EXPERIMENTAL INVESTIGATION AND EVALUATION OF HYBRID AMMONIA FUEL OPTIONS FOR POWER GENERATORS

by

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ABSTRACT

This research thesis aims to make use of ammonia as a possible fuel source for power generators by performing an experimental study on a gasoline generator with an ammonia based gasoline fuel blend. Then, the combustion is modelled by using different types of fuel sources which are; hydrogen, gasoline, diesel, ethanol, methanol, propane, butane and natural gas to see the effects of ammonia on these fuels. In the experimental studies the exhaust temperatures, power output, CO_2 emissions, overall energy and exergy efficiencies of the generator are measured in between 369.9 C^o to 480.1 C^o, 3689.2 W to 3572.8 W and 2.535 g/s to 2.4916 g/s, 35.7 % to 28.74% and 44.85 % to 36.4 %, respectively with the increase of ammonia percentage in the fuel blend. The reduction in the performance measures are as expected but the reduction in CO_2 emissions will be worth using ammonia with a combustion promoter.

Keywords: Generators, ammonia, gasoline, hydrogen, fuel, Thermodynamic analysis, ammonia combustion.

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NOMENCLATURE

AF	Air/fuel ratio by weight
b_c	Gasoline fraction
C_p	Heat capacity (kg/m^3)
$\dot{E}x$	Exergy rate (kW)
$\dot{E}x_d$	Exergy destruction rate (kW)
ex	Specific exergy (kJ/kg)
$GtCO_2$ - eq	CO_2 equivalent ($n \times 10^9$ tonnes of CO_2)
h	enthalpy (kJ/kg)
h_c	heat transfer coefficient (kW/m^2K)
I	Current (amp)
LHV	Lower heating value (kJ/kg)
N	Number of moles
P	Power (kW)
P	Pressure (kPa)
$\dot{Q}$	Heat rate (kW)
s	Specific entropy (kJ/kg K)
T	Temperature (°C or K)
t	Time (s)
U	Thermal conductivity (kW/m K)
u	Energy density (kJ/L)
V	Voltage (V)
$\dot{W}$	Work rate (kW)
W	Work (kJ)
Z	Compressibility factor
Greek letters	
η	Energy efficiency
ψ	Exergy efficiency
Δ	Change
ρ	Density (kg/m^3)
Subscripts	
ch	Chemical
en	Energy

ex	Exergy
i	State
in	Input
max	Maximum
min	Minimum
mix	Mixture
out	Outlet
ovr	Overall
tot	Total
0	Ambient condition

Acronyms

B100	100% pure biodiesel
CI	Compression ignition
DAP	Diammonium phosphate
EES	Engineering equation solver
GHG	Greenhouse gas
HB	Haber-Bosch
ICE	Internal combustion engine
LHV	Lower Heating Value
MAP	Monoammonium phosphate
PM	Particulate matter
SMR	Steam methane reforming
SI	Spark ignition
SSA	Solid state ammonia
SSAS	Solid state ammonia synthesis

CHAPTER 1: INTRODUCTION

As a known fact fossil fuel sources are affecting the environment in a bad way and utilizing the use of different clean fuel sources have been highly encouraged for research purposes. Hydrogen and ammonia are amongst the most significant clean fuel sources with no carbon print and in the future with the improvements in technology, it seems that these fuels will be used even more [1,2].

Generators have been used to produce electricity by combusting fossil fuels for many years but these fuels used in the process caused deleterious emissions and a possible solution may lie within the usage of ammonia as the primary fuel source. An option is designing a new generator that operates concerning the fuel properties of ammonia but as there are generators already available on the market, using these generators and transforming them to be used with ammonia may be a more feasible solution. Unfortunately, as these generators are primarily manufactured for other types of fuels some challenges occur for the possible usage of ammonia in these generators. The thesis focuses on these challenges and offers possible solutions for them by investigating the issue both experimentally and theoretically by combining ammonia with various types of fuel sources.

1.1. Environmental issues concerning energy

The environment profoundly affected by the greenhouse emissions and the global warming concerns of the society may become a reality in a time even sooner than expected. The use of fossil fuels has been crucial for the development of human race regarding inventions, transportation and electricity generation. In situations where a power outage occurs the generators operate to keep a sufficient and safe environment, which can be labelled as the basis for a well functioning society. In these kinds of situations generators come into play to produce electricity by directly combusting a fossil fuel source. The harmful emissions caused by these fuel sources should always be taken into consideration [3]. The resources used in energy production in the world in 2017 are listed in Figure 1.1, where the fossil fuel sources such as oil, coal and gas takes up the vast majority amongst all sources with percentages of 33%, 29% and 24%, respectively. The remaining portion is mostly taken up by renewable energy sources such as hydro, wind, solar and nuclear that add up to 14% of the total resources used in energy production.

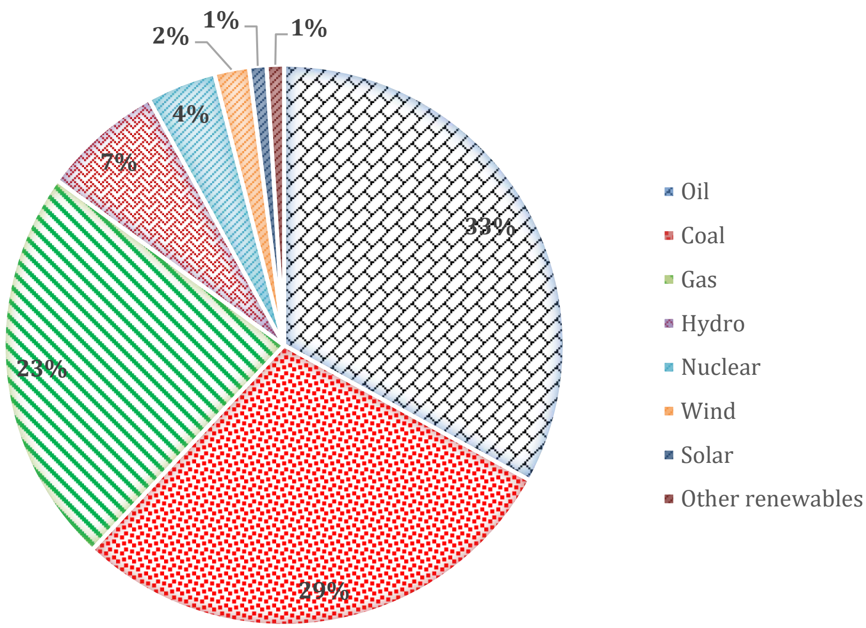

Figure 1.1: Percentage resource usage for energy production in the world at 2017 (Modified from [4])

Many countries plan to increase the percentage share usage of renewable energy amongst their total energy supply due to its clean and renewable nature, renewable energy sources have received great attention to replace fossil fuels in the future. Other than the renewable energy options fuel sources such as ammonia and hydrogen have the advantage of being both an energy storage medium and a clean energy carrier when produced from clean energy sources. Which means that using the combustion of these fuels will result in fewer pollutants and at the same time will allow storing the excess energy in hydrogen that will be more efficient in comparison with the usage of available fossil fuels. A large percentage of hydrogen and nitrogen can be readily found on earth in the form of air, so the composition of these elements will result in ammonia synthesis that is further discussed in the upcoming chapters of the thesis. Another aspect to foresight the energy production in the upcoming future, the possible depletion of the fossil fuels should always be taken into consideration as this may also occur earlier than expected (e.g. global warming). So possible ways to generate energy has been considered amongst the main issues and research fields for human beings at this stage.

1.2. Ammonia as a fuel source

Ammonia can be considered as an alternative fuel source that has no carbon print in its composition and as a result when it burns, it emits no CO_2 emissions that is one of the major issues with fuel sources nowadays as mentioned in the previous section of the chapter. However, even though there are reductions in deleterious emissions compared to the combustion of fossil fuels, the performance of ammonia should be taken into consideration before using it as an alternative fuel source. There are certainly some challenges that arise when ammonia is used. Mainly the slow flame speed and low flame temperatures of ammonia cause it not to ignite by itself and the combustion will not occur completely so using a different combustion promoter may be favoured when using ammonia in order to maintain the performance and reduce the emissions at the same time. Also the low autoignition temperature of the fuel makes its possible usage under combustion igniting engines hard as it the operating temperatures and pressures will be much higher for ammonia compared to conventional ones. However, its contribution to the environment makes this fuel source a possible contender to be a promising fuel alternative in the upcoming future regardless of its disadvantages. Also its ability to store hydrogen should also be taken in to consideration as the storage costs for hydrogen itself is 3 times the price for storing ammonia, so using it to store hydrogen will be safe and efficient way.

1.3. Motivation

Ammonia arises as being one of the most promising fuel sources for the future with its benefits to the environment known by its effect in reducing the greenhouse house emissions as mentioned previously in the chapter. As a result, there are many developments and research projects in the area funded by countries such as Japan and Australia. Japan has formed an alliance with the collection of companies and research institutions which have come together to form ‘Green ammonia consortium’ that intends to form a strategy for ammonia fuel as published in the global information portal ‘Ammonia energy’ [5]. So the funding and interest in the field makes ammonia an exciting topic for research purposes. There have been different types of researches going in about the possible usage of the fuel for different purposes but the main aim was using this fuel to generate electricity by emitting less pollutants. Regarding its usage in power generators further research was conveyed in this field and an extinction in diesel generators were observed in Canada. This observation made the possible conversion of these generators with ammonia fuel a gap in the literature. The negative impact that the combustion of fossil fuels used in these power generators cause to the environment and the possible depletion of the fossil fuels in the upcoming future has raised up the interest in the search for alternative clean fuel sources such as ammonia. As previously discussed in the chapter ammonia and hydrogen are labelled as some of the most popular and viable options. One of the ways of generating electricity with the usage of fuels can be accomplished with the use of power generators. The thesis study aims to make the usage of ammonia possible to produce electricity with the readily available generators that can be found in the market. The main problem with the use of ammonia as the primary fuel source for generators is the slow flame speed of ammonia/air mixtures, which makes it difficult to ignite and make the usage of another combustion promoter to be used in the ammonia generator a practical solution. The other challenges are further discussed in the upcoming parts of the thesis. Even though these challenges have caused ammonia to be overlooked as an alternative for storing the energy obtained from nuclear power or renewable sources it can still be a reasonable alternative for generators that will result in less greenhouse emissions.

1.4. Objectives

The main objective of the thesis is to investigate the possible ways to use ammonia in power generators to produce electricity with less emissions. The thesis takes on both experimental and theoretical approaches in order to achieve the desired results that will make the ammonia generator concept viable. The specific objectives aimed for this research thesis can be listed as follows;

- Investigating the possible usage of ammonia as a possible fuel source for electricity generation experimentally by using a commercially sold spark igniting gasoline generator. The experimental setup should be built and modified in a way that ammonia's usage in the generator will not cause any problems regarding its operation. The FIRMAN company should be contcted regarding the information necessary for the generator concerning the materials used for the wetted parts and its key properties.
- Decreasing the CO_2 emissions to minimum and observing the changes in exhaust emissions comparatively by trailing with various fuel sources. Experimenting the

usage of gasoline as a potential combustion promoter for ammonia combustion as the flame temperatures of ammonia will not be high enough to combust by itself completely. Stating the necessary changes that the transformation from a spark ignition or compression ignition generator will require to operate with ammonia.

- Making the necessary modifications for the engine part of the generatort to protect it against corrosion, which is investigated part by part in the upcoming chapters of the thesis. Also before doing the experiments setting the necessary safety measures regarding the procedures concerning the usage of ammonia and combustion of fuels against all kinds of potential fire situations before starting any types of experiments.
- Experimenting using different ratios of gasoline and ammonia fuel blend while measuring the changes in temperature, power output and exhaust emissions in order to understand the influence of ammonia for spark igniting gasoline generators. These results and findings will be used to calculate the thermodynamic properties and assess the performance of the generator.
- Modelling the combustion of ammonia thermodynamicaly with various fuel blends by using EES software to analyze the optimal fuel ratios and making comparative analysis regarding their emissions. The selected fuels for analysis are hydrogen, diesel, gasoline, ethanol, methanol, propane, butane and natural gas because of their possible usage in commercially sold generators.
- Lastly, validating the experimental results found by modelling the combustion of gasoline and ammonia blend, then finding the possible losses in the power output by finding the values at optimal combustion conditions. The percentage loss in the power in this sense can be used for other blends for thermodynamic calculations. Also calculating the performance measures for possibly generating electricity without emitting any carbon related emissions by blending ammonia with hydrogen and calculating the energy, exergy efficiencies and exhaust temperatures. Finding the ammonia’s possible contribution to the environment when blended with different fuel sources by calculating the exhaust emissions of each blend and at the same time comparing the experimental emission measurements with the emissions occurring from a possible gasoline blend.

CHAPTER 2: LITERATURE REVIEW

A literature review is conveyed in this chapter concerning the possible usage of ammonia as a fuel source in a gasoline generator by discussing the advantages and challenges from various aspects such as socio-economic, energetic and environmental with the addition of different methods used to produce clean ammonia. The main aim in using ammonia as a potential fuel source is to achieve better sustainability and produce electricity with minimum carbon emissions. In the first part of the thesis, the methods for clean ammonia production are comparatively assessed and discussed by regarding their technical, economic, and environmental performance criteria's in order to identify the potential ways to improve each method. The clean ammonia production methods considered here are namely, liquid electrolyte based systems, composite membrane based systems, solid state electrolyte, ceramic/inorganic proton conducting solid electrolyte based systems, polymer membrane based systems, O_2 conducting membrane materials and ammonia synthesis systems, ammonia synthesis via molten salt based electrochemical systems. In the second part of the present study, the ways to transform different types of commercially used generators are introduced, and their potential benefits are discussed by including the recent studies and improvements in the literature.

2.1. Ammonia synthesis

There are various types of production methods for clean ammonia synthesis which can either be listed regarding the source of production or the electrolyte type used in the synthesis can be used to filter the production methods. Figure 2.1 represents the main sources used in ammonia synthesis where natural gas takes up the majority of the sources where steam reforming method is used. Other than natural gas the conventional sources such as coal, fuel oil and naphtha takes up the rest of feedstock used in ammonia synthesis, which will be explained in a detailed fashion in the upcoming parts of the review.

Conventional fuel sources are always known with their usage for vehicular purposes but there are also many other uses of these fuel sources such as their usage in electricity generation and one of the simplest ways to do so this through generators [6]. The generators can be listed under spark ignition and compression ignition, which operate in a different way regarding their ways of combusting the fuel source in order to produce electricity.

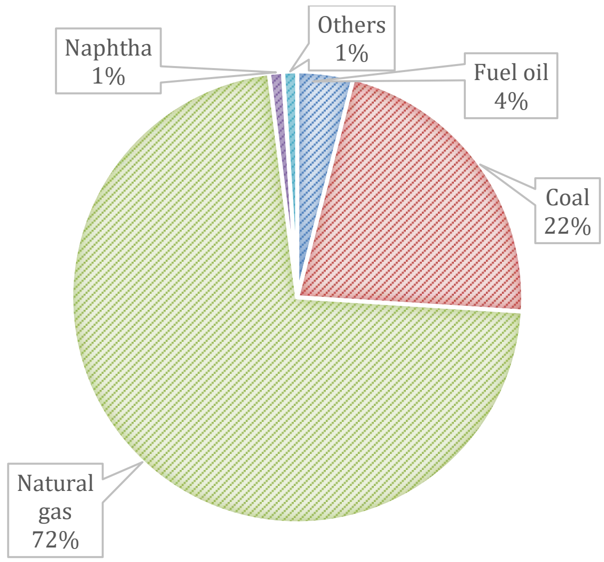

Figure 2.1: Sources of ammonia production (Modified from [7])

The generators are manufactured regarding the fuel that will be used in the generator where parameters such as the autoignition temperature, operating pressures, exhaust temperatures and the material. The most used fuel sources for generators are diesel and gasoline, there are also some examples for propane generator conversions. All of these cause CO_2 emissions but as mentioned previously these emissions are affecting the environment in a negative way. The idea of ammonia generators, in this case, makes a revolution regarding the hazardous emissions but rather than manufacturing a new generator transforming a gasoline or diesel generator will be a better and more feasible idea [8].

The possible usage of ammonia as a fuel source for a generator will require some changes and replacements. This transformation comes with the challenges that needed to be overcome in order to make the use of ammonia in an already manufactured generator possible. The main challenges are labelled as higher autoignition temperatures, higher pressures, corrosion, cooling systems and lastly the only possible toxic emission that occurs in ammonia combustion which is the NO_x emissions. This review covers the options regarding the use of clean ammonia as an alternative fuel for various power generating applications. Then discusses the possible solutions found for these challenges in the literature comparatively by digging down to clean ammonia synthesis methods and other conventional fuels sources used for generators [9].

Worldwide ammonia production by steam reforming of natural gas takes up to 72% of the total ammonia production based on the feedstock used [7]. The main sources used in ammonia synthesis are naphtha, heavy fuel oil, coal, natural gas coke oven gas and refinery gas. The most used conventional resource differs from country to country for example in China, coal is considered as the primary source for ammonia production and as a result, the greenhouse gas emissions and energy consumptions are higher than the rest of the world. But still as natural gas is the main conventional resource for ammonia synthesis the price of ammonia is directly related to the price of natural gas, as represent almost 70-90% of the production cost of ammonia for steam methane reforming method [10].

The most common methods used for ammonia production can be labelled under, Haber-Bosch process and solid state ammonia synthesis process as shown in Figure 2.2. Air separation process is used for delivering nitrogen to the system. Another method is cryogenic air separation, which is regarded as one of the most effective and economical method when it comes to delivering high amounts of oxygen and nitrogen. This method can also yield nitrogen with higher purities at relatively lower costs.

Compared to other air comparison methods used for ammonia synthesis the most industrialized and established method can easily be labelled as the cryogenic air separation process as ammonia is manufactured in bulks with lower costs and higher efficiencies [11]. Even though cryogenic process is labelled as the most industrialized one the Haber-Bosch process is still the most common method to produce ammonia. Hydrogen and nitrogen with the ratio of 3:1 is combined in an exothermic process in order to yield ammonia around a temperature and a pressure range of 450 to 600°C and 100 to 250 bar, respectively [12]. The following thermo-catalytic reaction is formed for the Haber–Bosch process:

$$\frac{3}{2}H_2 + \frac{1}{2}N_2 \rightarrow NH_3 + 45.2\ kJ/mol$$

Table 2.1: GHG emissions and the energy usage of ammonia production in the world

Region	**MJ/ ton NH_3**	**ton CO_2-eq/ ton NH_3**
Western Europe	41.6	2.34
North America	45.5	2.55
Russia and Central Europe	58.9	3.31
China and India	64.3	5.21
Rest of the World	43.7	2.45
World Average	52.8	3.45

Source**:** [13]

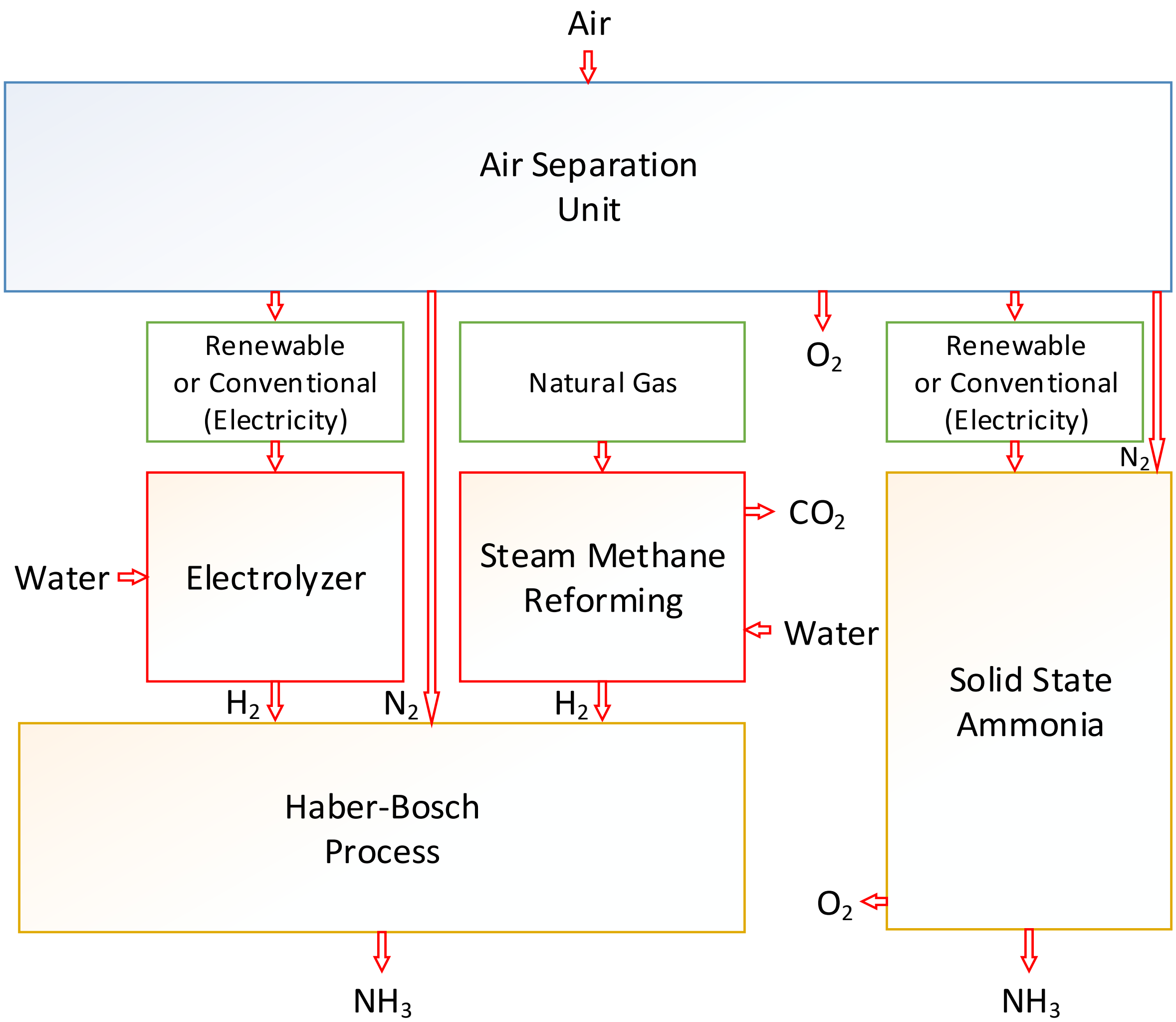

Figure 2.2: Main ammonia production routes with conventional or renewable sources (Modified from [14])

Table 2.1 represents the average energy use and environmental impact of various commercial ammonia plants in the world. As the consumption of different fossil fuel mixtures and ammonia in other regions of the world results in different varieties in emissions per tonne ammonia manufactured and the greenhouse gas emissions.

