbonate fuel cell. It is approximately equal to 22% saving per year.

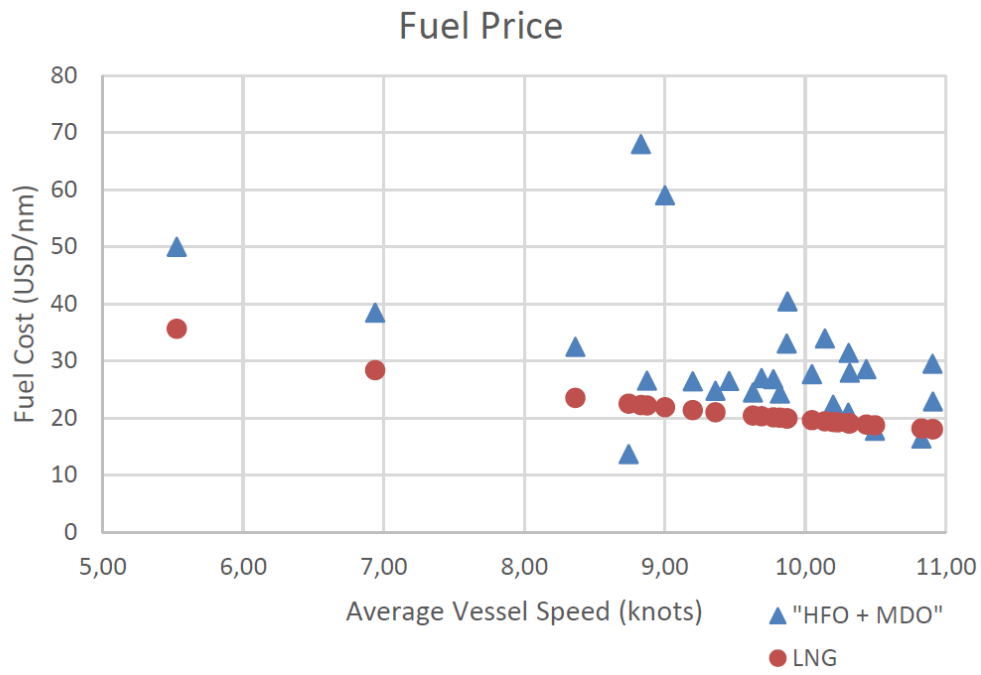


Figure 4.13 : Fuel price difference between diesel engine and fuel cell.

5. CONCLUSION

There is several methods for reducing the ship-sourced emissions in shipping industry; however, their high operational and installation costs and diminishing of fossil fuel reserve are forcing ship owners to invest in new environmental friendly power plant/unit sources. Due to tightened international regulations on GHG and air polluting emissions in shipping, main power source of vessels must be switched from diesel engines to zero emission power producing technologies. The hydrogen fuel cells are important alternatives with their water emissions but high cost of hydrogen production and difficulties on storage of hydrogen make their usage difficult in ship. Therefore, MCFC, a high temperature working fuel cell, is investigated in this thesis thanks by considering to its capability of using LNG as a fuel.

M/T YM Neptune, a chemical tanker, was dealt with case study using real routes, fuel consumption and emission data in 2018 that were received from the company. LNG fuelled MCFC, which has same power output with diesel engine, is studied for the ship main propulsion system. Approximately, more than 99% of SO_x and NO_x and 17% of CO_2 emission reduction is calculated. In addition, the decreased cost of fuel due to the switch from heavy fuel oil and diesel oil to LNG is found 270.000 USD annually. Totally, 1500 tons of fuel oil and 190 tons of diesel oil is saved in ten months via transformation. Furthermore, as a conclusion of system changing, lesser operational and periodic maintenance expenditure and labour force need add more financial gain and diminish the risk due to human factor in the system as well. However, the lifetime and carbon footprint of the fuel cells should be investigated and therefore the difference with diesel engines and costs for the renewing the electrolyte should be identified.

The new system is designed with respect to auxiliary system components like compressors or additional pumps. Hence, previous equipment such as fuel separators, lubricating oil tanks and related pumps and heat exchangers will be out of use. The transformation of the fuel tanks to LNG is another challenge for the new system, at least LNG use in shipping is a mature technology than hydrogen usage and there is enough experience to handle it. The heat transfer rate is calculated and with high

isolation performance, tanks do not need any cooling system equipment during the working process, because of the fuel consumption of FC is more than the vaporized fuel. The electrical motor and motor driving units are also chosen for the system to satisfy the most completed and coherent system design. Specifically, IP certificates and compatibility with marine conditions are taken into account to find the most efficient electrical units. The electrical components are very reliable systems for years, so, their failure and maintenance need is neglected.

As a disadvantage, the fuel cell systems weight can be demonstrable and it is clear that for the same power output MCFC power density is half of the diesel engine. This situation is related to the technological maturity of the system, for instance, PEM fuel cells are showing much more efficiency under power density perspective but the high purity hydrogen requirement as a fuel puts them in second place for the selection.

The regulations for the applicability of fuel cells are also considered in this thesis. Obviously, the lack of rules for the hydrogen usage and/or on board production ways for the system is directed this thesis case study to the LNG usable fuel cells. In addition, suitability for co-generation systems for the MCFC and opportunity of the thermal efficiency raising was another motivating reason.

For further studies, similar cases can be investigated under economical perspective with considering supply chain and bunkering operations of hydrogen or LNG. Moreover, noise and vibration effects and response for instantaneous load changes of the system can be investigated for the fuel cell powered ships. Lifecycle of fuel cells from the manufacturing until the end of power production should be identified. Besides, potential risk and risk assessment of the fuel cell ships can be another subject for further studies.

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