The interest in deploying ammonia is increasing day by day and it is projected that in the upcoming 10 years the ammonia market will grow approximately 3% and will be labelled as one of the conventional fuel sources [15]. The main usage of ammonia in various applications can be labelled underutilizing it as fertilizer, non-fertilizer, ammonia nitrate, urea, DAP/MAP and indirect applications.

Another method to produce ammonia is solid state ammonia synthesis (SSAS). A solid state electrochemical process is used to produce ammonia using nitrogen, water, and electricity. Compared to other methods SSAS works with higher efficiencies which means that it consumes less energy. The Haber-Bosch combined with an electrolyzer costs approximately 12,000 kWh/tonne-NH_3 where the required electricity for SSAS process is 7,000-8,000 kWh/tonne- NH_3 [16].

The usage of ammonia for different types of applications has been shown in Figure 2.3. Its main usage in the market is being a fertilizer and a refrigerant. Also ammonia is used as a fuel source in engines and fuel cells for research purposes.

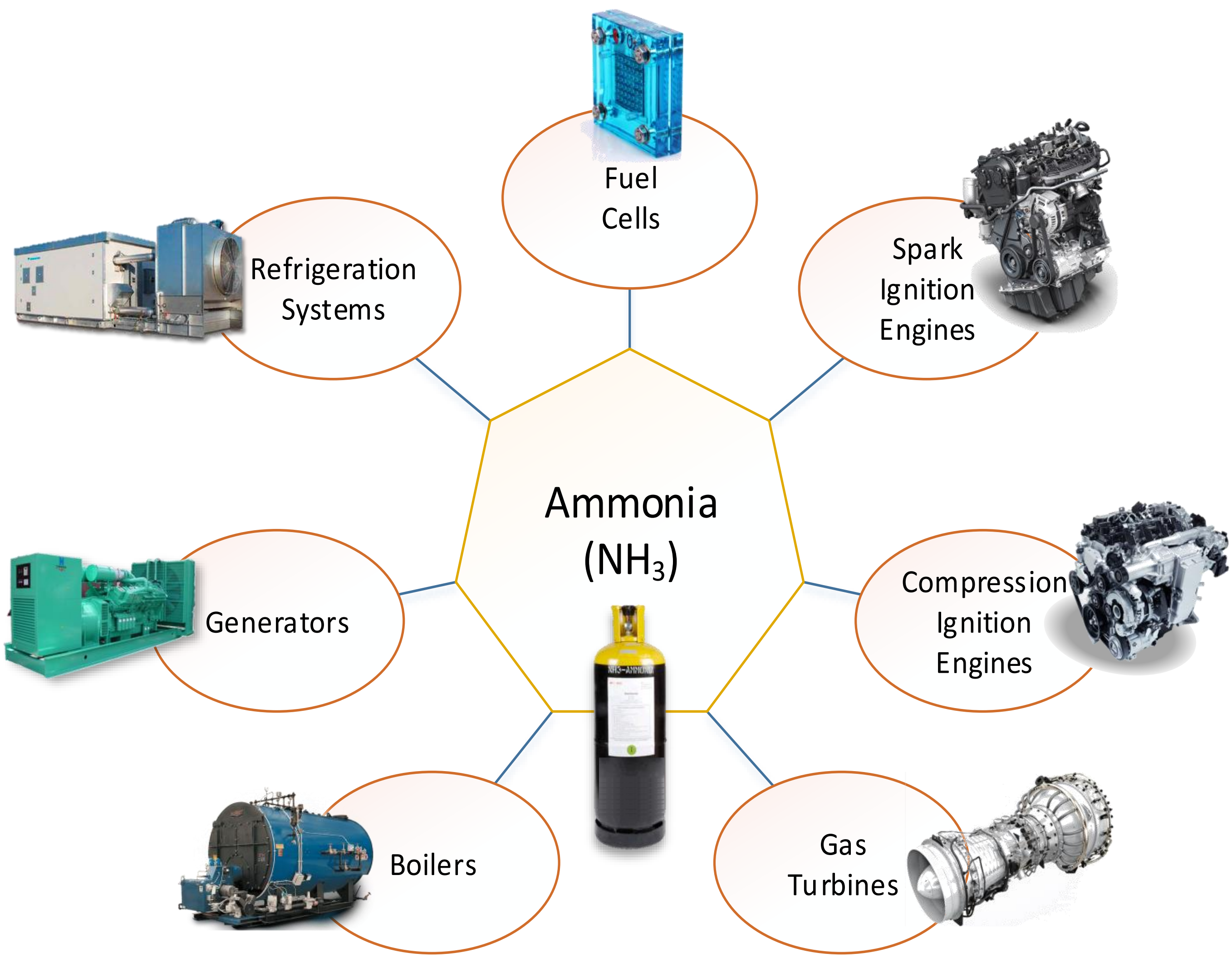

Figure 2.3: Uses of ammonia in various practical applications.

As mentioned previously there are different ways to produce ammonia and the most popular method is the Haber-Bosch process in the market. When it comes to the electrolytic ways which, require hydrogen that can be supplied from natural gas similar to the electrolysis of water or the decomposition of an organic liquid. In cases where water electrolysis is used in producing hydrogen using a renewable source such as solar energy and wind energy, the synthesis would be environmentally friendly, causing the pollutant emissions recede [17]. When used as a storage, ammonia can be utilized for concentrated solar energy as the occurring reaction is reversible and there are no side products. The reaction can be written as $NH_3 \leftrightarrow 1.5\ H_2 + 0.5\ N_2$ which can either provide heat or receive thermal energy from the sun when necessary under pressures up to 200 bar [18]. Figure 2.4 represents the usage of ammonia in various applications such as: non-fertilizers, other fertilizers, ammonia nitrate, urea, DAP/MAP and direct applications.

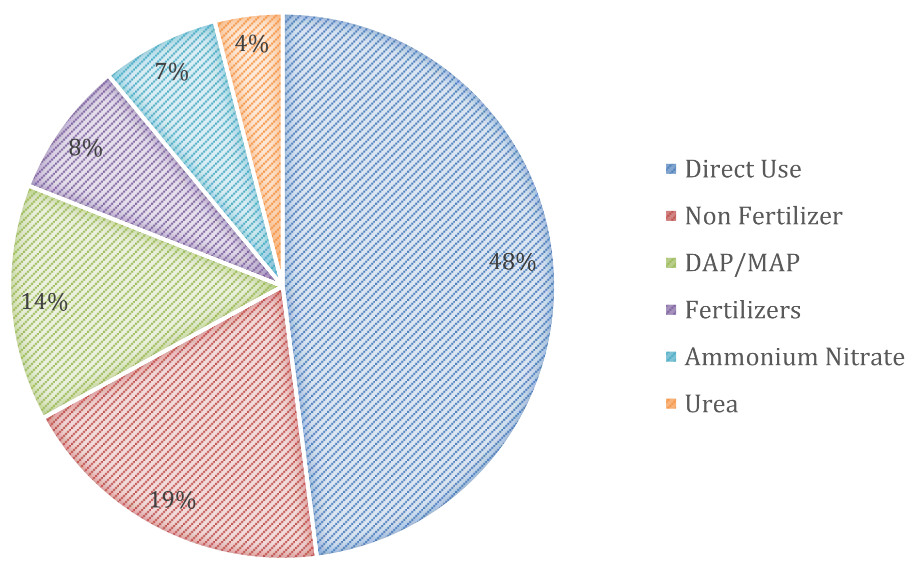

Figure 2.4: Applications of ammonia (Modified from [19,20])

Optionally ammonia is considered a contender for being one of the conventional fuel sources used in the industry for vehicles that is explained accordingly to the ways it can be used for different types of engines in Figure 2.5. With minor changes in possible corroding parts ammonia can easily be used in pipelines, especially the steel ones which are used to transfer natural gas and oil [21]. Transporting liquid ammonia will deliver up to 50 % more energy compared to the transportation of compressed natural gas. As a fuel source ammonia can be used in spark ignition engines, compression ignition engines, gas turbines and fuel cells with minor changes that will be discussed in the further chapters of the review. Due to the low reforming energy of hydrogen from ammonia, it is used in many applications in the industry as hydrogen storage [22].

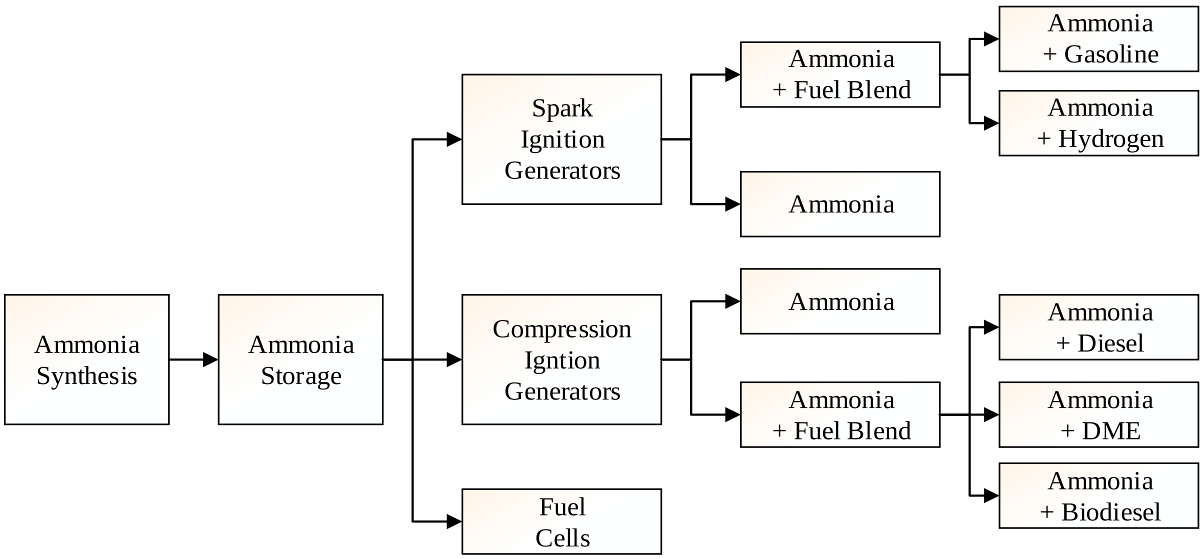

Figure 2.5: Ammonia's possible usage in generators applications (Modified from [23])

Also, electrochemical processes can be used to supply hydrogen for ammonia synthesis inside an electrolytic cell. Producing hydrogen from natural gas may require catalysts such as Sulphur compound or CO which may cause poisoning for the system it will be used so using water as the source will be an excellent way to eliminate this effect. These processes concerning water may be conveyed under ambient temperatures or at higher temperatures regarding the electrolyte material used. For the exothermic reaction where hydrogen and nitrogen is used to produce ammonia at high pressures and low temperatures will determine the production rates of ammonia [24].

Figure 2.6 represents the electrolytes used in the ammonia synthesis can be labelled under four categories which are;

- Solid electrolytes with a wide operating temperature range of 80 to 750˚C,
- Composite electrolytes with a temperature range of 400 to 650˚C,
- Molten salt electrolytes operating at temperatures around 300˚C,
- Liquid electrolytes that operate around the room temperature [25].

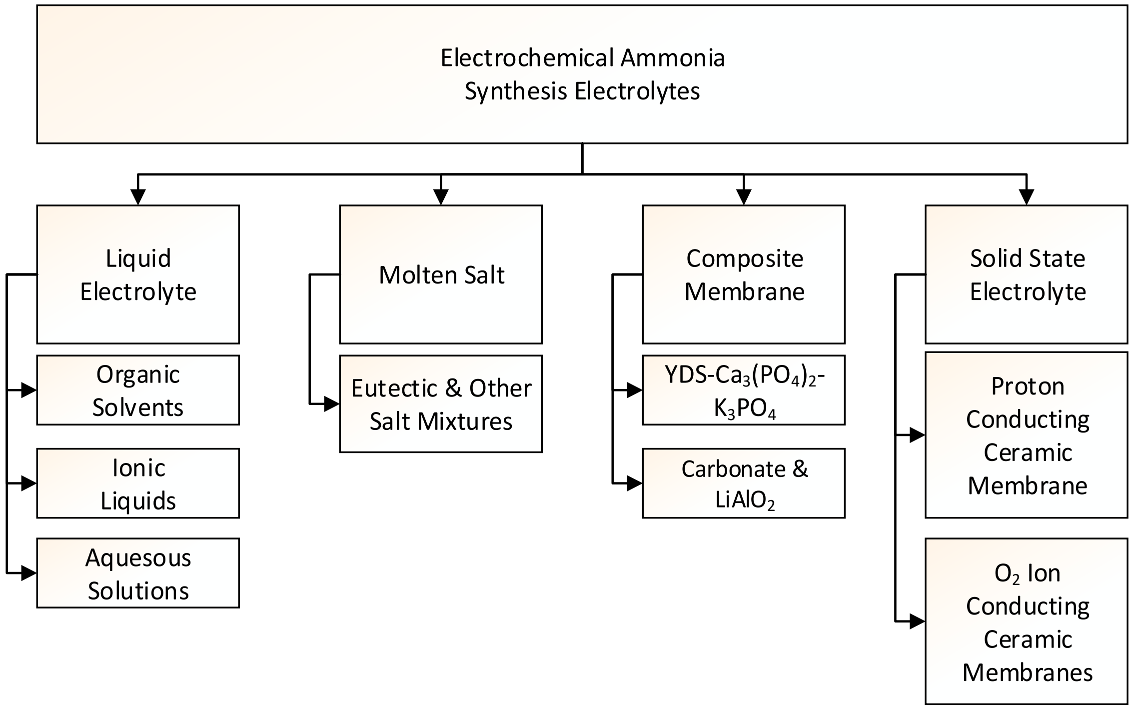

Figure 2.6: Electrolyte types used in ammonia synthesis (Modified from [16])

In cases where hydrogen is used as the reactant in ammonia synthesis the source must be considered starting from fossil fuels and a small portion from electrolysis with an efficiency rate around 75% [26]. Also for some fuel cells that require pure hydrogen gas, ammonia must be cracked at around temperatures above 500°C. Li [27] conveyed a method where H_2 and NH_3 are cogenerated through electrochemical ammonia production using an iron intermediate. Water, N_2 and hydroxide are used for electrolysis process for ammonia synthesis. An alternative ammonia production method was presented by Lan [28] where N_2 separation and H_2 production phases with a maximum ammonia production rate of 1.14×10^{-5} mole m^{-2} s^{-1} when a voltage of 1.6 V was applied.

Both researchers have forecasted that in the upcoming years other low cost ammonia synthesis catalysts will possibly be introduced. The studies regarding the methods for ammonia production in the literature is given in Table 2.2. Many studies have been made on the electrolyte materials and the catalysts used in the reactions. Garagounis [34] have conveyed experiments on at least 30 electrolyte materials with 15 different catalysts in a time period of 15 years. A different approach was introduced by Skodra [36] where nitrogen and steam are available together at the cathode with the addition of oxygen ion conductors. Also using molten salt electrolyte based systems can result in high conversion ratios which can also be utilized by polymer based membranes. System operating temperature, pressure, density and conductivity are the factors that will affect the ammonia production rate and are needed to be taken in to account when selecting the cell material. Giddey [16] have presented that the conductivity of a solid electrolyte is, directly and indirectly, related with temperature and cell thickness, respectively. The conversion ratios up to 70% of Li_3N into NH_3 for the system around temperatures of 350 to 400°C as reported by Serizawa [37]. The recent updates about the effects of temperature on electrochemical NH_3 synthesis routes show that the synthesis rates can reach up to 3.3×10^{-8} mole/s.cm^2 which was reported by Kyriakou [25]. Regarding developments in an electrochemical NH_3 production presented by Shipman [38] who have used water, hydrogen as proton donors and noted that operating with temperatures around 100 to 300°C will yield higher efficiencies when molten salt is used.

Table 2.2: The methods for ammonia synthesis in the literature.

Method	Results	Sources
Liquid Electrolyte Based Systems	Nitrogen was supplied to iron which is the cathode at a temperature and pressure of 50°C and 50 atm respectively with an efficiency of 58%.	[16], [29]
Ceramic Proton Conductor Based Systems	These systems use vacancies in the chemical structures with a conversion efficiency of 50% because of the decomposition of ammonia back to hydrogen and nitrogen.	[30], [31]
Molten Salt Electrolyte Based Systems	Water and air are used as reactants with an efficiency of 30%. Nanoscale Fe_2O_3 is used as a catalyst for the molten NaOH-KOH mixture.	[32], [33]
Polymer Membrane Based Systems	The highest rate of ammonia formation reported was 1.13 × 10-8 mole s^{-1} cm^{-2} at 80°C from a solid Nafion membrane with $SmFe_{0.7}Cu_{0.1}Ni_{0.2}O_3$.	[34], [35]

2.1.1. Liquid electrolyte based systems

For liquid electrolyte based system that is used in ammonia synthesis, hydrogen was supplied from ethanol and lithium perchlorate in tetrahydrofuran is utilized as the electrolyte [16]. The efficiencies are around 3-5% in the recent studies and were achieved regarding the current densities as low as 2 mA/cm^2. The efficiency theoretically may improve by optimizing the pressure and temperature values but with the conditions given by Bicer [14]. It was also noted that ionic liquid electrolyte was also present during the experiments which means that some problems may be occurring in the long term for the process. Another experiment was performed by Kim [39] on the electrochemical synthesis of ammonia in the molten electrolyte with $CoFe_2O_4$ and nano-Fe_2O_3 as the catalysts. The optimum conversion rate was achieved where water and nitrogen were used for the reaction at 3×10^{-10} mole/s cm^2.

2.1.2. Composite membrane based systems

Various ionic conducting phases gather up to build the composite electrolytes then second or third phases are added to the main phases to identify the properties of the produced ammonia such as thermal, mechanical and electrical. An alkali metal carbonate and an oxide under experimental conditions have been shown to have oxygen-ion, carbonate ion and even proton conductivity [16]. As reported by Kim [39] conveyed regarding the potential electrolytes for intermediate temperatures around 400 to 800°C fuel cells also these electrolytes are trailed with different operating conditions to find the relation between these conditions and the ammonia production rate.

2.1.3. Solid state electrolyte based systems

Regarding the researches done on electrochemical ammonia synthesis, the electrolytes are trailed by the selection of proton and mixed proton/oxygen-ion conducting solid systems as reported by Di [40]. For these systems, there are cathodes and anodes present with a compact solid electrolyte that separates them and permits ion transportation of either protons or oxide ions in between, while acting like a barrier to gas diffusion. Solid-state proton conductors are labelled with the ability to transfer and directly use hydrogen ions and are identified as a class of ionic solid electrolytes but still the inevitable high operating temperatures and the need for secondary phases make the method less favourable [41].

2.1.4. Ceramic/inorganic proton conducting solid electrolyte based systems

The proton conducting membrane coated from both sides by catalysts which depositing electrode that are fabricated with a typical electrolytic cell for ammonia synthesis. The methods used to produce these electrodes can be summarized as screen printed and brush coated electrodes, which are usually on ceramic proton conductor membranes that is then heat treated [30]. The ammonia production is utilized on the cathode side of the cell which is supplied by nitrogen, where water or hydrogen is supplied to the anode. In the setup metallic sheets are placed in contact with the electrodes to hold the collection together. The most critical components in these system are mainly the cathode, the catalyst and the ceramic membrane. The proton conductivity at above temperatures of 400°C reveals substantial proton conductivity. Skodra [42] reported that a proton-conducting solid electrolyte with Ru based catalyst at temperatures between 450 to 700°C resulted in conversion rates that are lower compared to nitrogen or steam supplied systems as a result of low conductivity properties of the operating electrode.

2.1.4.1. Polymer membrane based systems

In electrochemical ammonia synthesis cells the electrolyte is utilized by different types of polymer ion exchange membranes that can operate within a temperature range of 35 to 120°C. For the alkali industry the most popular and used proton conducting membrane is labelled as the Nafion membranes, which are also popular for electrolysis cells and the polymer electrolyte membrane based fuel cells [34]. The main advantages for these membranes are utilizing high proton conductivities at lower temperatures and being compatible with fuel cells. But there are also some disadvantages such as being unstable when in contact with ammonia [28]. As the operations are occurring in lower temperatures compared to other ammonia synthesis methods as a result the decomposition rate is relatively reduces and the problems related to temperature is being dealt with in this method. In the experimental studies conveyed by Kordali [43], using polymer membrane based systems with a gas diffusion layer on both electrodes and utilizing Nafion as the electrolyte at room temperature yields an ammonia production rate of 1.1×10^{-9} mole s^{-1} cm^{-2}, a columbic efficiency of 0.6% that expends water and air at the anode and cathode.

2.1.4.2. O_2 conducting membrane materials and ammonia synthesis systems

One of the most known usage purposes for O_2^- conducting ceramic electrolytes are in oxygen sensors and also in solid oxide fuel cells. There are also some examples where it has been utilized in high temperature steam electrolysis processes. The material used in the process profoundly affects O_2^- conductivity feature and as a result the production rates of ammonia declines. For some materials such as $BaSrO_3$ and $SrCeO_3$ develop electronic conductivity when in contact water but still there are some materials that can retain O_2^- conductivity at different pressures, temperatures and gas compositions [44].

2.1.5. Ammonia synthesis via molten salt based electrochemical system

For this method the electrolysis occurs when a reactor is used to supply the electric current that requires a cathode, anode, and ionic conducting membrane. The reactor works continuously with the membrane conducting an ion in the form of H^+ and combining it with chemical reactions where the reduction occurs on one side and the oxidation on the other. Once again the chemical reaction makes ammonia synthesis possible with an activation potential and two reactants that are conducted by varying different of types of cathodes, anodes, and membranes. The wide range for operations regarding the pressures and temperatures makes it possible to work under atmospheric conditions [45].

When molten salt NaOH-KOH is combined with water and nano-Fe_2O_3 is being used as the catalyst at atmospheric air the efficiency yields as 30% as reported by Licht [32]. Eventhough the efficiencies for proton conducting membranes are higher compared to this method the low material costs makes it viable to use this method with possible improvements in the upcoming future regarding the reactor. The salt mixture should contain a consistent concentration throughout the process with the inclusion of a catalyst inside the mixture such as nano-iron oxide. In the literature there are conceptual designs conducted on small cells in experimental environments with the usage of hydrogen, methane or water as the reactants. As reported by Murakami [46] the efficiencies of the current researches on the possible usage of hydrogen oxidation reaction have yielded around 72% and ammonia production rate of 3.3×10^{-9} mole cm^{-2} s^{-1}.

2.2. Conventional and alternative fuels

As mentioned previously fossil fuels are the primary fuel source for vehicular purposes. Eventhough these fuels are considered to affect the environment in a negative way there are some fuel sources such as biodiesel which are considered less harmful to the environment [47]. But still the new developments in carbon free fuels such as ammonia and hydrogen are only increasing each and every day. Regardless of the environmental effects petroleum also offers some advantages that makes it lead the fuels market since its implementation to various daily applications. The characteristics to look for in a fuel source can be listed as operate under a wide range of temperatures, being transportable, being storable, low manufacturing costs, wide supply sources, low CO_2 emissions and most importantly safe [48]. One of the most critical issues in selecting a viable fuel source for vehicular usage is the energy density of the fuel, which can determine the overall energy contained by a given mass, and the energy stored per volume of fuel. By using these the information gathered from the energy density of a fuel source the average range that a vehicle can go with the fuel can be calculated. Also the fuel sources with higher volume per energy density needs less space is to store the fuel in the vehicle that will be beneficial both in manufacturing and in the design of lightweight vehicles [49].

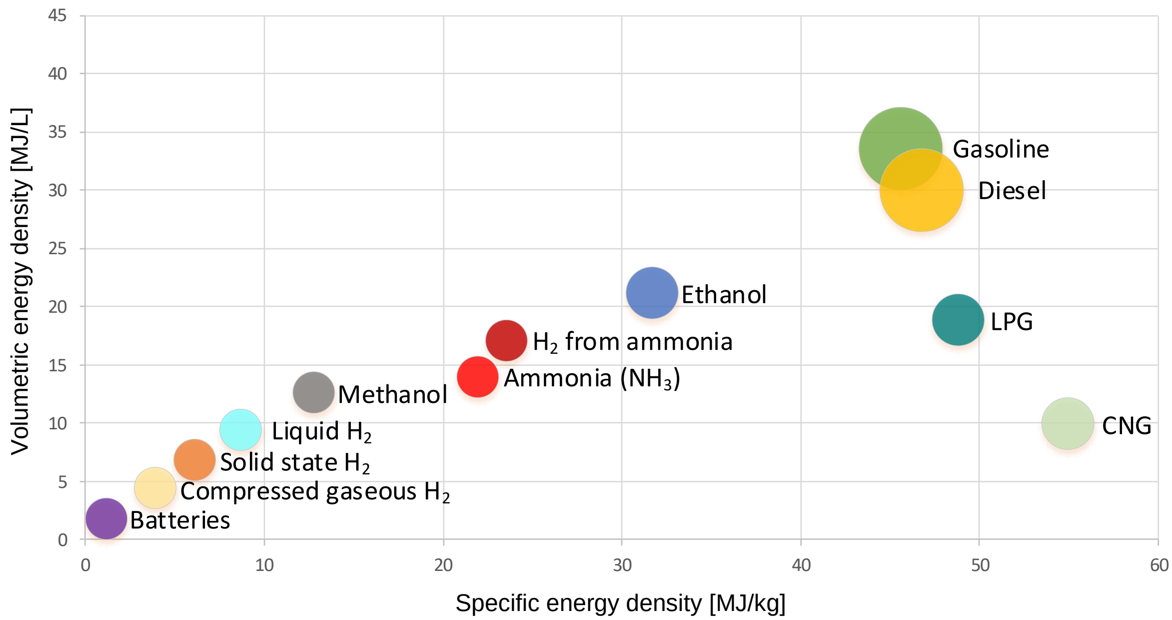

Figure 2.7: Energy densities of various fuel types (Data from [49–52])

Figure 2.7 gathers the energy densities of different fuel types such; gasoline, diesel and ethanol that seem viable for vehicle use. Other than the fossil fuels listed on the figure there are also ammonia and hydrogen which are carbon free fuel sources which unfortunately has less energy density values and ranges compared to the conventional fossil fuels. But still the adverse environmental impacts of these fossil fuels make the carbon free fuel sources as possible candidates to replace them [53]. In the rest this section various fuels will be comparatively discussed in a detailed way by highlighting the advantages and disadvantages of each fuel source. Eventhough the graph can give an approximation regarding the power output that can be exctracted from each fuel source, the energy density itself will not be enough to calculate these values. In the upcoming chapters of the thesis the energy densities of the fuel blends will be combined with the energy efficiencies of eacuh blend to find the shaftwork with respect to energy density to give a better understanding of ammonia's possible contribution to the power generators.

Gasoline have been labelled as the most used and known fuel source for many different applications (mainly for vehicular usage). Using gasoline as a fuel source presents some advantages such as eliminating the emission possibilities of lead particles that may occur in leaded fuel sources, being compatible with most of the engine block materials, reducing the hazardous emissions by being compatible with the use of most of the catalytic converters and operating at lower auto ignition temperatures compared to other types of fuel sources. The octane rating is an important factor when selecting the appropriate fuel source necessary for the needed operation, the correct octane rating selection for an operation increases the lifetime of an engine by decreasing the occurrence of wear and tear and at the same time it can be a facilitator for higher engine efficiencies [54].

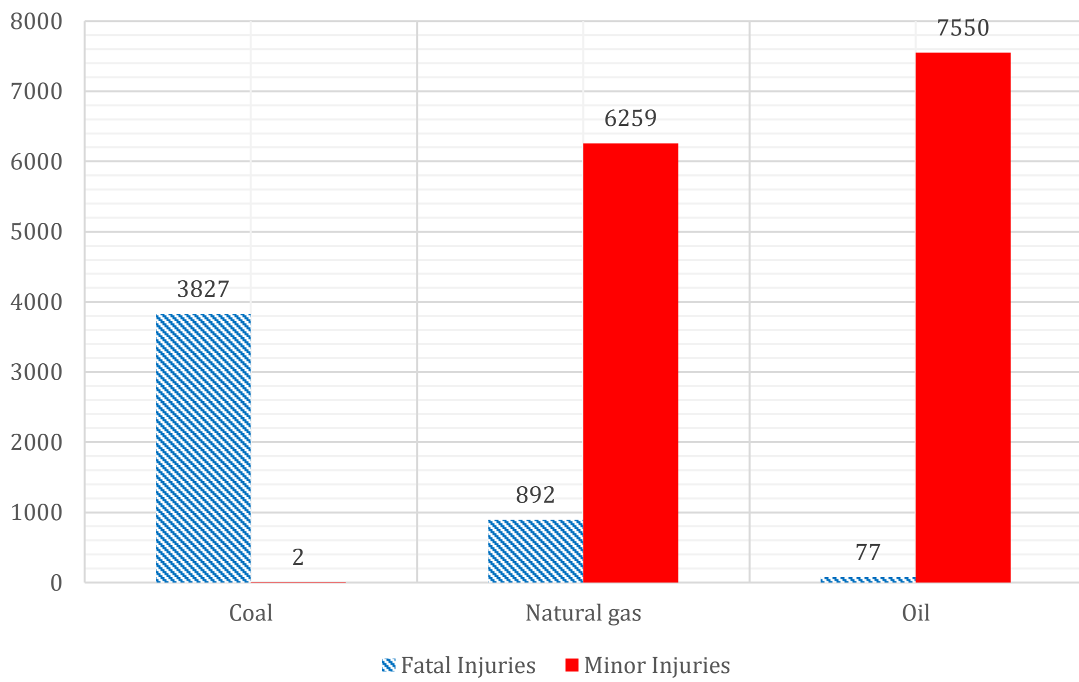

Figure 2.8: Fossil fuel related accidents in US between 1968 to 2011 (Modified from [54])

Since its first usage there have been critical factors such as consumer, technical, and regulatory factors that have affected the development of gasoline the automotive market. The improvements in engine technologies allowed improvements regarding the transportation efficiency. Figure 2.8 shows the occurrence of fossil fuel related accidents between years 1968 to 2011 in US. It is evident that the accidents related to oil takes up the vast majority of the occurring accidents. Also during the implementation period of gasoline to the commercial market the rate of incidents were much higher than it is now [55]. From an historical point of view up until the 1970's, enchantments to fuel refining technologies and octane rating have been made for gasoline fuel. In mid-1970's lead removal began for gasoline, which made it less harmful against the environment and people than it is before but unfortunately the CO_2 emissions were still in effect that is accepted as the primary negative impact caused by gasoline combustion [56]. Regarding the changes performance improvements after the removal of lead from gasoline the octane number has remained the same where the engine efficiency have improved with the addition of digital controls and design enchantments. After that the regulations set regarding the CO_2 emissions, new challenges have raised concerning the need in some improvements in engine technology and vehicle efficiencies that got reconsidered and redesigned to keep the performance levels and decrease the deleterious emission rates. As mentioned before gasoline is still the most used and popular fuel type for spark ignition engines, even though the CO_2 emissions will always be a problem gasoline will be in the automotive market until the depletion of fossil fuels [57].

Diesel fuel is the most popular and used fuel for compression ignition engines where the combustion of the fuel occurs without any spark. Regarding its properties that yield in more efficient use of fuel and higher thermodynamic efficiencies it is often selected for compression combustion situations [58].

Afterwards in the upcoming years the amount of sulphur that was present in the diesel fuel was thinned which brought advantages such as decreasing the sulphur oxide emissions and as a result increasing the engine life with the utilization of emission control technologies.

Nowadays the compression combustion engines are operating at high pressure values up to 29,000 psi and operate with low Sulphur diesel fuel that emit low NO_x emissions when a catalytic converter is installed [59]. The main disadvantage of diesel combustion is the CO_2 emissions that effect the environment and health of human beings in a negative way. The pollutant emissions standards require the usage diesel particulate filters all around the world to decrease the amount of particulate matter emissions to help protect the quality of air and as a result the human health.

Table 2.3: Comparison of similar gasoline and diesel vehicles

Criteria	Gasoline vehicles	Diesel vehicles	Difference
Vehicle weight (kg)	1452	1500	48kg
Fuel economy (km/L)	11.5	16.2	+41%
CO_2^-emissions (g/km)	205	201	-3%
PM emissions (g/km)	--	0.022	0.022

Source**:** [60]

When the average weight is compared for gasoline and diesel vehicles regarding the components used for the engine and the exhaust system it seems that the diesel engine weight more but with the improvements in fuel consumption with the diesel technology the fuel economy benefits are higher up to 40%. The climate benefits of diesel vehicles are also better for diesel vehicles which are only 3% on a CO_2^- equivalent basis. So not only it is more economical in terms of the fuel but it also emits CO_2 near the same amount that will not improve the air quality, health and will not be reaching the climate goals that are set these engines [60].

Low sulphur diesel is required for diesel particulate filters to function appropriately with the utilization of emissions control systems which is introduced in Europe and U.S. since 2007 to eliminate the negative health impacts of diesel vehicles [61]. Table 2.3 presents the differences for criteria such as the curb weight (kg), fuel economy (km/L), CO_2 emissions (g/km) and particulate matter emissions (g/km).

Propane can only be used in modified engines or generators that can operate with stored ammonia that is in compressed liquid form. When compared to other fossil fuels propane emits less harmful pollutants and can help better the life-cycle of GHG emissions up to 20%. Low sulphur percentage in propane emits minimal amounts of sulphur oxides. The main disadvantage that propane proposes is the low energy density value compared to gasoline and diesel fuel which increases the amount of fuel necessary to travel a certain distance compared to these fuels which makes it less cost effective [62].

Regarding its usage in generators there are conversion kits available on the market that makes it usable in gasoline generators with minor changes. Propane can operate with the spark igniting engines installed for the gasoline generators with the changes in the injection system and the fuel delivery system of the generator as proposed by Ledjeff-Hey [63]. Biofuels aim to reduce the carbon CO_2 emissions during the combustion of the fuel but it should be taken into consideration that when biofuels are generated from a feedstock the reaction causes CO_2 emissions so eventhough it is not direct there are still some deleterious emissions occurring from biofuels. The feedstock's are mainly plants or organic waste but if the demand increases the production of biofuels may require large amounts of plow land and as a result the diversion process from crops used for food production to biofuel may affect food prices in a negative way if it becomes more popular. This is one of the reasons that it is not getting that much attention from the society and the researchers at this time.

But in the upcoming years if new methods can be utilized for the production of biofuels without any CO_2 emissions it will have a positive impact on the environment as it leaves no carbon print when it combusts [64].

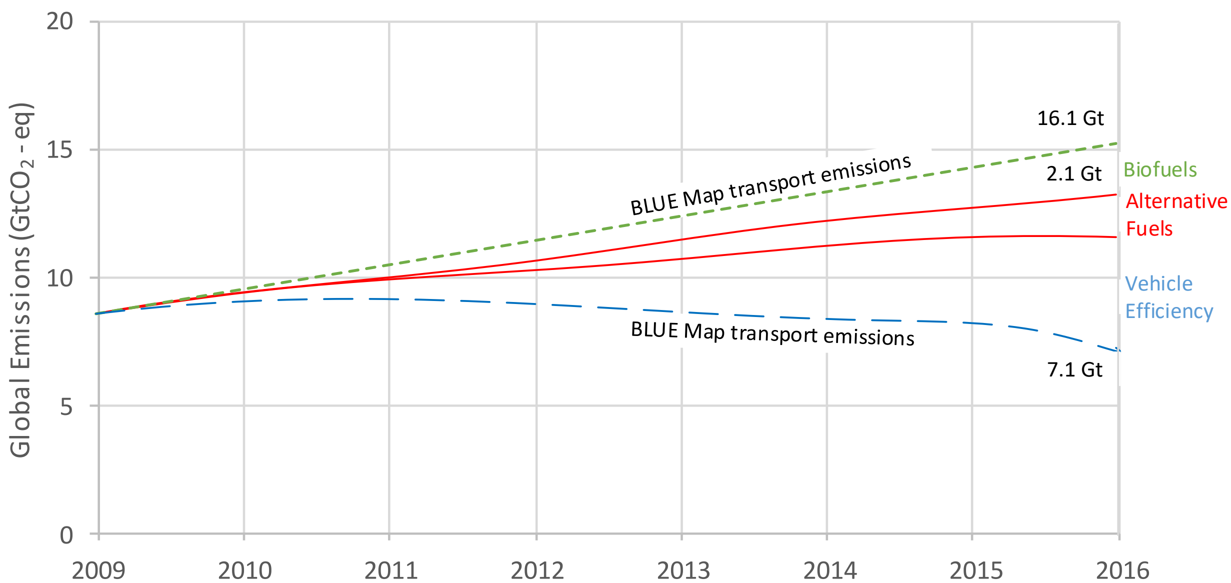

Figure 2.9: Emissions of biodiesel and alternative fuels between 2009 to 2016 in US (Modified from [64])

Figure 2.9 shows the percent changes in emissions in between biodiesel and alternative fuel sources. Biodiesel has up to 20% less emissions in terms of Carbon dioxide equivalent (CDE) resulting improvements in vehicle efficiency which takes up to 30% of emission reduction in the vehicle industry that makes biofuels the second-largest contributor for emissions saving [65]. The use of biofuels are usually in the form of blends with gasoline or diesel up around 5 to 10% but with necessary engine modifications there are some designs where the concentration can go up to 85% such as the work done by Lee [66] the reason behind this is that the energy densities of biofuels are seemingly lower than gasoline or diesel which result in higher autoigniton temperatures and pressures. The most commonly used and known biofuels can be labelled as biodiesel and ethanol.

The main biodiesel production method used is transesterification where the main ingredient is used, waste oil such as waste cooking oil, vegetable oil or animal fat where methanol and sodium hydroxide used to be mixed up with the oil type resulting in a biodegradable non-toxic fuel source. Even though the method seems like a waste reproduction method it is still considered to an expensive one that highly depends on the feedstocks price which may nearly double the cost of conventional diesel [67]. One of the most significant advantages that the biodiesel offers in comparison with the conventional diesel fuel is emitting less pollutants. When used in compression ignition diesel engine as the work done by Basha [68], the pollutants compared to conventional diesel combustion is highly reduced. But once again as shown in Figure 2.9 it may cause an increase in NO_x emissions compared to conventional diesel fuel emissions.

Figure 2.10 represents the production rates of biodiesel mainly in European countries such as Germany, France and Italy between years 2000 to 2005 that are the years when biodiesel entered the commercial market. The production rate of US is also included in the graph which was zero to none in 2000 but started to become more popular starting with 2002 [69]. The primary production occurs in Germany and the total production has almost doubled since 2010 from 0.63 million litres to 2.48 million litres. After that the production rates of biodiesel got up to 8 million litres in 2010 and fluctuated around that rate through the years since then [70]. At the same time the carbon emissions are much lower compared to other fossil fuel sources that are commercially used. But its impact on engine durability is a concern that should be taken in to consideration before using this fuel source. In much the same way cooking oil can solidify when too cold, biodiesel can solidify too, making it nearly impossible to start a vehicle [71].

The 100% pure biodiesel fuel is referred as B100 which is the purest and least polluting for of biodiesel which unfortunately has a significant advantage of crystallizing at cold temperatures because of the higher gelling temperatures than conventional diesel fuel. Regarding its possible usage for ammonia generators B100 auto ignites under compression around temperatures of 400°C that is less than the values for ammonia. So it can be used as the second fuel source for the generator that will operate with ammonia to decrease the combustion temperatures.

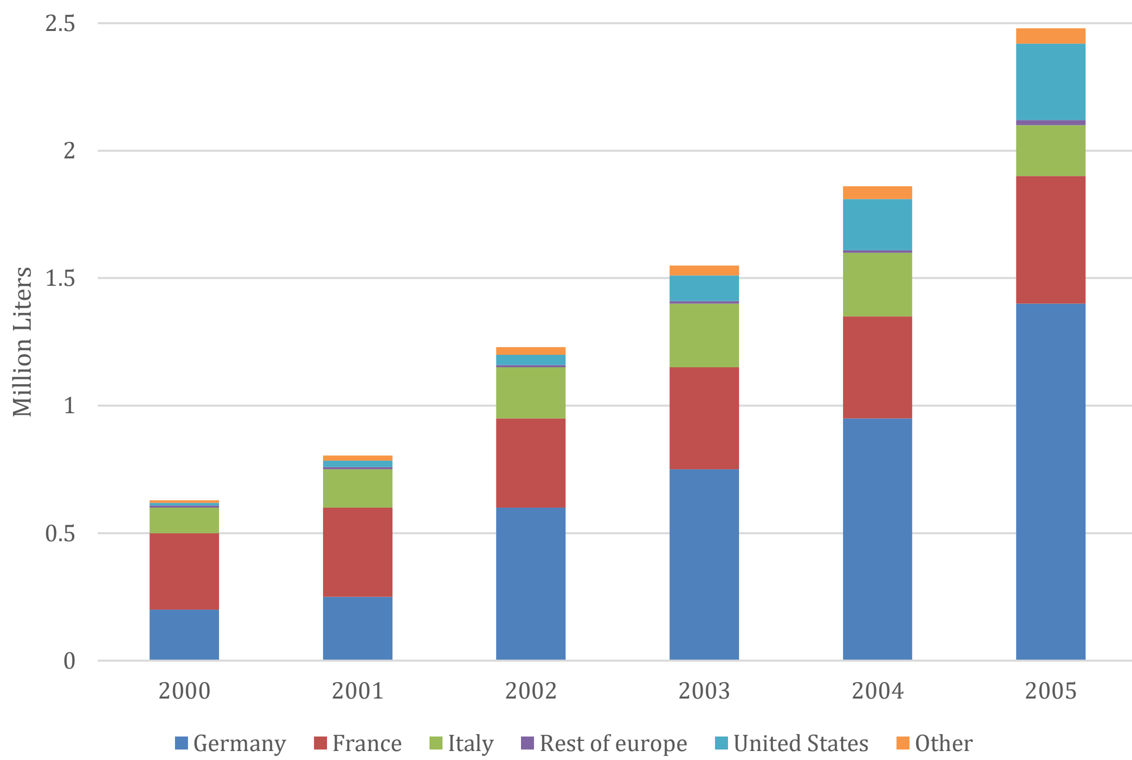

Figure 2.10: Biodiesel production from 2000 to 2005 in Europe (Modified from [69])

Ethanol is another type of biofuel which is produced by either corn, grains or the waste from sugar can serve as feedstocks. In US corn is used for production but in Brazil the primary feedstock used in the process is sugar cane waste that nearly costs half the price necessary for the production from corn or grains [72]. As a fuel source ethanol is used in engines with different petroleum fuel blends.

Ethanol works well with spark ignition engines and after its combustion it emits less pollutants such as hydrocarbons and CO_2 compared to conventional gasoline fuel emissions as reported by Costa [73] but as being a biofuel it bears the potential to increase food prices if it becomes more and more popular in the upcoming future. At ambient conditions it can be stored in liquid form and can quickly form blends with gasoline in order to take advantage of the higher energy density level of gasoline which is about 30 percent more compared to ethanol's energy. The mole percentage of ammonia in these blends range from 10 to 25 percent but there are also some experimental vehicles that can run with blends up to 85% of ammonia such as the work done by Fang [74] where ammonia is used up to 20 percent in the blends which does not require any changes to the conventional gasoline engine. For blends higher than these percentages may require some changes such as adjusting the spark ignition timing and some changes in the fuel delivery system.

2.3. Power generator types

In the literature the generators have been classified with respect to the type of ignition occurring in the engine. Mainly the two type mostly used in these generators are compression ignition and spark ignition generators, where different mechanisms are used in order to ignite to fuel and combust it. Each of these types have some advantages and disadvantages when compared with each other which will be explained further in the upcoming sections of the chapter by referencing the previous work done by other researchers in the field of energy and internal combustion engines.

2.3.1. Compression ignition power generators

A compression ignition engine operates by increasing the pressure of the fuel with the reduction to its volume inside the cylinder block, than the increased pressure results in increases to the temperature up until the auto ignition point for the fuel source and lastly the combustion occurs which turns the crankshaft and activates the electromagnets which result in electricity production [75]. Table 2.4 presents some crucial properties for ammonia in both liquid and gaseous form that affects its combustion. Density values are given for ammonia in both states where the compressibility factor, heat capacity and thermal conductivity values are presented for ammonia in gas form. Pressure tanks usually store ammonia in liquid form at a pressure of at least 10 bars, at room temperature and the liquid gas equivalent ratio with respect to their volume is found as 1:947. Lastly the most important property that is used in the thermodynamic equations for any combusting fuel which is the latent heat of vaporization also given for ammonia. As presented by Rieter and Kong [76] whom have trailed with ammonia in a compression ignition engine with direct injection using 1 to 5 and 2 to 3 ratios of ammonia and dimethyl ether blend that reduces the combustion temperature but results in higher CO and HC emissions.

Table 2.4: Chemical Properties of Gaseous and Liquid Ammonia

Property	SI Units
Ammonia, Gas	
Density	0.73 kg/m^3 (1 bar, 15 ˚C)
Compressibility factor	0.9929 (1 bar, 15 ˚C)
Heat capacity (C_p)	0.037 kJ/(mole K) (1 bar, 15 ˚C)
Thermal conductivity	22.19 mW/(mK) (1 bar, 0 ˚C)
Ammonia, Liquid	
Density	682 kg/m^3 (10 bar, -33.5 ˚C)
Liquid/gas equivalent	1:947 (10 bar, 15 ˚C)
Latent heat of vaporization	1371.2 kJ/kg (10 bar, -33.5 ˚C)

Source**:** [21]

2.3.2. Spark ignition power generators

A spark ignition engine combusts fuel with the help of a spark plug and as a results generates electricity in generators. The spark plug inserted inside the engine helps ignite the fuel and as a result combusts it, the most popular fuel source used in these types of engines are gasoline fuels as mentioned previously in the paper. There are not many experimental setups in the literature mainly for generators but there are some examples where, ammonia is right away trailed in its possible usage in spark igniting engines rather than generators such as the work done by Ryu [77].

Table 2.5: Properties of ammonia and gasoline

Property	Ammonia	Gasoline
Lower heating value	18.6 MJ/kg	42.45 MJ/kg
Octane rating	>130 RON	92.4 (R+M)/2
Specific gravity of fuel (Liquid form)	0.64 g/cm^3	0.73 g/cm^3
Stoichiometric air/fuel mass ratio for single fuel	6.1	14.5
Flammable equivalence ratio range	0.72-1.46	0.55-4.24
Flame speed at stoichiometric	12 cm/s	62 cm/s

Source**:** [78]

Another example is Grannell [79] who has successfully built an ammonia fuelled vehicle that operates with a blend of gasoline and ammonia, where the vehicle uses a blend of approximately 70% ammonia and 30% gasoline on a lower heating value energy basis in order to lower the high auto-ignition values of ammonia. Table 2.5 presents the combustion properties of ammonia and gasoline which are both gathered and experimentally calculated by Grannell [78]. In the study dual fuelled operation is used where gasoline behaves as a combustion promoter for ammonia. The equation given below indicates the stoichiometric combustion of ammonia and gasoline where b_c is the gasoline fraction. When b_c is set to 1 the equation simply becomes the combustion of gasoline and when set to 0 it gives out the combustion equation for ammonia, where LHV energy yield per mole of air:

$$(88.7 - 4.0\times b_c)\ \text{kJ}.(0.790\ N_2 + 0.210\ O_2) + 0.024\times b_c\ C_6H_{11} + 0.280\times(1-b_c)\ NH_3 \Rightarrow$$
$$(0.930 - 0.140\times b_c)\ N_2 + (0.420 - 0.288\times b_c)\ H_2O + 0.144\times b_c\ CO_2$$

When compared with the stoichiometric vaporized gasoline/air mixture the energy yield per mole of both the intake mixture and exhaust products for the stoichiometric gaseous ammonia/air mixture is about 17% less efficient. On chemical equivalence basis and LHV energy basis are nearly the same for the gasoline fraction as noted by Grannell [79].

2.4. Challenges for ammonia power generators

Table 2.6 summarizes all the possible problems for ammonia generator conversion and offers a road map for the possible solutions offered for these challenges in the literature. Ammonia is currently used as a fuel source for gas turbines to generate electricity without any carbon emissions. There are many various ways to produce clean ammonia that are also sold on the market as mentioned in the previous sections of the paper. But when it comes to generator systems that operate with ammonia fuel, there are not that many options available on the market excluding the experimental setups built for research purposes. The reason behind this probably lies on the high temperature and pressure values that the ammonia fuel requires for combustion purposes. The generator setups where ammonia is experimented as a fuel source usually another agent, substance or fuel source is used to lower the combustion temperatures as reported by Ryu [77].

Table 2.6: Challenges and possible solutions map for ammonia generator transformation

Problem	Description	Possible Solutions
High pressures & temperatures	The auto ignition temperature for ammonia is 651^{o}C where this value is 256^{o}C for diesel fuel. As the generator system was designed for diesel fuel the material used for the engine, cylinder block, should withstand these very high temperature and pressure values.	• Adding another agent, substance or fuel source to lower the combustion temperatures and pressures. • Changing the combustion ratios by replacing the cylinder heads and steel cylinders. • Changing the whole system to work under very high temperature and pressure values.
Corrosion	Using ammonia as a fuel source will result in water propagation, which might corrode the parts (inside the engine block, fuel delivery systems) that get in touch with the fuel source.	The corroding parts used in a diesel generator should be replaced with non-corroding (ex: stainless steel) ones.
Cooling system	The cooling system for the diesel engine is designed to operate around temperatures much lower compared to ammonia fuel's combustion.	After the problem for high pressures and temperatures are dealt with the cooling system should be modified.
NO_x emissions	The only adverse effect for ammonia combustion for the environment is NO_x emissions, which should be taken in to consideration for the conversion.	Using a slightly fuel rich mixture and a catalytic converter where one mole of NH_3 is added for each mole of NO_x in the exhaust.

Source**:** [76,77,80]

2.4.1. High temperatures and pressures

Ammonia only auto ignites under combustion at very high pressures and temperatures around 651^{o}C compared to diesel fuel which auto ignites at 256^{o}C under combustion, so if aluminium is used for the steel cylinders this might cause a problem as these are not designed to operate at those temperatures. There are couple of solutions trailed in the literature for this problem such as changing the aluminium alloy cylinder to a stainless steel one, changing the compression ratios or adding another agent, substance or fuel source into ammonia fuel to decrease the auto ignition temperatures under combustion. In the project done at Iowa State University a small amount (~5% energy basis) of high cetane fuel is injected with the ammonia to promote combustion.

As a result Reiter and Kong [76] reported that the engine operated with 5% biodiesel and 95% ammonia, at 110% of rated load compared to diesel fuel. The critical solutions to overcome any issues related to high temperatures and pressures are discussed in this research.

2.4.1.1. Ammonia fuelled generator with the addition of hydrogen

Just like ammonia, when hydrogen is used, as a fuel source there are no carbon emissions as it was reported in the work done by Mørch [80]. The auto ignition temperature of hydrogen under combustion is around 500^0C, where the ammonia's auto ignition temperature is around 651^0C as mentioned previously in the report. This can be used to lower the combustion temperature for the generator that will be beneficial in many ways such as shortening the combustion times and avoiding to change the combustion ratios, which is a significant process. Hydrogen fuel improves burning performance with moderate burning velocity and will have an accelerated effect on the systems combustion time as it will be lowering the combustion times, which will increase energy generation. Eventhough hydrogen will offer some positive impacts for the conversion it will also increase the NO_x emissions which is considered to be the only deleterious effect for the combustion of ammonia fuel [81].

2.4.2. Material selection and possible replacements

As a known fact elements, such as brass and copper corrodes under ammonia, so the parts that are made from these materials and get in touch with the fuel used in the generator should be replaced with stainless steel or aluminium composite parts [82].

The parts inside of the engine block, the fuel delivery systems will be interacting with fuel during its operation, so it is crucial that these parts are non-corrosive. The parts such as gas controllers and ancillary devices are usually made from brass or copper in a diesel generator but there are also stainless steel options available for these parts in the market. Figure 2.11 represents the parts of a diesel generator and the parts are numbered accordingly in Table 2.7 regarding the type of material used in the production of the generator so the parts that need caution can be easily labelled from this list. Only wetted parts are the engine block and the parts inside it, such as the cylinder heads and steel cylinders that get in touch with the fuel used in the generator. These parts should be taken in to consideration when making the necessary changes for the ammonia conversion [82].

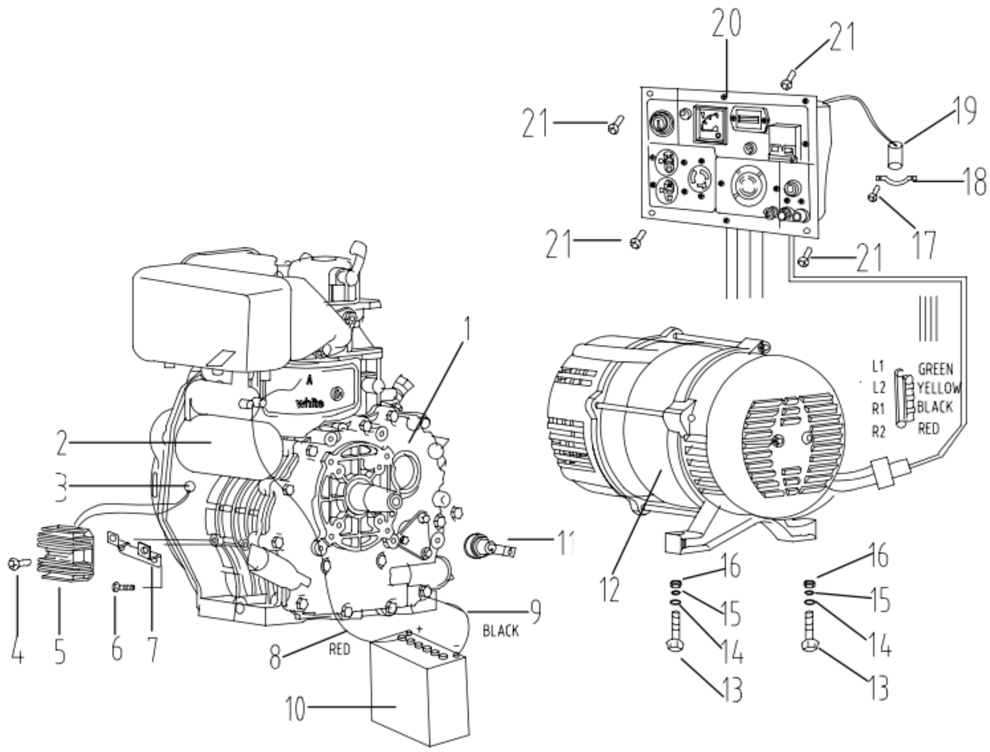

Figure 2.11: Diesel generator assembly (Taken from [83])

Table 2.7: Part list for the diesel generator assembly

Number	Part	Material (mostly used)
1	Engine block	Grey cast iron or Al Composite
2	Starter motor	Steel
3	Engine flywheel	Grey cast iron
4	Bolt of voltage regulator	Stainless steel
6	Bolt of voltage regulator bracket	Stainless steel
7	Voltage regulator bracket	Stainless steel
8	Battery cable (red)	Plastic
9	Battery cable (black)	Plastic
12	Magnetic Generator	Grey cast iron
13-17	Bolts	Stainless steel
14-15	Washers	Stainless steel
16	Nut	Stainless steel
18	Capacitor bracket	Stainless steel
21	Bolt of output panel assembly	Stainless steel

Source**:** [83,84]

2.4.3. Cooling system

The cooling system may also need some modifications after the usage of ammonia fuel in the generator because of the higher temperature values that the system will operate under, which will be much higher as explained previously. Regarding the work done by Berman [85] who have proposed the idea of a new lubricant, graphene which makes cooling at higher temperatures possible and can also be utilized for ammonia converted generators that will combust at much higher pressure and temperature values.

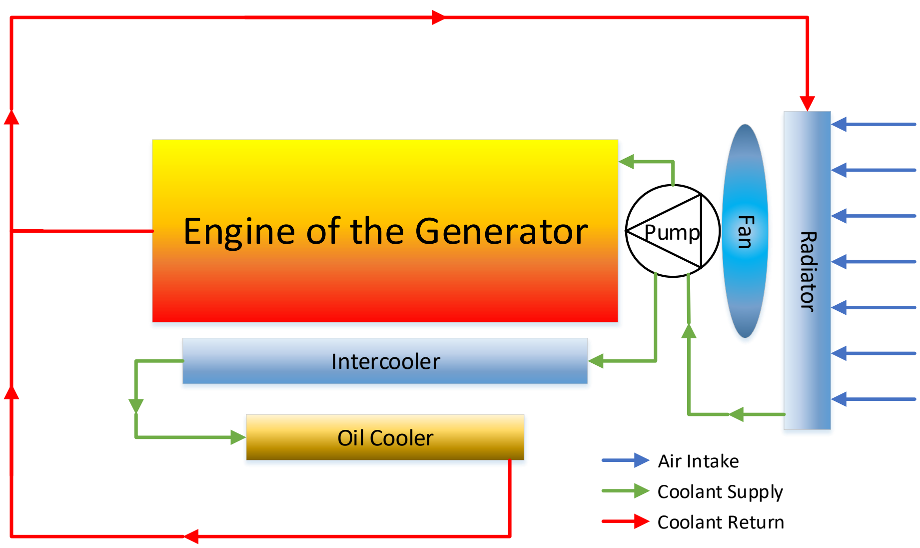

Figure 2.12: Modelling of generator cooling system

As plotted in Figure 2.12 the cooling system for a generator simply works this way where the ambient air enters the radiator the coolant used in the system enters the pump with the addition of a fan to decrease the temperature of the coolant. Then the coolant enters the engine, the intercooler then the coolant returns back to the radiator to repeat the process. The conventional generators operate at lower temperatures so the coolant will be replaced and will operate in the same system [86].

2.4.4. NO_x emissions

Using ammonia will result in no carbon footprint but the NO_x emissions should be taken into consideration as it also has negative effects on the environment. Nakahira [87] reported a possible solution for the problem is using a slightly fuel rich mixture and a catalytic converter where one mole of NH_3 is added for each mole of NO_x in the exhaust and this results in the propagation of nitrogen and water. This method is currently being used on all high-performance engines, which employ a high compression ratio such as ammonia engines. The selective catalytic reduction process is in generally used for the reduction of nitrogen oxides emissions occurring in the exhaust after the combustion of the fuel source used in the operation [88]. For the reduction process the injected ammonia forms a mixture with the emitted NO_x particles and passes through a catalyst at temperatures ranging from 300 to 420 °C in which the nitrogen oxides are converted to nitrogen and water vapour [89]. The basic idea and concept used these catalytic converters can be seen in Figure 2.13.

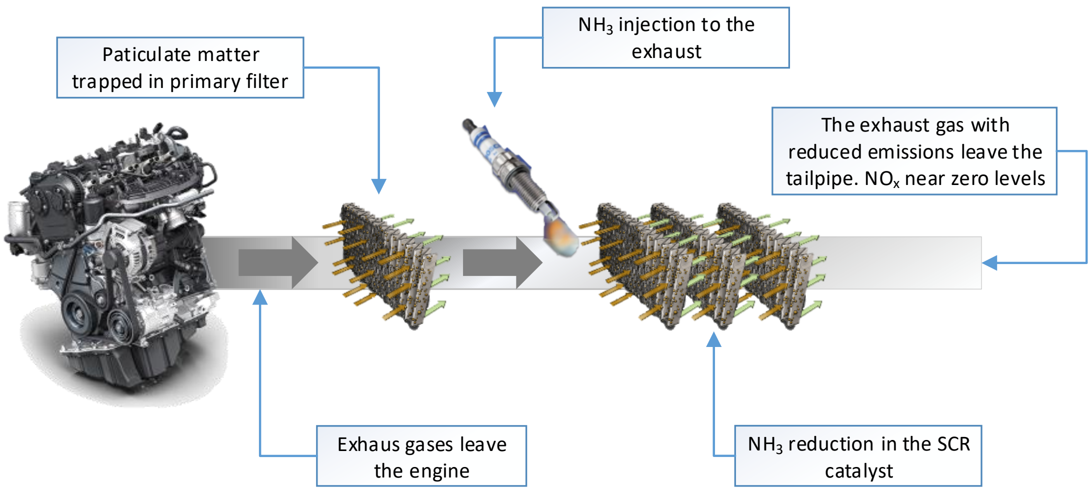

Figure 2.13: Selective catalytic removal process for NO_x emissions (Modified from [90])

The conversion of nitrogen oxides does not create any secondary pollution, as the products formed are only nitrogen and water vapour, which are already present in the atmosphere in large quantities. The conversion efficiency is typically 90% but may be as high as 99%. The ammonia source for the reduction of NO_x may be anhydrous ammonia, aqueous ammonia or an aqueous solution of urea. Anhydrous ammonia is considered the cleanest and most cost effective reducing agent, but storage of anhydrous ammonia under pressure may imply a potential hazard [89]. So regarding the work done by the researchers that is mentioned in the chapter for the possible combustion of ammonia and the progress made on the topic. The main problems for its possible usage have been because of the high autoigniton temperature which usually requires a secondary fuel source in order to start the combustion process and at the end work as a spark for the ammonia fuel to combust it at lower temperature and pressure values. But with the improvements in the technology and regarding the popularity of the topic in the upcoming future the combustion of ammonia will be dealt with at lower pressures.

CHAPTER 3: EXPERIMENTAL APPARATUS AND PROCEDURE

In this chapter, the detailed explanation of experimental setup is presented with the materials and instruments used in the experiments are briefly described regarding their properties and purpose of usage. Lastly the experimental procedure is explained step by step in a detailed fashion.

3.1. Experimental apparatus

The setup consist of a gasoline generator and a cylinder tank full of gaseous ammonia at 1 atm. The generator have gone under some changes and modifications in order to be readily available to operate with ammonia as the main fuel source. These modifications, changes and all of the steps followed to convey the experiments on the generator will be explained in the experimental procedure part of the chapter.

3.1.1. Gasoline generator

The gasoline generator used in the experiments were selected for a couple of reasons such as being commercially sold in the market and also being easy to dissemble and put back together with the way it is designed.

Figure 3.1: FIRMAN P03602 portable gasoline generator used in the experiments

The P03602 portable gasoline generator used during the experimental studies can be seen in Figure 3.1 that is manufactured by FIRMAN Company. The generator combust the fuel with the help of a spark plug and has a power capacity of up to 3.56 kW. The key properties and specifications of the generator is gathered on Table 3.1.

Table 3.1: Specifications of the FIRMAN P03602 portable gasoline generator

Engine type	Single cylinder, 4-stroke OHV air cooled
Starting watts	4550
Running watts	3650
Rated AC voltage	120V
Rated current	30A
Rated frequency	60Hz
Phase	Single
Voltage regulator	AVR
Power factor	1
Alternator type	Brushed
Engine	FIRMAN
Displacement	208 cc
Low oil shutdown	Yes
Engine power	3.65 kW
Ignition system	Spark ignition type
Starting system	Recoil
Fuel	Unleaded automotive gasoline (min 87 octane)
Fuel tank capacity	5.0 gallons
Carburetor type	Float
Air cleaner	Polyurethane type
P.T.O. shaft rotation	Counter clockwise
Spark plug	TORCH F6RTC/NGK BPR6ES/CHAMPION RN9YC
Product weight	101.5 lb
Idle speed	3000 rpm
Compression ratio	7:1

Source**:** [91]

As mentioned previously, a generator consists of two main parts which are the engine and the electromagnetic converter. These parts and their specifications will be investigated separately before getting on to the steps followed during the experimental procedure.

3.1.1.1. Generator engine

The engine consists of various parts that each act in the process of igniting the fuel and make the combustion possible for the generator and create a motion that later can be transformed to electricity. The engine used in the FIRMAN P03602 generator is a spark ignition one that is specifically designed to operate with gasoline fuel. As the generator will be operating with ammonia there are some challenges arising as discussed back in Chapter 2, so as a result there will be modifications that are necessary for the engine part of the generator before using ammonia. These modifications that are made on the generator will be explained in a detailed fashion in the experimental procedure part of the Chapter.

Figure 3.2: Spark ignition engine of FIRMAN P03602 portable gasoline generator

The engine is visible after the removal of the gas tank and can easily be seen in Figure 3.2. The engine parts consist of components such as the spark plug, carburetor, piston, cylinder head, exhaust and other parts. The rated power of the generator is 3.65 kW and the displacement property is values at 208 cc and the fuel is injected with use of a carburetor as it can be seen on Table 3.1.

3.1.1.2. Electromagnetic converter

The electromagnetic converter takes advantage of the motion occurred by the combustion reaction in the engine and with the help of the magnets installed, it produces electricity. This part of the generator will not go under any changes as it only transforms the motion occurred by the engine regardless of the fuel used in combustion. But the properties of this part of the generator will be used in the thermodynamic analysis regarding the energy and exergy efficiencies of the generator. The electromagnetic converter part of the generator can be found by removing the panel in front of it and this part of the generator is used to measure the changes in voltage and ampere during its operation. The part can be seen in Figure 3.3.

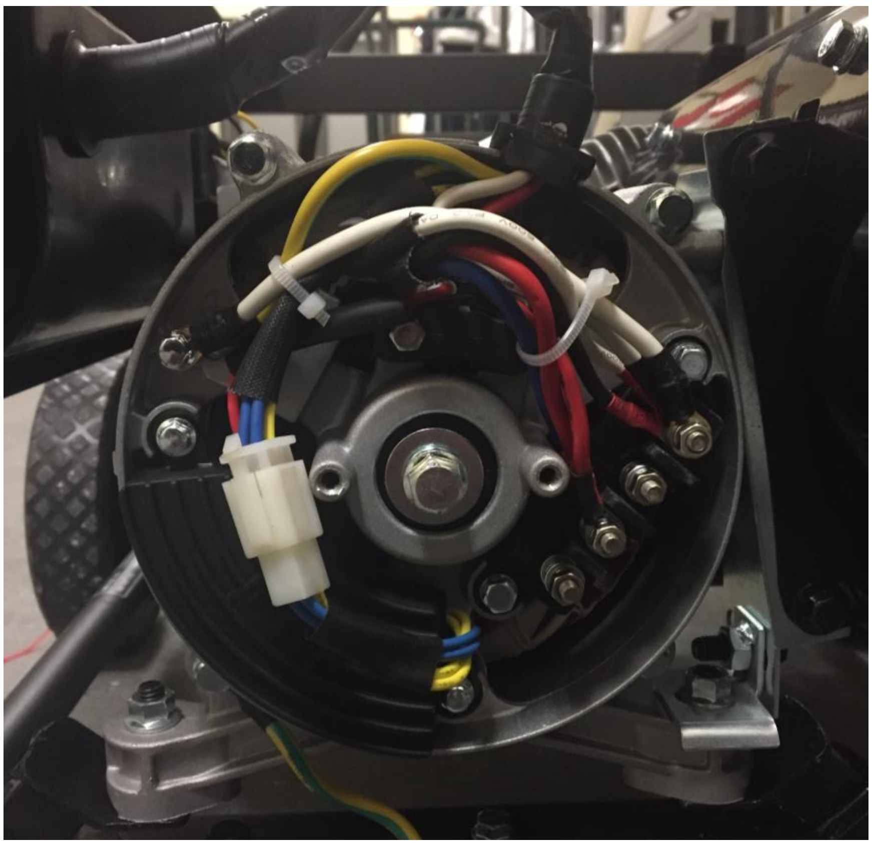

Figure 3.3: Electromagnetic part of FIRMAN P03602 portable gasoline generator

The measurements concerning the electricity production can be done from the plugs that are available on the front of the panel but using the electromagnetic converter part of the generator to measure the changes in voltages and current might be an easier way to observe the changes power output of the generator.

3.2. Experimental procedure

The experimental procedures and all of the setups followed during the preparation of the setup is included in the following flowchart labelled as Figure 3.4.

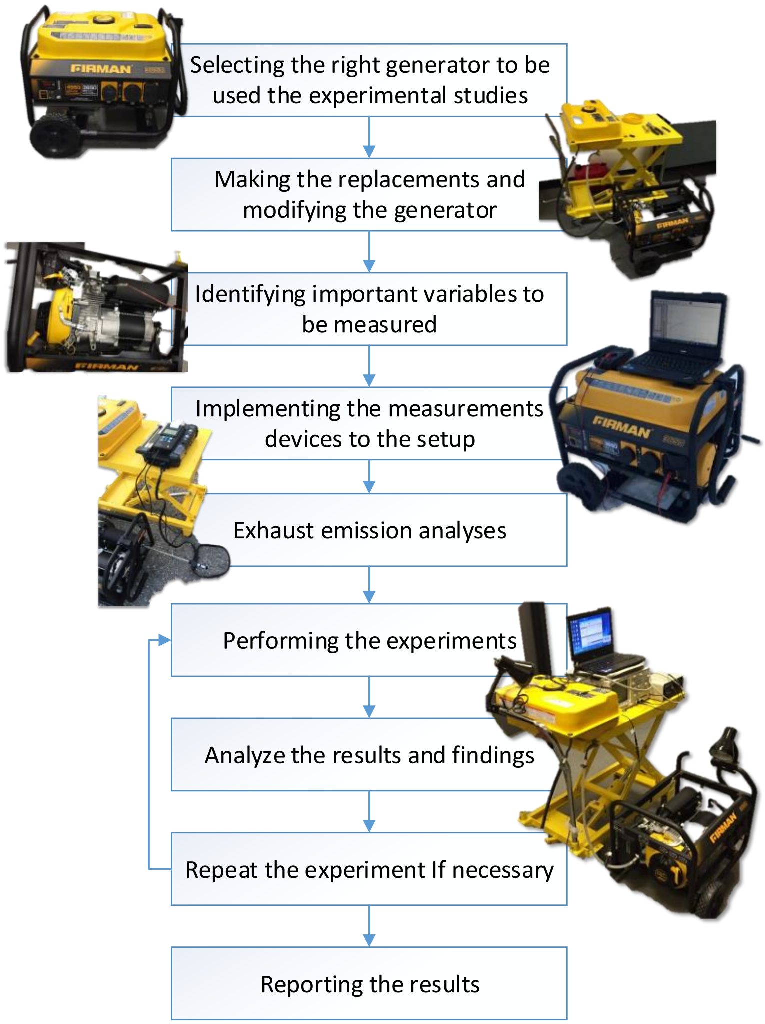

Figure 3.4: The flowchart for experimental analysis of the scientific work

After defining the need for the experiment and the objectives that are selected for the scientific work the important variables and the possible selections for the experimental setup have been discussed in with respect to the previous work conveyed by other researchers in the field. The following steps and methodology have been followed during the experimental analysis part of the work. After each experiment the assessment of the findings were discussed before moving on to the next step, If else that part of the experiment have been repeated up until the acceptable results have been achieved and there are minimum occurrence of errors.

The experiments have been conveyed outside the Clean Energy Research Lab (CERL) with necessary precautions to prevent causing harm to others and keep safety as the first priority. Firstly the plan was to convey the experiments inside one of the engine labs but afterwards because of the regulations regarding engines and the combustion of ammonia, it was decided that the changes and modifications will be done in CERL but the experimental will be conveyed outside of CERL without interacting with the ventilation systems of the building. Figure 3.5 shows the experimental setup that is used with only gasoline, as it is the fuel that is appropriate for this generator no changes were done at this point.

Figure 3.5: The setup without any engine modifications trailed with only gasoline at this stage of the experimental studies

The measurement devices such as the thermocouples and multimeter were used in this part of the experiment to measure the exhaust temperature and the changes in voltage. The main aim in conveying the experiments at this point is to make sure that the generator is operating and to calibrate the measurement instruments.

The devices and instruments used in the experiment are mainly used to contain the fuel and make the necessary measurements for the system. The power output and the temperatures of the generator is measured with an oscilloscope, a multimeter and a couple of thermocouples. The usage and the properties of the devices are discussed in a detailed way in the chapter. The thermocouples are sensors known with their ability to measure temperature. In the experiments the thermocouples will be placed on the generator to see the affect that varying the ratio of a fuel blend will make to the combustion process.

Table 3.2: Specifications of the Omega OM-CP-QUADTEMP-A thermocouple

Number of channels	4	
Thermocouple types	J, K, T, E, N, R, S, B	
Calibrated accuracy	∓ 0.5°C	
Temperature range of device	-20 to 60°C	
Thermocouple ranges of each type of thermocouple	Type J	-210°C to 760°C
	Type K	-270°C to 1370°C
	Type T	-270°Cto 400°C
	Type E	-270°C to 980°C
	Type R	-50°C to 1760°C
	Type S	50°C to 1760°C
	Type B	+50°C to 1820°C
	Type N	-270°C to 1300°C

Source**:** [92]

The thermocouple, used in the experiments to measure the change in temperature with respect to time during the operation of the generator under different fuel blend ratios and the specifications for the device can be seen on Table 3.2. Oscilloscope is a device that observes the change of electrical (AC and DC) signals over time, such that voltage and time describe a shape which is continuously graphed on a calibrated scale. A mixed-signal oscilloscope usually has two or four analog channels and a larger number of digital channels. These generated waveforms can be analysed for properties such as voltage, ampere, frequency, time and amplitude. There are modern digital instruments that calculate and display the combination of these properties directly such as a multimeter measuring the voltage. These devices will also give the correct estimates for that particular property but the oscilloscope has the ability to plot the momentarily changes in the property with respect to time. The open circuit voltage can be measured by directly using the probe but to measure the current of the closed circuit a simple load resistant circuit was built and was measured using the second probe. The Agilent branded oscilloscope that is used in the experiment to plot the changes in voltage and ampere with respect to time which will be used to calculate the power output of the generator. The key properties and specifications of the mixed-signal oscilloscope can be seen on Table 3.3.

Table 3.3: Specifications of the Agilent 54622D Digital Oscilloscope

Number of channels	2+16
Frequency range	DC to 100 kHz (-3dB with current de-rating)
Current range	100 mV/A; 100 mA to 10 A peak, 10 mV/A: 1 to 100 A peak
Working voltage	600 V max
AC current accuracy	100 mV/A (50 mV to 10 A peak) - 3% of reading ≥50 mA 10 mV/A (500 mA to 40 A peak) - 4% of reading ≥50 mA 10 mV/A (40 A to 100 A peak) - 15% max at 100 A
Sampling speed	25 million vectors/sec

Source**:** [93]

As mentioned previously in the chapter there are devices that can directly measure a specific property and a multimeter will be used to measure the voltage changes during the operation of the generator simultaneously to make sure that the power output of the oscilloscope are correct. The digital multimeter is used to measure the changes in voltage during the experiments. After observing that the setup and the measurement instruments calibrated and are operating in perfect condition the next step was bringing ammonia in to the play. Before doing so the modifications are made to the generator concerning mainly on the possible increase in temperature and corrosion. For the possible increase in temperature all of the fasteners and connecters are replaced with high temperature resistant ones as the temperature may possibly increase more than it supposed to compare to gasoline combustion. Regarding the corrosion concern the corroding parts under the influence of ammonia such as brass and copper parts should be replaced with stainless steel ones. After the talks with FIRMAN [91], the company confirmed that all of the parts used inside the engine are made of stainless steel, which makes the transformation process even easier and possible. After the removal and reconnection process of the fuel tank. The reason behind this is to open the air intake and make the engine part of the generator readily available for temperature measurement. The ammonia will be used in gaseous form in the experiments and will be injected to the system through the air intake with premixing it with air at ambient conditions. Regarding the air filtering system all of the filters and plastic covers are removed and cropped to have the space for the piping connected to the ammonia cylinder.

Figure 3.6: The setup after with necessary modifications to be used with different ratios of ammonia and gasoline blends at this stage of the experimental studies with the inclusion of the instruments that will be used in the measurements

After the modifications measurement instruments such as the oscilloscope, 2 thermocouple data logger devices and the laptop were installed to the experimental system on top of a hydraulic table where the fuel tank full of gasoline and was mainly placed as shown in Figure 3.6. The hydraulic table has the ability to change its height as the fuel tank full of gasoline should be placed up higher than the engine even though the engine will be sucking the fuel from the pipings, which will prevent knocking caused by fuel insufficiency. After all the changes and modifications are made to the generator, the next step was injecting gaseous ammonia to the system. Gaseous ammonia was stored in a cylinder tank and kept at 1 atm but as the experiments will be conveyed outside for safety precautions the tank should be kept far away from the experimental setup. To do so a piping with a length of 25 meters was used and the ammonia cylinder was stored inside the building and was fixed to the wall for safety precautions with the experimental setup placed outside the building as shown in Figure 3.7.

Figure 3.7: The setup placed outside CERL building with the ammonia cylinder stored inside the building and connected with the use of extra piping

As all of the safety measures were followed step by step the next step is to run the generator and use the fuel blend for measurements. As mentioned previously because of slow flame speed and low flame temperatures ammonia will not ignite by itself and the combustion will not occur completely so gasoline will be used as the combustion promoter for the process. At first the operation of the engine started with only gasoline fuel and kept running for up to 30 minutes up until the exhaust temperature and power readings were as stable as possible at the instant when the picture of the setup was taken as displayed in Figure 3.8. Then the gaseous ammonia was injected to the generator from the air intake starting at 1 atm and was increased up until 2.5 atm. While the mass flow rate for the ammonia was increasing the gasoline input was decreased at the same rate up until the point where the only fuel operating in the system was gaseous ammonia. During the changes of the fuel blend ratios the engine operated without any knocking but as the gasoline input was depleted in the system the generator continued on operating for approximately 10 to 15 more seconds but then because of the slow flame speed and low flame temperatures the engine of the generator stopped working as the fuel could not ignite by itself with the absence of a combustion promoter.

Figure 3.8: During the operation of the experimental setup operating at varying fuel blend ratios of gasoline and ammonia placed outside the CERL

The analysis for gas emissions was conveyed using a gas analyser that can measure the CO_2 emissions of the exhaust. The main aim in doing this is to observe the positive impact that ammonia addition to gasoline combustion has on greenhouse emissions. Unfortunately the gas analyser used the in the analysis did not have the necessary calibrations set to measure NO_x emissions, which would have been another right way to observe the impact of ammonia fuel.

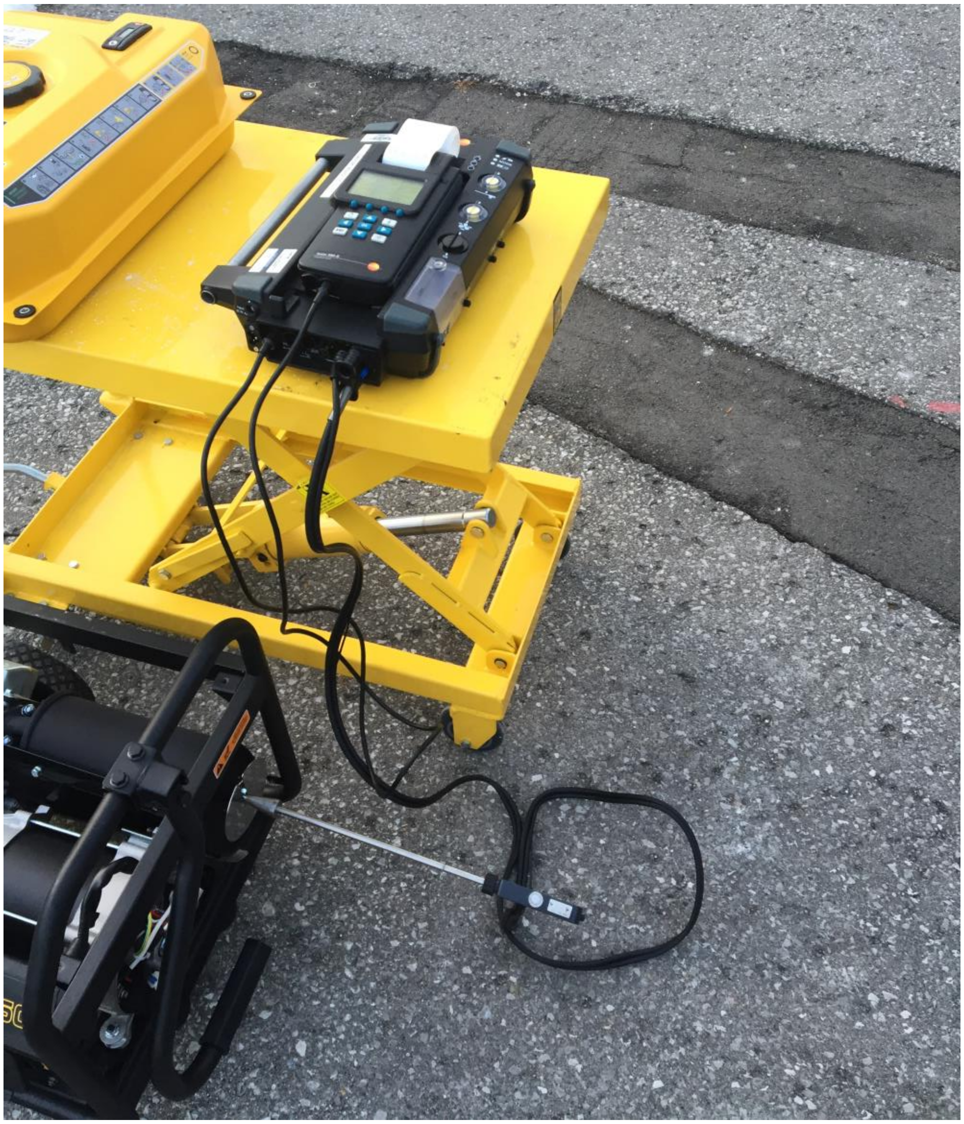

Figure 3.9: CO_2 gas analysis of the experimental setup

These devices aim to measure the types of gases available in that environment and it will be used to measure the changes in CO_2 emissions of different fuel blend ratios trailed during the experimental operation of the generator. Figure 3.9 represents the device used during the experiments to measure the emissions under different fuel ratios. The measured voltage, current, power, temperature and exhaust emission values are plotted and discussed on Chapter 5 of the thesis with the thermodynamic analysis of the combustion process with respect to varying ratios of gasoline and ammonia fuel blend.

CHAPTER 4: ANALYSIS AND MODELLING

In this chapter the theoretical analysis of ammonia combustion is conveyed with various combustion promoters to find the optimal amount of fuel that should be combined with ammonia by finding the energetic and exergetic efficiencies of different blend ratios. Also other properties such as the exhaust temperature and the energy outputs of each blend is examined in the chapter. The process flow diagram for ammonia combustion that was used in the modelling can be seen on Figure 4.1.

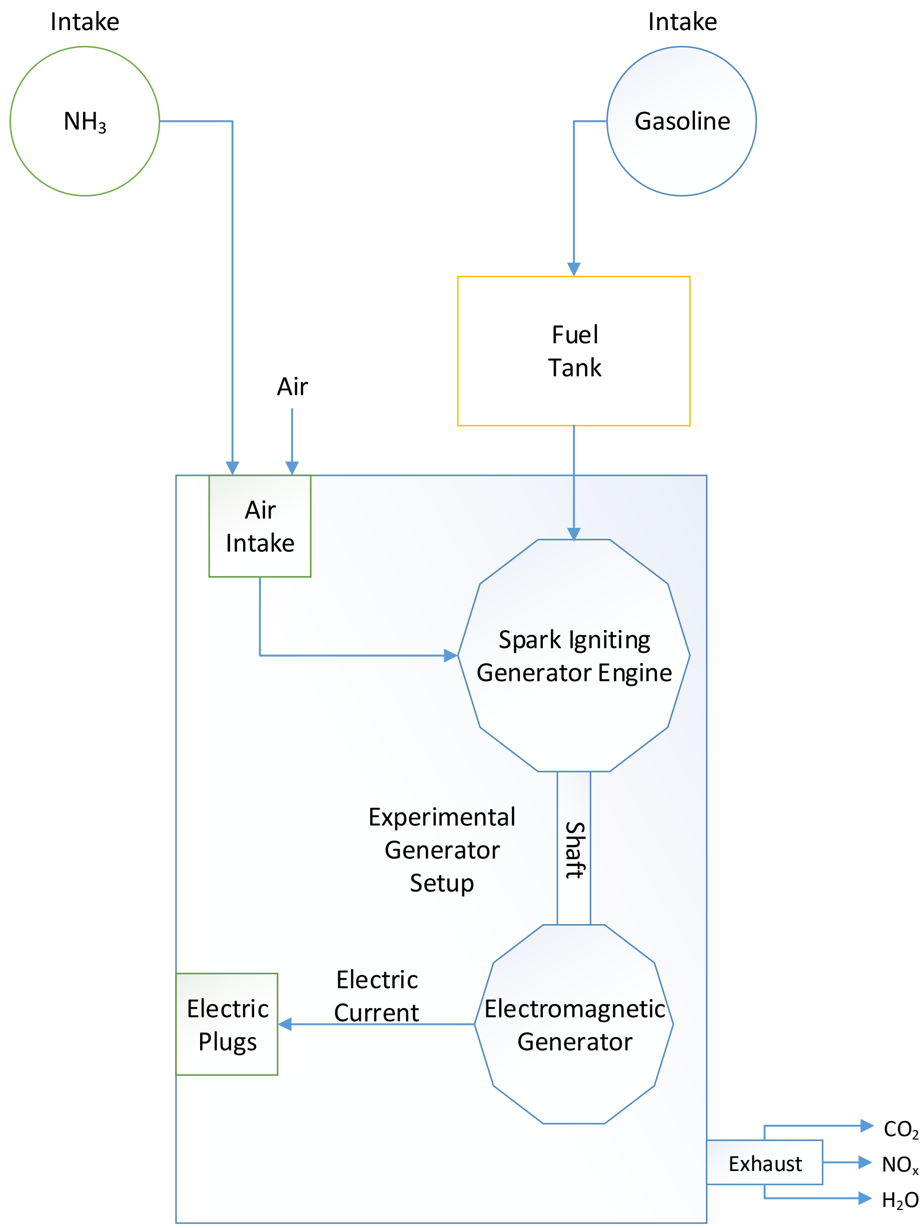

Figure 4.1: Process flow diagram of ammaonia based fuel blend combustion

The diagram includes all of the parts that will be used in the modelling of combustion for the power generator where an ammonia based fuel blend has been used for thermodynamic modelling purposes of the combustion reaction. Secondary fuel has been kept in a separate fuel tank that was disassembled from the experimental generator device, where the ammonia fuel was injected to the system through the air intake directly from the pressurized ammonia cylinder in gaseous form.

4.1. Thermodynamic Analysis

In thermodynamic analyses, overall mass, energy, entropy and exergy balance equations are written for the fuel that will be blended with ammonia. In order to understand the combustion process, how the generator operates and its performance, a comprehensive thermodynamic analysis is carried out regarding energy and exergy studies stated by Dincer and Rosen [94], to evaluate efficiencies of the system. The modelling of the combustion is built up in the Engineering Equation Solver (EES) for analysis purposes.

The general assumptions taken in to account for the thermodynamic analysis and calculations of the system can listed as:

- The reference temperature is selected as T_0 = -15 ºC (outside temperature during the experimental studies) and reference pressure P_0 = 101.325 kPa.
- The variations in the kinetic and the potential energies and exergies are ignored.
- The ideal gas laws apply for the gases operating in the system.
- Air used in the system is an ideal gas with constant specific heat.
- The relative humidity of the inlet air and hydrogen is taken as 90%.
- A 20% of the produced heat is assumed to be lost by convection and radiation.
- The generators maximum output power is set to 3.65 kW as this is the maximum value for the experimental generator device.
- Complete combustion occurs.

4.1.1. Combustion reactions of fuels

The combustion of a fuel occurs when it burns with air. At stoichiometric ratio 1 mole of fuel is burnt with 100% air intake accordingly to combustion product. But alternatively different chemical equations can be written for the combustion of these fuels with different air intakes as shown in Table 4.1 for 100%, 150% and 200% for various fuel sources.

Table 4.1: The combustion reactions for various fuel types under different air intakes

	Stoichiometric (100% air intake)	150% air intake	200% air intake
Combustion of ammonia	$NH_3 + 0.75(O_2 + 3.76N_2) \rightarrow 1.5H_2O + 3.32N_2$	$NH_3 + 1.125(O_2 + 3.76N_2) \rightarrow 1.5H_2 + 1.125O_2 + 4.23N_2$	$NH_3 + 1.5(O_2 + 3.76N_2) \rightarrow 1.5H_2 + 1.5O_2 + 6.14N_2$
Combustion of hydrogen	$H_2 + 0.5(O_2 + 3.76N_2) \rightarrow H_2O + 1.88N_2$	$H_2 + 0.75(O_2 + 3.76N_2) \rightarrow H_2 + O_2 + 2.82N_2$	$H_2 + (O_2 + 3.76N_2) \rightarrow H_2 + O_2 + 3.76N_2$
Combustion of diesel	$C_{12}H_{23} + 17.75(O_2 + 3.76N_2) \rightarrow 12CO_2 + 11.5H_2O + 66.74N_2$	$C_{12}H_{23} + 26.625(O_2 + 3.76N_2) \rightarrow 12CO_2 + 11.5H_2 + 14.625O_2 + 100.11N_2$	$C_{12}H_{23} + 35.5(O_2 + 3.76N_2) \rightarrow 12CO_2 + 11.5H_2 + 23.5O_2 + 133.48N_2$
Combustion of gasoline	$C_8H_{18} + 12.5(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 47N_2$	$C_8H_{18} + 18.75(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2 + 10.75O_2 + 70.5N_2$	$C_8H_{18} + 25(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2 + 2O_2 + 94N_2$
Combustion of ethanol	$C_2H_5OH + 3(O_2 + 3.76N_2) \rightarrow 2CO_2 + 3H_2O + 11.28N_2$	$C_2H_5OH + 4.5(O_2 + 3.76N_2) \rightarrow 2CO_2 + 3H_2 + 2.5O_2 + 16.92N_2$	$C_2H_5OH + 6(O_2 + 3.76N_2) \rightarrow 2CO_2 + 3H_2 + 4O_2 + 22.56N_2$
Combustion of methanol	$CH_3OH + 1{,}5(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 5.64N_2$	$CH_3OH + 2.25(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2 + 1.25O_2 + 8.46N_2$	$CH_3OH + 3(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2 + 2O_2 + 11.28N_2$
Combustion of propane	$C_3H_8 + 5(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2O + 18.8N_2$	$C_3H_8 + 7.5(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2 + 4.5O_2 + 28.2N_2$	$C_3H_8 + 10(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2 + 7O_2 + 37.6N_2$
Combustion of CNG	$CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 7.52N_2$	$CH_4 + 3(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2 + 2O_2 + 11.28N_2$	$CH_4 + 4(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2 + 3O_2 + 15.04N_2$
Combustion of butane	$C_4H_{10} + 6.5(O_2 + 3.76N_2) \rightarrow 4CO_2 + 5H_2O + 24.44N_2$	$C_4H_{10} + 9.75(O_2 + 3.76N_2) \rightarrow 4CO_2 + 5H_2 + 5.75O_2 + 36.66N_2$	$C_4H_{10} + 13(O_2 + 3.76N_2) \rightarrow 4CO_2 + 5H_2 + 9O_2 + 48.88N_2$

With the use of a catalyst and under the correct conditions of temperature, ammonia reacts with oxygen to produce NO, which is oxidized to NO_2, which is considered as deleterious emissions. The combustion characteristics of various fuel sources that will be blended for analysis have been listed in Table 4.2. The air-fuel ratio by weight can be calculated using the equation given in the thermodynamics book by Cengel [95] as follows:

$$AF = \frac{m_{air}}{m_{fuel}} \tag{1}$$

Table 4.2: Combustion characteristics of various engine fuels

Fuel	Formula	Storage Temp. [ºC]	Storage Pressure [kPa]	Density [kg/m³]	Lower Heating Value [MJ/kg]	Air/Fuel Ratio by Weight	Energy Content [MJ/kg]	Autoigniton Temp. [ºC]
Ammonia	NH_3	25	101.3	600	18.8	6.05	2.64	651
Ethanol	C_2H_5OH	25	101.3	790	27	8.95	2.70	423
Gasoline	C_7H_{17}	25	101.3	700	42.5	15.29	2.58	370
Hydrogen (gas)	H_2	25	24,821	17.5	120	34.32	3.40	571
Hydrogen (liquid)	H_2	-253	102	71	120	34.32	3.40	571
Diesel	$C_{12}H_{23}$	25	101.3	850	45	14.32	2.77	254
Methanol	CH_3OH	25	101.3	780	19.5	6.44	2.69	464

Source**:** [96–98]

4.1.2. Energy analysis

The energy analysis can be defined by starting from the basic principles and formulas of thermodynamics. The general equation for the conservation of mass in a control volume for any system can be presented as:

$$\sum \dot{m}_{in} - \sum \dot{m}_{out} = \frac{dm}{dt} \tag{2}$$

In equation (2) the subscripts 'in' and 'out' specify the control volume for the inlet and the outlet, respectively. If the operation is considered as steady state, then there is no accumulation or consumption of mass which results in $\dot{m}_{in} = \dot{m}_{out}$.

The common steady state form of the energy balance equation (neglecting the potential and kinetic energy) can be written as

$$\dot{Q} - \dot{W} + \sum \dot{m}_{in} h_{in} - \sum \dot{m}_{out} h_{out} = 0 \tag{3}$$

where $\dot{Q}$ and $\dot{W}$ represent the heat transfer and work rate crossing the boundaries and $\dot{m}$ and h represent the mass flow rate and the specific enthalpy of the streams of the system, respectively. The entropy is a quantity of the disorder for a thermodynamic system and the change in entropy occurring as a result of a chemical reaction that is given by the difference in entropy of the products and the sum of the entropies of the reactants and it is defined as

$$\Delta S_R = \sum\nolimits_p v_p\, \Delta S_{R_p} - \sum\nolimits_r v_r\, \Delta S_{R_r} \quad (4)$$

The lower heating value of the fuels are used in the calculations to find the Energy output of the combustion reaction and can be written as

$$Q = n_{fuel}(LHV_{fuel}) \quad (5)$$

As mentioned previously the mechanical power produced by the engine is converted to electrical power by the electric generator. The electrical output power by the electric generator can be calculated by using Equation (6) where the product of current and voltage waveforms measured by the oscilloscope is integrated to find the real power produced by the electric generator;

$$P_E = \frac{1}{T}\int_0^t (i.v)dt \quad (6)$$

4.1.3. Exergy Analysis

Exergy can be defined as the amount of work obtained when a piece of matter is brought to a state of thermodynamic equilibrium with respect to its surroundings by a reversible process. The total exergy Ex of a system is given by:

$$Ex = (U - U_o) + P_o(V - V_o) - T_o(S - S_o) + \sum_k Nk(\mu_{ko} - {\mu_k}^o) \quad (7)$$

where U is the total energy, V is the volume, S is the entropy, Nk is the number of moles of component k and μ is the chemical potential. Subscript o are relates to values regarding the system, superscript o presents the chemical potential of the substance with respect to the environment. For a control volume, the exergy flow Ex_f can be written as

$$Ex_f = (H - H_o) - T_o(S - S_o) + \sum_k Nk(\mu_{ko} - {\mu_k}^o) \quad (8)$$

where H represents the enthalpy and the chemical exergy is represented by the term that depends on the chemical potentials and can be calculated for different fuel blends according to the methodology presented by Morris and Szargut [99]. For a mixture of substances or fuels in this case, the chemical exergy in molar basis can be calculated as

$$\overline{ex}_{mix}^{ch} = \sum_i y_i \, \overline{ex}_i^{ch} + \bar{R}T_0 \sum_i y_i \, \ln y_i \tag{9}$$

The total exergy flow of a mixture of ideal gases can then be written as

$$\overline{ex}_{f\,mix} = \sum_i y_i \, \overline{ex}_i^{ch} + \bar{R}T_0 \sum_i y_i \, \ln y_i + \sum_i y_i \int_{T_0}^{T} \bar{c}_{p\,i} dT - T_0 \sum_i y_i \int_{T_0}^{T} \bar{c}_{p\,i} \frac{dT}{T} - \bar{R} \ln \frac{P}{P_0} \tag{10}$$

where the first, second terms of equation (10) represent the chemical exergy of the mixture and the third, fourth terms present for the physical exergy flow.

The total exergy in molar basis can be obtained from the definitions of total exergy and total exergy flow and is given by

$$\overline{ex}_{mix} = \overline{ex}_{f\,mix} + \bar{R}\mathrm{T}_0 \left(\frac{P}{P_0} - 1\right) \tag{11}$$

The exergy balance for a given system in terms of irreversibility can be written as

$$I = Ex_1 - Ex_2 - W_{net} + \sum_r Q_r \left(\frac{T_r - T_0}{T_r}\right) \tag{12}$$

where the last term of equation (12) presents the exergy associated to the heat transfer between the system and a thermal reservoir at temperature, T_r and W_{net} is the net work available.

4.1.4. Performance Analysis

The energy efficiency can be defined as an indicator of how efficiently the input is converted to the product. The energy efficiency is defined by η_{en} and it can be written as:

$$\eta_{en} = \frac{Energy\ output\ in\ product}{Energy\ Input} = 1 - \frac{Energy\ loss}{Energy\ input} \tag{13}$$

The exergetic efficiency can be specified to evaluate exergy conversion in a process where the first law thermodynamics is applied to define energy conversion. The evaluation of exergy conversion defines a relation between energy losses to environment and internal irreversibilities of the combustion process [100]. The exergetic efficiency can be written as

$$\psi = \frac{Useful\ exergy\ production}{Exergy\ consumption} \tag{14}$$

From the concepts of exergetic efficiency, a general expression was obtained by Gallo and Milanez [96] for combustion reactions. A combustion engine is analysed where the expressions for the exergetic efficiencies are separately defined for compression, combustion, expansion, exhaust, and intake that can be written as

$$\psi_{cp} = \frac{-\Delta Ex}{|W_{cp}|} \tag{15}$$

$$\psi_{cb} = \frac{\Delta Ex + W_{cb}}{Ex_i} \tag{16}$$

$$\psi_{exp} = \frac{W_{exp}}{\Delta Ex} \tag{17}$$

$$\psi_{exh} = \frac{\Delta Ex}{Ex_{f_i} + |W_{exh}|} \tag{18}$$

$$\psi_{in} = \frac{\Delta Ex}{Ex_{f_0} + |W_{in}|} \tag{19}$$

The complete closed part of the cycle, complete open part of the cycle and for the overall exergetic efficiencies can be written as

$$\psi_{cyc} = \frac{W_{cyc}}{\Delta Ex} \tag{20}$$

$$\psi_{op} = \frac{Ex_f}{Ex_{f_0} + |W_{op}|} \tag{21}$$

$$\psi_{ov} = \frac{W_B}{Ex_{f_{mix}}} \tag{22}$$

In these expressions ΔEx is the exergy variation between initial and final states, Ex_{f_0} is the exergy flow entering the cylinder. $Ex_{f_{mix}}$ is the exergy flow associated to the air-fuel mixture and W_B is the brake power.

The exergetic efficiency of combustion process considers the network of the process where the exergetic efficiency of the intake is similarly to volumetric efficiency. The exergetic efficiency of the open part of the cycle simply combines the exhaust and intake processes. Lastly, the overall engine efficiency neglects the conditions inside the cylinder but to the brake conditions considered regarding the effect of engine's frictional losses.

CHAPTER 5: RESULTS AND DISCUSSION

In this chapter, the results of the experimental and theoretical analysis have been presented and the important points have been discussed by plotting the necessary graphs gathered from both instruments and simulations. Part 5.1 discusses the experimental results of the gasoline engine conversion, where part 5.2 investigates the usage of each fuel blends of ammonia separately by trailing different ratios and comparing their efficiencies both energetically and exergetically.

5.1. Ammonia based gasoline blend in FIRMAN generator

As explained previously in Chapter 3 that the measurements have been conveyed on a spark ignition generator by varying the fuel ratio of ammonia and gasoline blend and some measurements have been made using the instruments introduced. The thermocouples were placed around the exhaust to get the overall exhaust temperature under the influence of different fuel blend ratios. The influence of changing the mass ratio of the gasoline ammonia blend on the exhaust temperatures of the generator is plotted in Figure 5.1 from the measured experimental data.

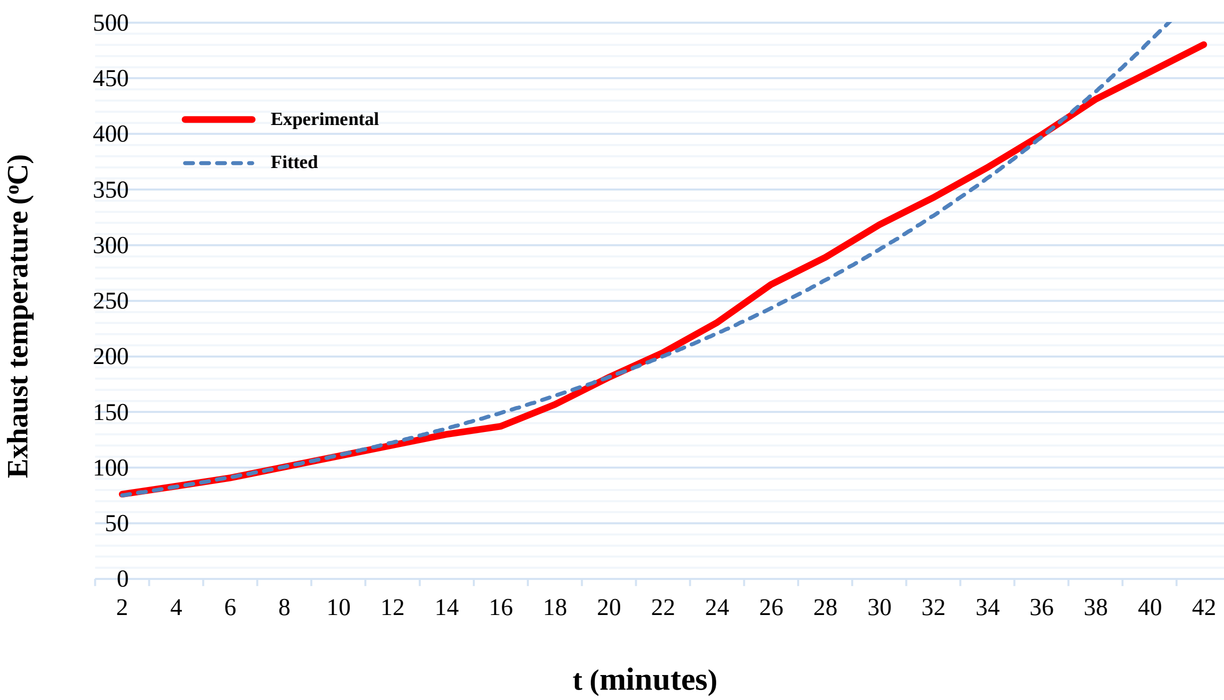

Figure 5.1: The influence of changing the mass ratio of the gasoline ammonia blend (with respect to the experimental procedure) on the exhaust temperatures of the generator

As expected the temperature increases with respect to time as the generator kept on operating, the measurements were made starting from 100% gasoline fuel that kept on operating up to 30 minutes then the ammonia injection has begun in an increasing mass flow rate manner where the injection of gasoline was reduced at the same rate the ammonia increases. The ratios investigated starting at 100% gasoline, 80% gasoline to 20% ammonia, 60% gasoline to 40% ammonia, 40% gasoline to 60% ammonia and 20% gasoline to 80% ammonia with temperature measurements of approximately 369.9 C^o, 399.3 C^o, 431.2 C^o, 455.7 C^o, and 480.1 C^o, respectively. But after this point because of the low flame temperatures of ammonia the fuel did not ignite and the generator stopped operating at that point. The lower flame temperature of the fuel may require a greater spark as it will require more temperature to ignite.

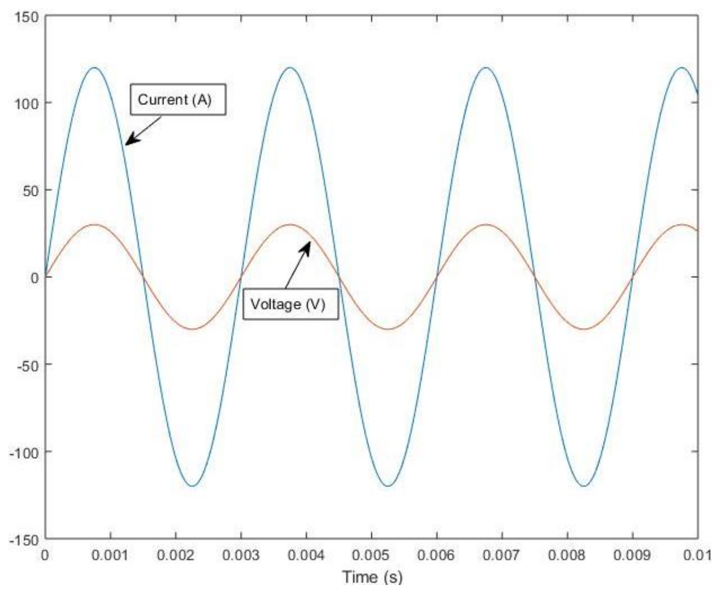

Figure 5.2: The plotted values for the voltage and current waveforms of the generator recorded using the digital oscilloscope

Figure 5.2 shows the instant changes observed in the oscilloscope during the experiments. The power that is generated for 100% gasoline, 80% gasoline to 20% ammonia, 60% gasoline to 40% ammonia, 40% gasoline to 60% ammonia and 20% gasoline to 80% ammonia is 3689.2 W, 3657.4 W, 3624.1 W, 3599.6 W, 3572.8 W, respectively. As the generator stopped working when the gasoline supply was less than 20% the electrical properties were not measured around ratios. When the ratio of ammonia in the fuel blend increased the power generated by the generator slightly decreases which is as expected.

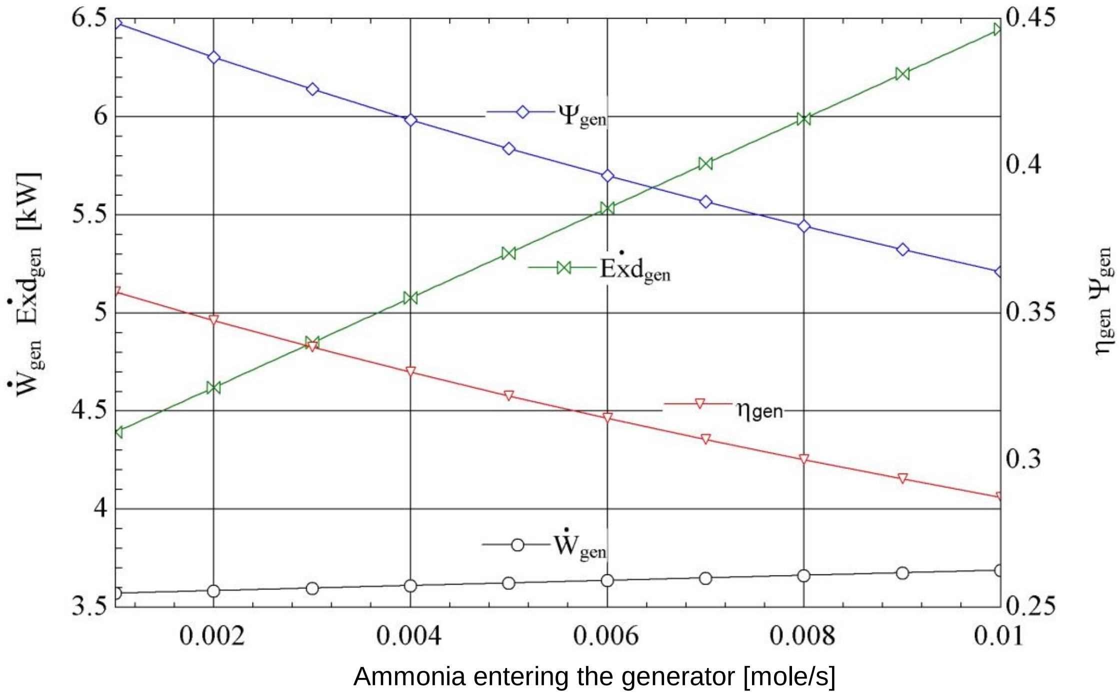

Figure 5.3: Effects of changing the ratio of the gasoline ammonia blend on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for gasoline and ammonia fuel blend experimentally

Figure 5.3 shows the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for gasoline and ammonia fuel blend that are calculated using the experimental findings with respect to the change in fuel ratio for gasoline and ammonia blend. Changing the fuel ratios starting from 100% gasoline, 80% gasoline to 20% ammonia, 60% gasoline to 40% ammonia, 40% gasoline to 60% ammonia and 20% gasoline to 80% ammonia increases the power output of the generator slightly from 3572.8 W to 3689.2 W. The same variation of molar variation resulted in a change in the exergy destruction rate of the generator from 4.392 kW to 6.447 kW. Regarding the results for the overall energy and exergy efficiencies of the generator reduced from 35.7 % to 28.74% and from 44.85 % to 36.4 %, respectively. Lastly the CO_2 and NO_x emissions of the generator operating with varying ratios of gasoline and ammonia blend was measure and plotted as it can be seen in Figure 5.4.

The reduction in CO_2 emissions from 2.535 g/s to 2.4916 g/s are related with the addition of ammonia to the combustion but at the same time the NO_x emissions have considerably increased with the addition of ammonia to the system that increases it ratio against gasoline in the fuel blend. After the completion of experimental analysis, theoretical analysis will be made using the EES software and mathematically modelling the thermodynamic equation written for the energetic and the exergetic performances of ammonia combustion with various fuel types.

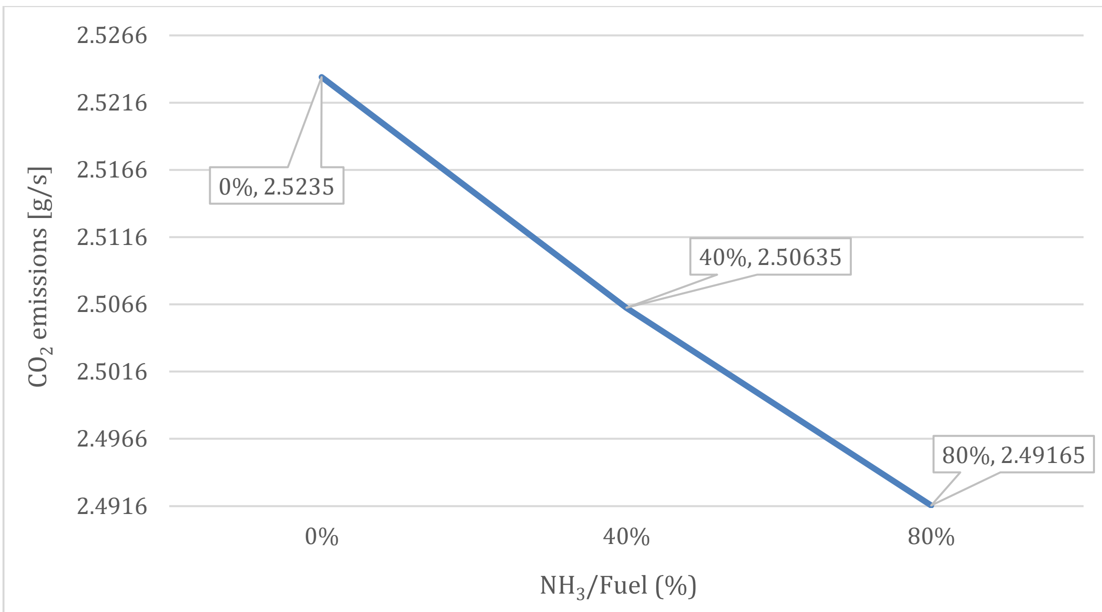

Figure 5.4: Effects of changing the ratio of the gasoline ammonia blend on CO_2 emissions

During the theoretical analysis the combustion process will be modelled using various types of fuels that can be used as combustion promoter to help ignite ammonia to combust fully. The optimal ratio and the thermodynamic properties of each fuel blend will be made to be used with ammonia in different types of generator to produce electricity. The verification of the theoretical analysis will be made with the comparison of experimental data gathered from the measured performance analysis results of ammonia and gasoline blend where the maximum power output is set to 3.65 kW. The results and graphs regarding each fuel blend will be investigated separately in the chapter with an overall comparison at the end of the chapter.

5.2. Ammonia based hydrogen blend

A parametric study is performed on the generator using hydrogen and ammonia blend to assess the system performance with changing operating conditions such as changing the ammonia and hydrogen molar flow rate entering the generator, varying the mass flow rate of ammonia entering the generator. The influence of changing the molar flow rate of ammonia supplied to engine on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.5. Changing ammonia molar flow rate from 0.01 to 0.04 mole/s increases the power output of the generator from 0.9159 kW to 3.737 kW. The same variation of molar variation resulted in an upsurge in the exergy destruction of the generator from 2.203 kW to 9.376 kW. Regarding the results for the overall energy and exergy efficiencies of the generator reduced from 24.91% to 24.87% and from 29.36% to 28.5% respectively. This reduction in the efficiency can be interpreted by the increase in the exergy destruction rate of the generator.

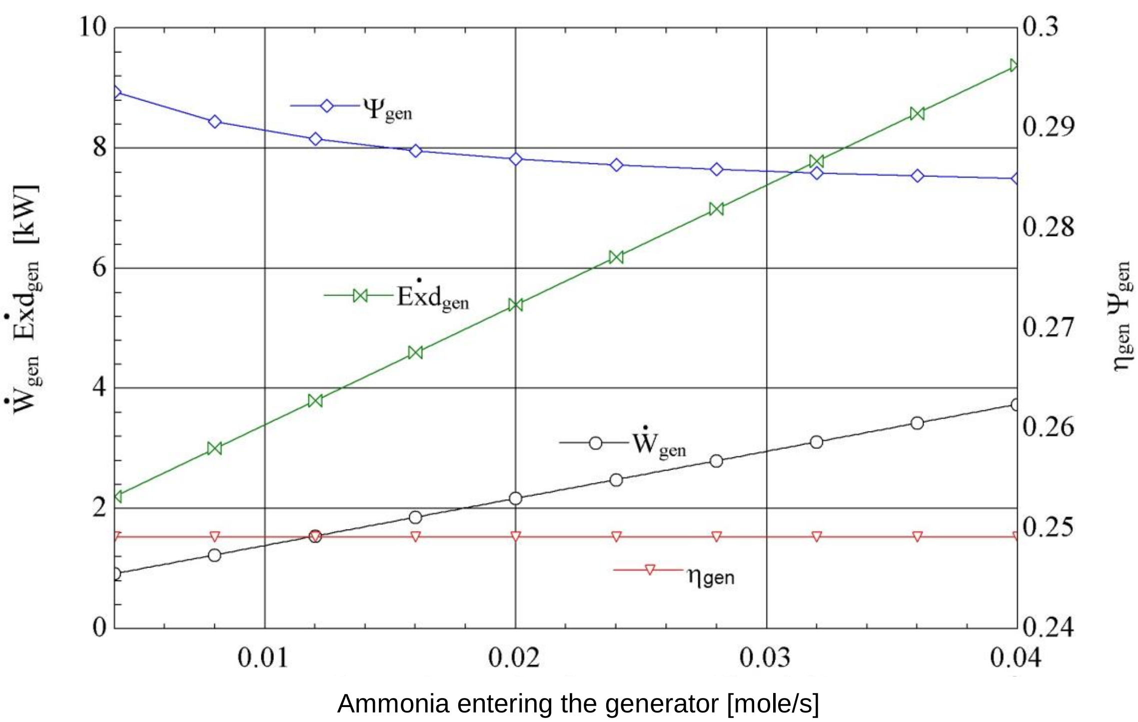

Figure 5.5: Effects of changing amount of ammonia entering engine on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for hydrogen and ammonia fuel blend

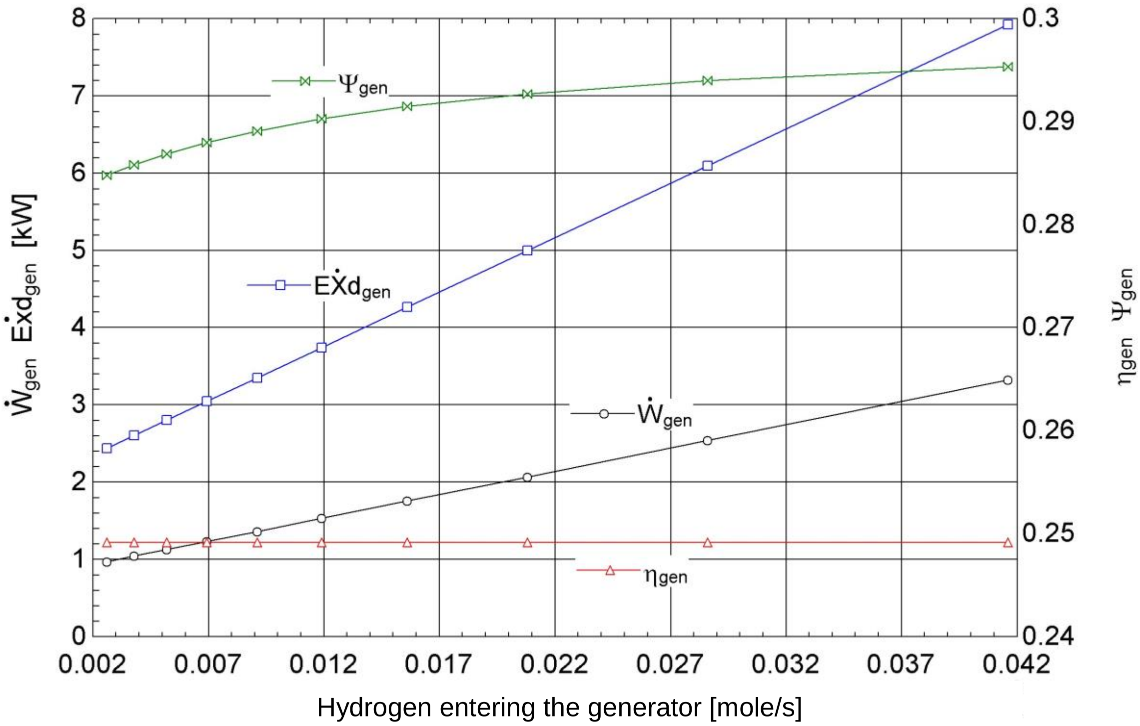

Figure 5.6: Effects of changing amount of hydrogen entering engine on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for hydrogen and ammonia fuel blend

Secondly for the ammonia hydrogen blend another parametric study is performed by changing the molar flow rate of hydrogen supplied to engine on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.6. Changing hydrogen molar flow rate from 0.02 mole/s to 0.42 mole/s the results for the overall energy and exergy efficiencies of the generator to increase from 24.71% to 24.80% and 28.4% to 29.53%.

The increase of the efficiency can be related to the increase in the lower heating value of the fuel blend with the addition of hydrogen fuel to the system. The same variation of molar variation resulted in an upsurge in the exergy destruction rate of the generator from 2.44 kW to 7.925 kW. Regarding the power output of the generator it increases from 0.971 kW to 3.321 kW. Which shows the impact of increasing the amount of ammonia fuel entering the generator will be increasing the power output at the same time.

Another parametric study have been performed on the generator by changing the ratio of the hydrogen ammonia blend starting from 80% hydrogen and 20% ammonia to 20% hydrogen and 80% ammonia to plot the changes in the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator.

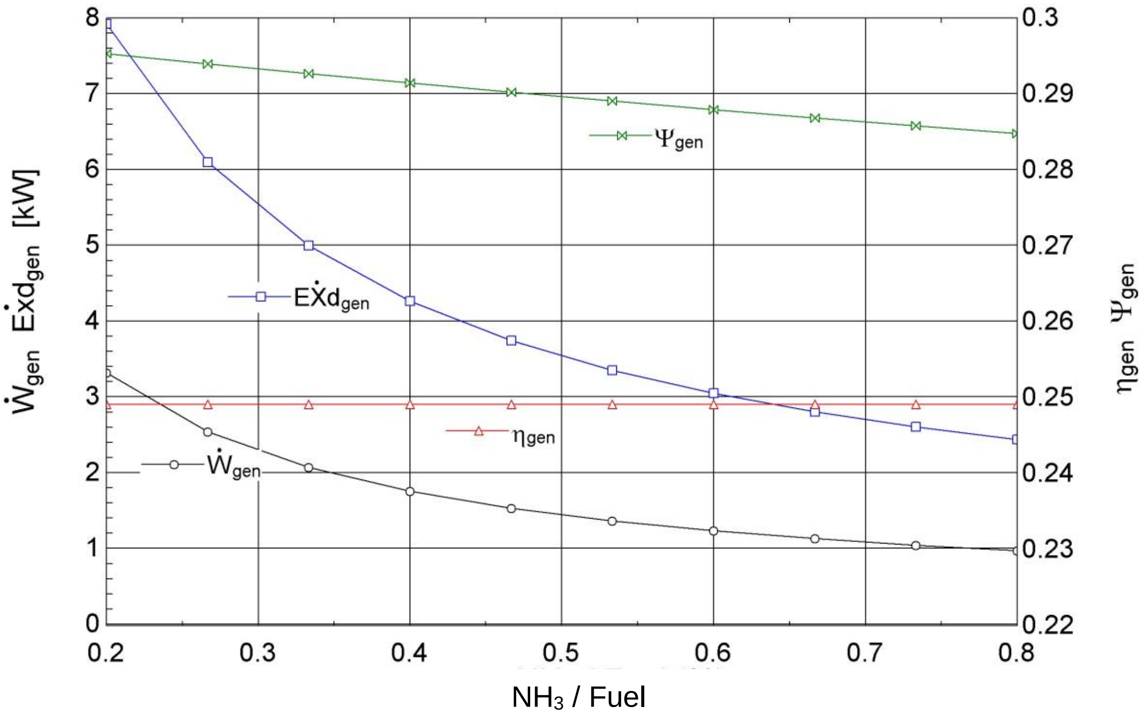

Figure 5.7: Effects of changing the ratio of the hydrogen ammonia blend on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for hydrogen and ammonia fuel blend

The effect of changing the ratio of the hydrogen ammonia blend on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.7. Changing the mass ratio of the hydrogen ammonia blend starting from 80% hydrogen and 20% ammonia to 20% hydrogen and 80% ammonia increases the power output of the generator from 1.01 kW to 3.45 kW. The same variation resulted in a reduction of the exergy destruction rate of the generator starting from 8.229 kW to 2.534 kW. Regarding the results for the overall energy and exergy efficiencies of the generator reduced from 24.7% to 23.8% and from 29.57% to 28.48% respectively.

Lastly another graph was plotted regarding the influence of changing the mass ratio of the hydrogen ammonia on NO_x emissions. During the studies once again the ratio of the hydrogen ammonia blend was changed starting from 80% hydrogen and 20% ammonia to 20% hydrogen and 80% ammonia.

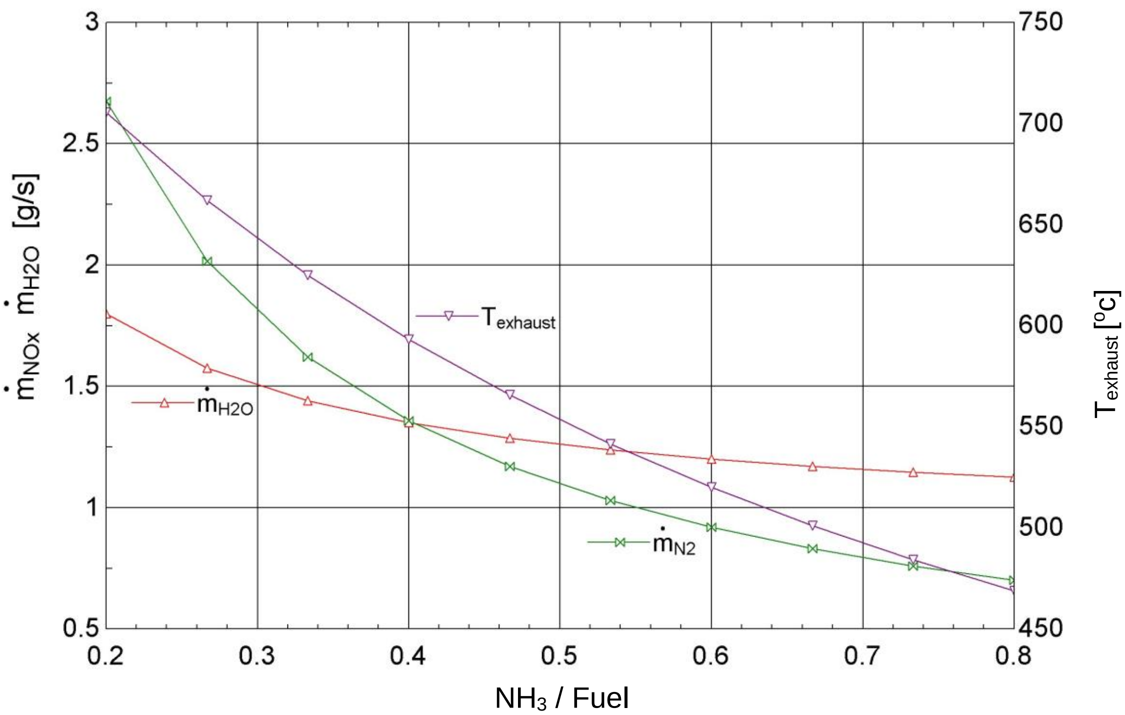

Figure 5.8: Effects of changing the ratio of the hydrogen ammonia blend on NO_x emissions

The effect of changing the ratio of the hydrogen ammonia blend on the exhaust emissions are plotted in Figure 5.8. Changing the ratio of the hydrogen ammonia blend starting from starting from 80% hydrogen and 20%ammonia to 20% hydrogen and 80% ammonia decreases the NO_x emissions starting from 2.57 g/s to 0.7 g/s. The decrease occurs by the increase in ammonia content even though it has nitrogen in its structure but still hydrogen itself causes more NO_x emissions. Eventhough the NO_x emissions occur the absence of CO_2 emissions reduces the negative impact towards the environment in comparison with the fossil fuel combustion emissions of CO_2. The reason why there are no CO_2 emissions lies on the fact that both fuel sources have no carbon print, which was the main aim of the studies but the reduction in power produce compared to other fossil fuel blends with ammonia favours the other fuel types to be used as combustion promoters.

5.3. Ammonia based gasoline blend

A parametric study is performed on the generator using gasoline and ammonia blend to assess the system performance with changing operating conditions such as changing the ammonia and gasoline molar flow rate entering the generator, varying the mass flow rate of ammonia entering the generator. The influence of changing the molar flow rate of ammonia supplied to engine on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.9. Changing ammonia molar flow rate from 0.01 mole/s to 0.1 mole/s that increases the power output of the generator from 2.901 kW to 3.722 kW. The same variation of molar variation resulted in an increase in the exergy destruction rate of the generator from 5.063 kW to 6.414 kW. Regarding the results for the overall energy and exergy efficiencies of the generator both slight increase from 29% to 29.07% and from 36.43% to 36.72% respectively.

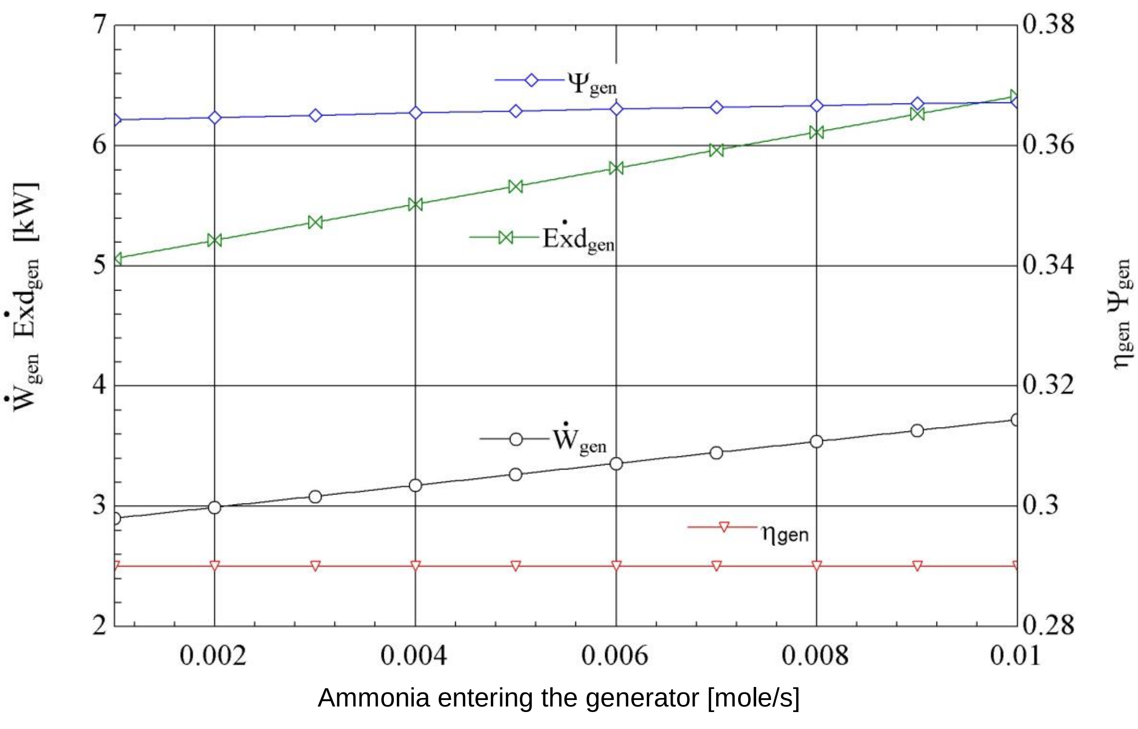

Figure 5.9: Effects of changing amount of ammonia entering engine on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for gasoline and ammonia fuel blend

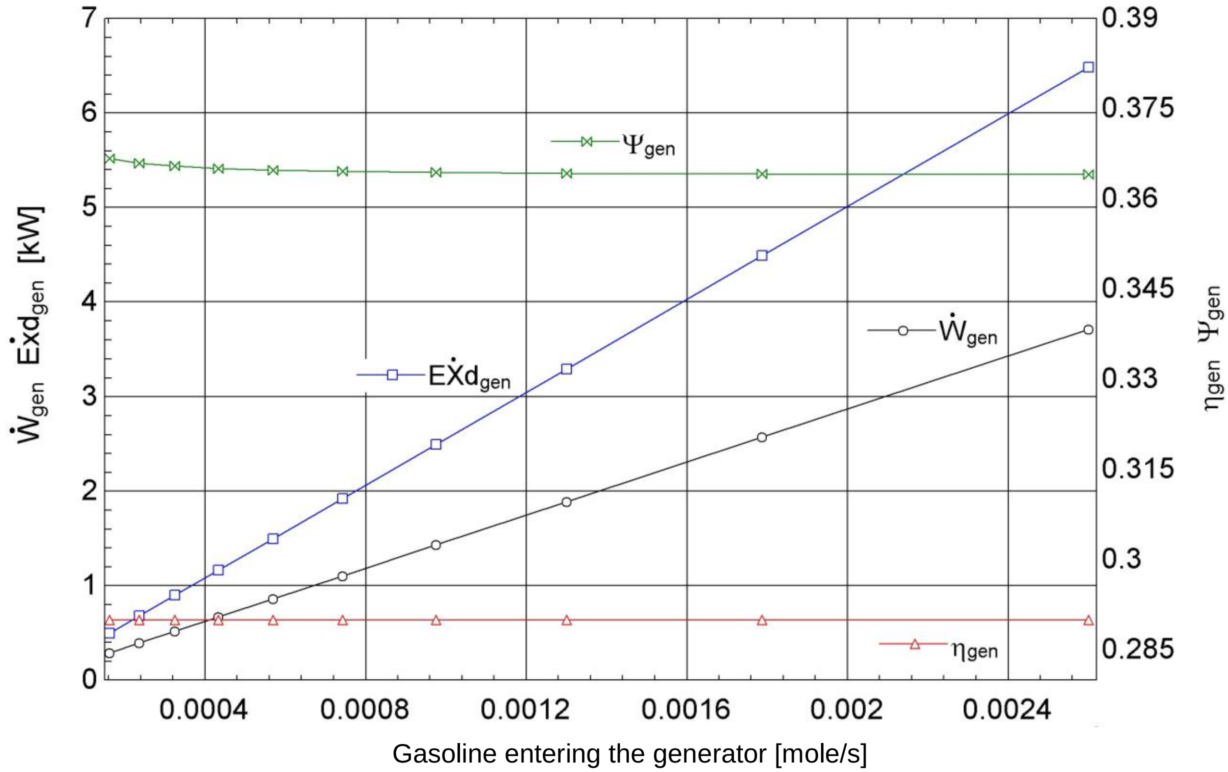

Figure 5.10: Effects of changing amount of gasoline entering engine on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for gasoline and ammonia fuel blend

Then for the ammonia gasoline blend another parametric study is performed by changing the molar flow rate of gasoline supplied to engine on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.10. Changing the gasoline molar flow rate from 0.04 mole/s to 0.24 mole/s the results for the overall energy and exergy efficiencies of the generator slightly reduce from 36.67% to 36.41% and from 28.82% to 29.01%.

The reduction in the efficiency can be related to the increase in the exergy destruction rate from 0.4967 kW to 6.485 kW. Regarding the power output of the generator it increases from 0.2876 kW to 3.712 kW. Which shows the impact of increasing the amount of ammonia fuel entering the generator will be increasing the power output at the same time.

Another parametric study have been performed on the generator by changing the ratio of the gasoline ammonia blend starting from 80% gasoline and 20% ammonia to 20% gasoline and 80% ammonia to plot the changes in the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator.

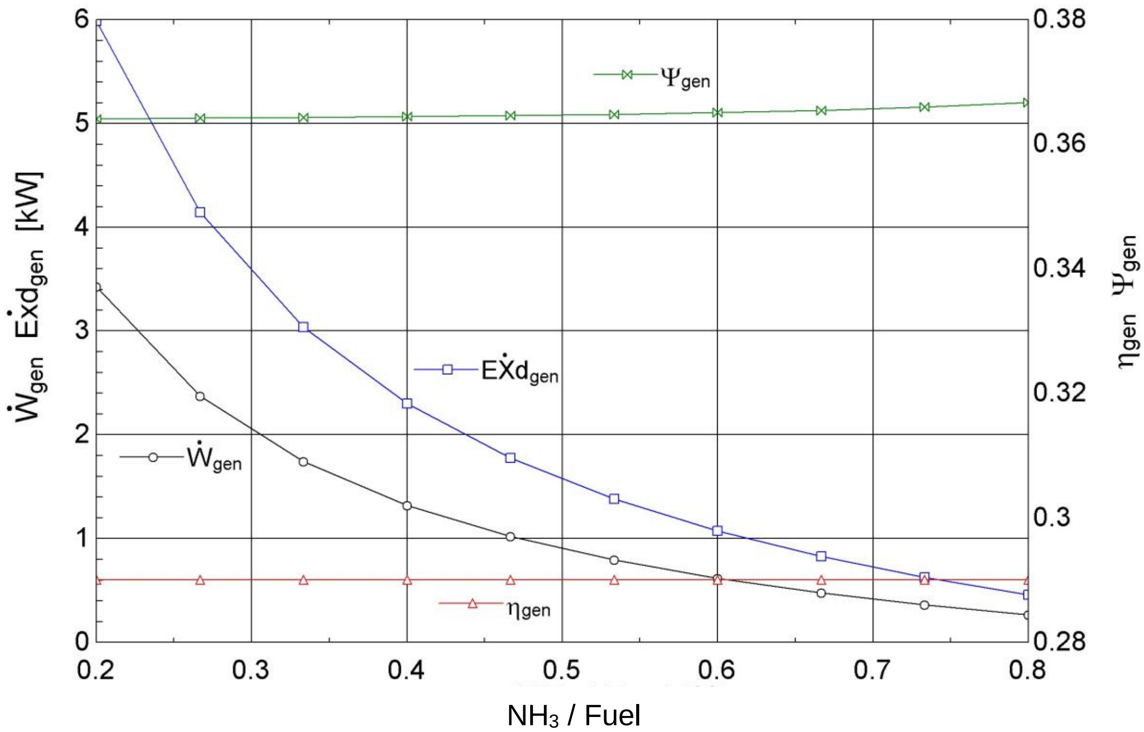

Figure 5.11: Effects of changing the ratio of the gasoline ammonia blend on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for gasoline and ammonia fuel blend

The effect of changing the ratio of the gasoline ammonia blend on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.11. Changing the ratio of the gasoline ammonia blend starting from 80% gasoline and 20% ammonia to 20% gasoline and 80% ammonia reduces the power output of the generator from 3.427 kW to 0.2655 kW. The same variation of molar variation resulted in a reduction in the exergy destruction rate of the generator from 5.986 kW to 0.4585 kW. Regarding the results for the overall energy and exergy efficiencies of the generator slightly increase from 29.01% to 29.06% and from 36.41% to 36.67% respectively. The increase in the efficiency can be interpreted by once again the quality content that gasoline offers.

Lastly another parametric study was performed on the generator model to see the influence of changing the ratio of the gasoline ammonia on CO_2 and NO_x emissions. During the studies once again the mass ratio of the gasoline ammonia blend was changes starting from 80% gasoline and 20% ammonia to 20% gasoline and 80% ammonia.

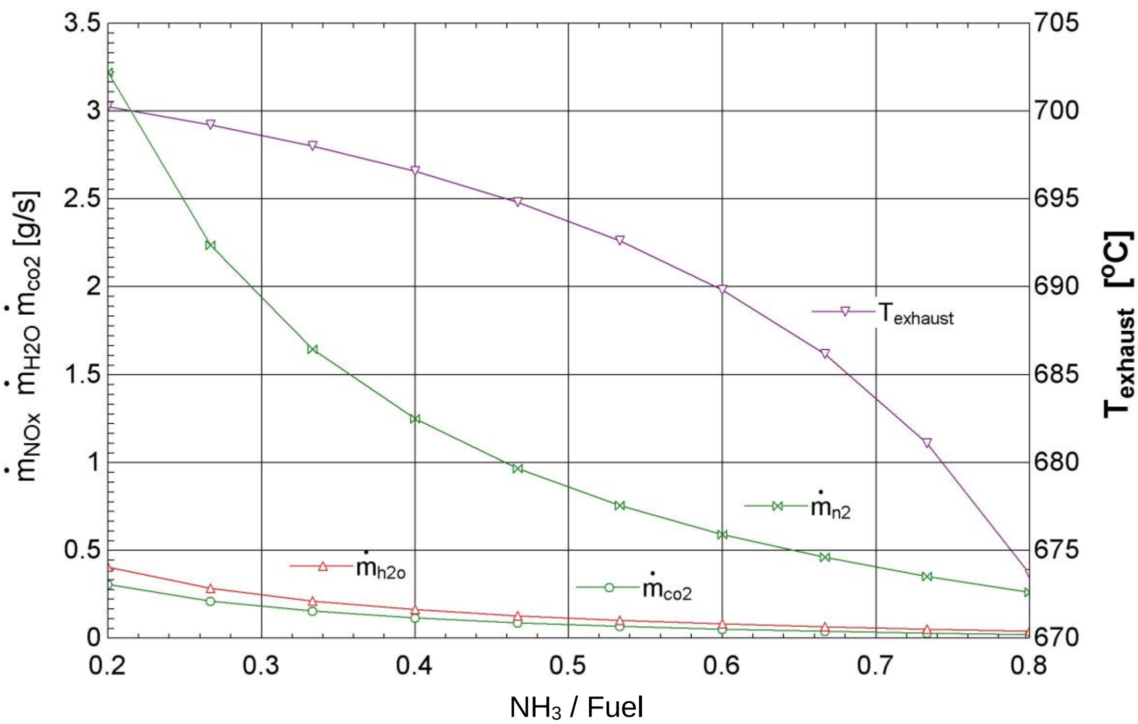

Figure 5.12: Effects of changing the ratio of the gasoline ammonia blend on CO_2 and NO_x emissions

The effect of changing the ratio of the gasoline ammonia blend on the exhaust emissions are plotted in Figure 5.12. Changing the ratio of the gasoline ammonia blend starting from 80% gasoline and 20% ammonia to 20% gasoline and 80% ammonia decreases the CO_2 emissions starting from 1.64 g/s to 1.28 g/s. The same variation of molar variation resulted in a reduction in NO_x emissions starting from 2.67 g/s to 0.69 g/s, respectively. The reduction in CO_2 occurs with the increase in ammonia ratio as it has no carbon print but at the same time the NO_x emissions were effected in a negative way with the increase in ammonia ratio as it contains nitrogen elements in the fuel. Eventhough the occurrence of NO_x emissions have increased the reduction in CO_2 emissions highly benefits the environment in comparison with the fossil fuel combustion emissions.

5.4. Ammonia based diesel blend

A parametric study is performed on the generator using diesel and ammonia blend to assess the system performance with changing operating conditions such as changing the ammonia and diesel molar flow rate entering the generator, varying the mass flow rate of ammonia entering the generator. The influence of changing the molar flow rate of ammonia supplied to engine on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.13. Changing ammonia molar flow rate from 0.01 to 0.1 mole/s increases the power output of the generator from 2.901 kW to 3.722 kW. The same variation of molar variation resulted in an upsurge in the exergy destruction rate of the generator from 5.063 kW to 6.414 kW. The results for the overall energy and exergy efficiencies of the generator changed from 28.01% to 28.07% and from 36.41% to 36.50% respectively. This reduction in the efficiency can be interpreted by the increase in the exergy destruction rate from 2.3 kw to 168 kW.

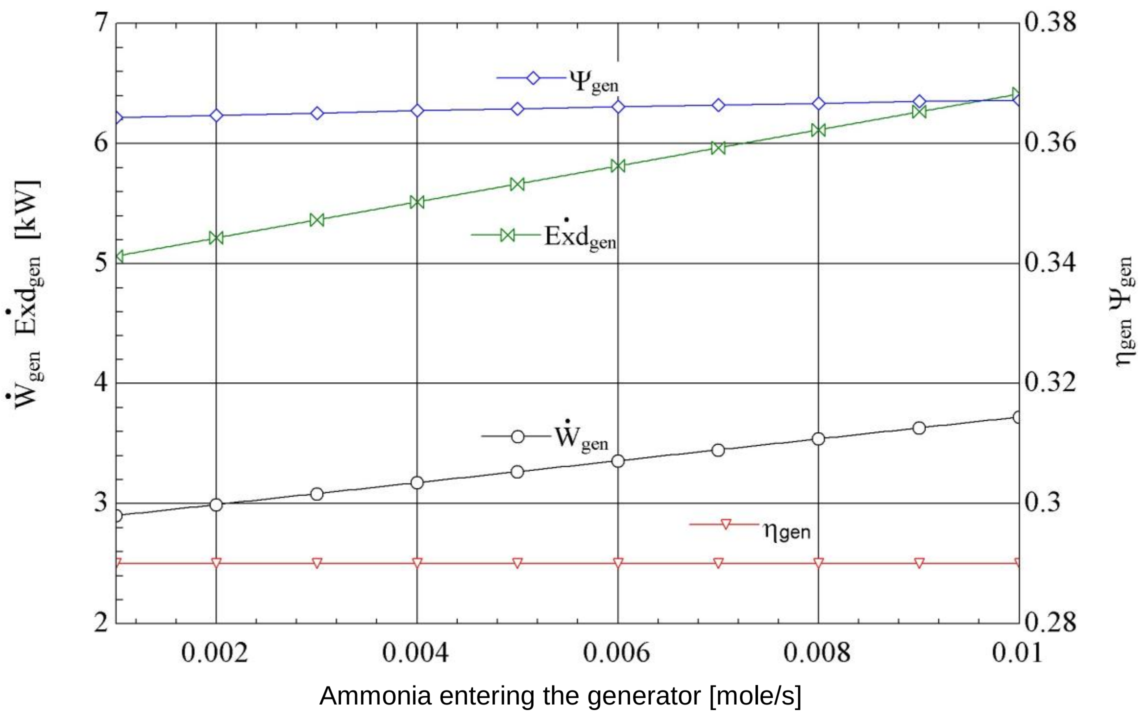

Figure 5.13: Effects of changing amount of ammonia entering engine on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for diesel and ammonia fuel blend

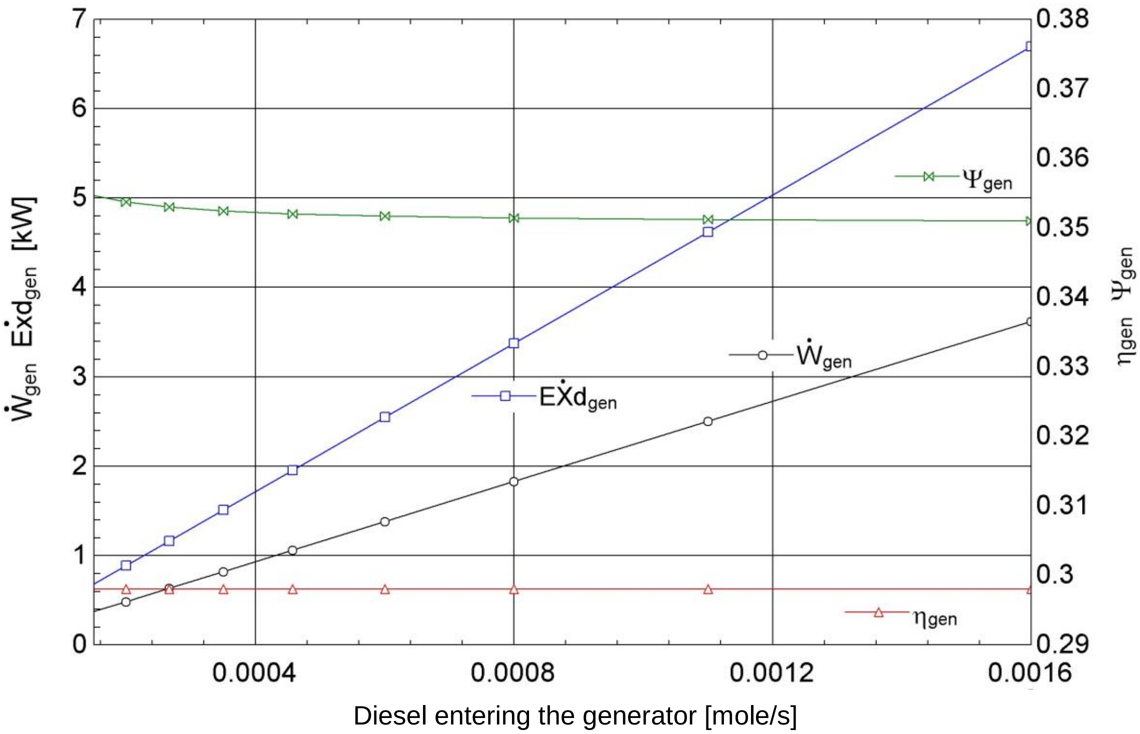

Figure 5.14: Effects of changing amount of diesel entering engine on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for diesel and ammonia fuel blend

Secondly for the ammonia diesel blend another parametric study is performed by changing the molar flow rate of diesel supplied to engine on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.14. Changing diesel molar flow rate from 0.0004 mole/s to 0.0016 mole/s the results for the overall energy and exergy efficiencies of the generator slightly reduced from 28.8% to 28.78% and from 35.5% to 35.01%.

The reduction in the efficiency can be related to the increase in the exergy destruction rate from 0.68 kW to 6.75 kW. The same variation resulted in an upsurge in the exergy destruction rate of the and at the same time the power output of the generator it increases from 0.465 kW to 3.76 kW. Which shows the impact of increasing the amount of ammonia fuel entering the power generator will be increasing the power output at the same time.

Another parametric study have been performed on the generator by changing the ratio of the diesel ammonia blend starting from 80% diesel and 20% ammonia to 20% diesel and 80% ammonia to plot the changes in the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator.

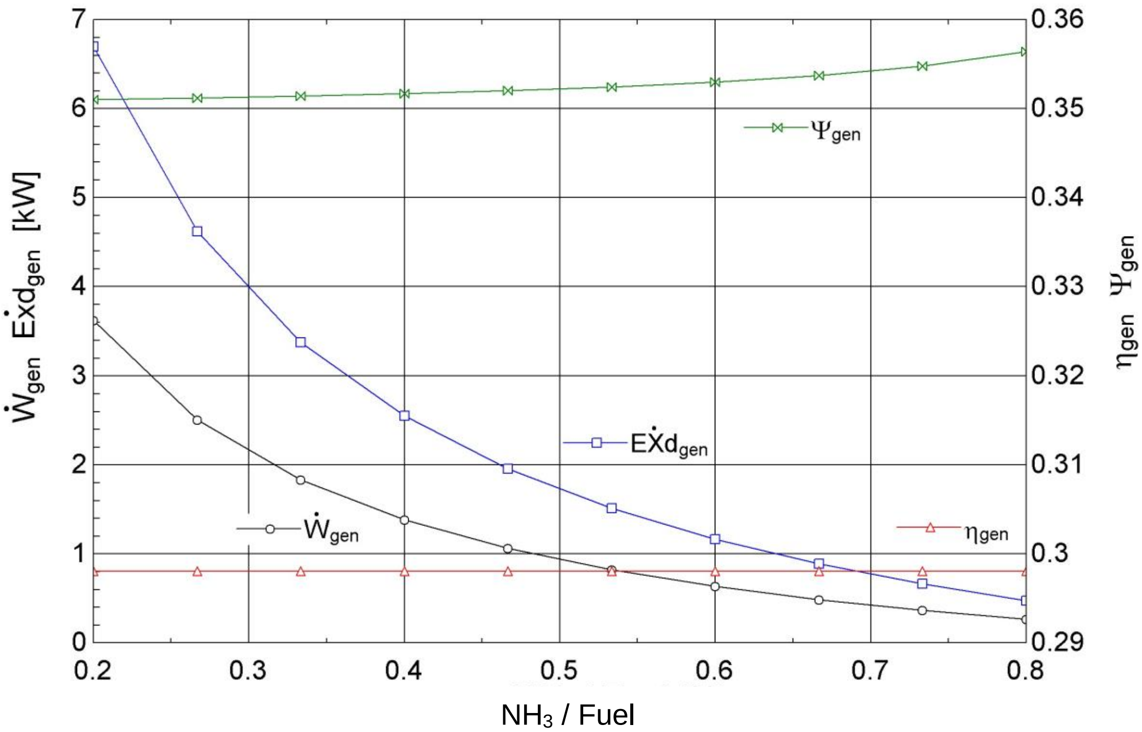

Figure 5.15: Effects of changing the ratio of the diesel ammonia blend on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for diesel and ammonia fuel blend

The effect of changing the ratio of the diesel ammonia blend on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.15. Changing the ratio of the diesel ammonia blend starting from 80% diesel and 20% ammonia to 20% diesel and 80% ammonia reduces the power output of the generator from 3.76 kW to 0.465 kW occuring as a result of low molar flow rates. The same variation of molar variation resulted in also a reduction in the exergy destruction rate of the generator from 6.89 kW to 0.648 kW. Regarding the results for the overall energy and exergy efficiencies of the generator slightly increase from 28.73% to 28.76% and from 35.05% to 35.41%.

Lastly another parametric study was performed on the generator model to see the influence of changing the ratio of the diesel ammonia on CO_2 and NO_x emissions. During the studies once again the ratio of the diesel ammonia blend was changes starting from 80% diesel and 20% ammonia to 20% diesel and 80% ammonia.

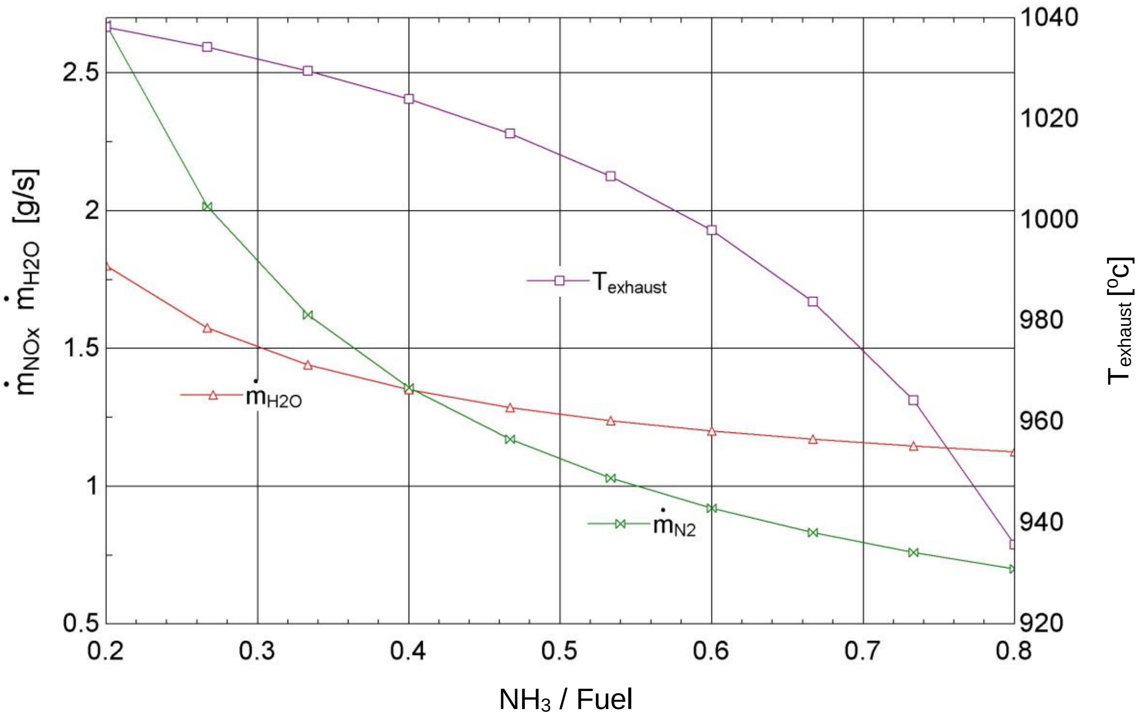

Figure 5.16: Effects of changing the ratio of the diesel ammonia blend on CO_2 and NO_x emissions

The effect of changing the ratio of the diesel ammonia blend on the exhaust emissions are plotted in Figure 5.16. Changing the ratio of the diesel ammonia blend starting from 80% diesel and 20% ammonia to 20% diesel and 80% ammonia reduces the CO_2 emissions starting from 1.63 g/s to 1.27 g/s. The same variation of molar variation resulted in a decrease in NO_x emissions starting from 2.57 g/s to 0.71 g/s respectively. The reduction in CO_2 occurs with the increase in ammonia ratio as it has no carbon print but at the same time the NO_x emissions were effected in a negative way with the increase in ammonia ratio as it contains nitrogen elements in the fuel. Eventhough the occurrence of NO_x emissions have increased the reduction in CO_2 emissions highly benefits the environment in comparison with the fossil fuel combustion emissions.

5.5. Ammonia based ethanol blend

A parametric study is performed on the generator using ethanol and ammonia blend to assess the system performance with changing operating conditions such as changing the ammonia and ethanol molar flow rate entering the generator, varying the mass flow rate of ammonia entering the generator. The influence of changing the molar flow rate of ammonia supplied to engine on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.17. Changing ammonia molar flow rate from 0.001 mole/s to 0.01 mole/s increases the power output of the generator from 2.98 kW to 3.72 kW. The same variation of molar variation resulted in an upsurge in the exergy destruction rate of the generator from 5.84 kW to 7.12 kW. The results for the overall energy and exergy efficiencies of the generator increased slightly from 27.06% to 27.17% from 33.06% to 33.23% and respectively. This slight increase in the efficiency can be interpreted by the increase in ammonia entering the generator.

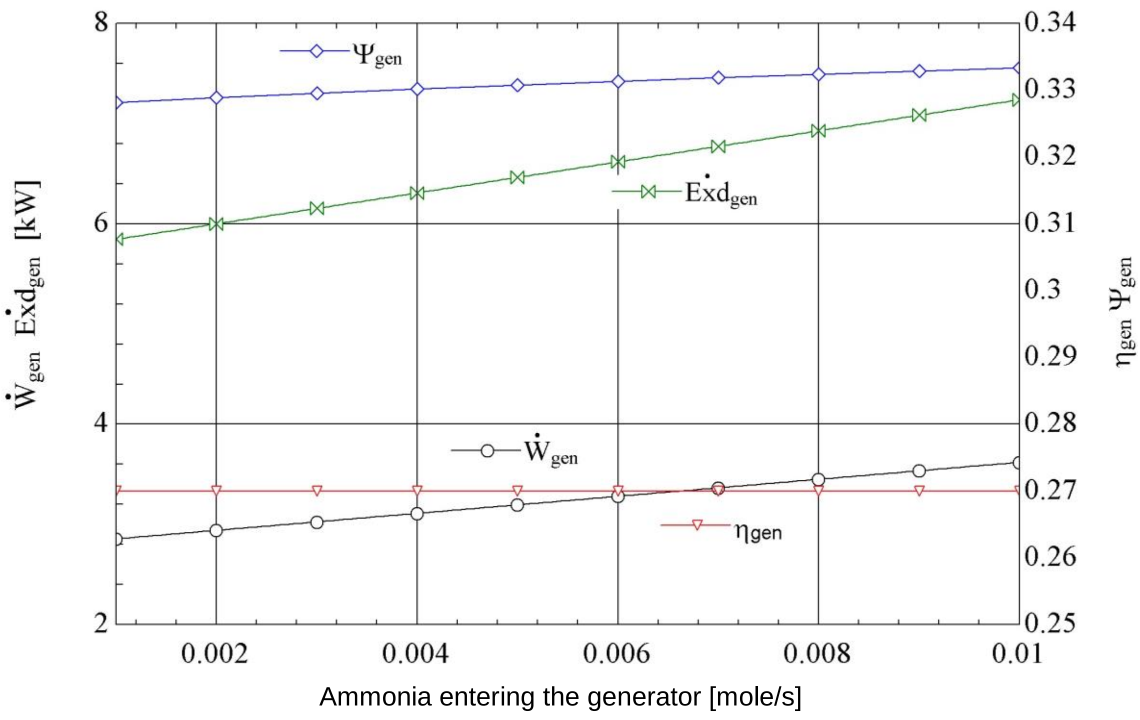

Figure 5.17: Effects of changing amount of ammonia entering engine on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for ethanol and ammonia fuel blend

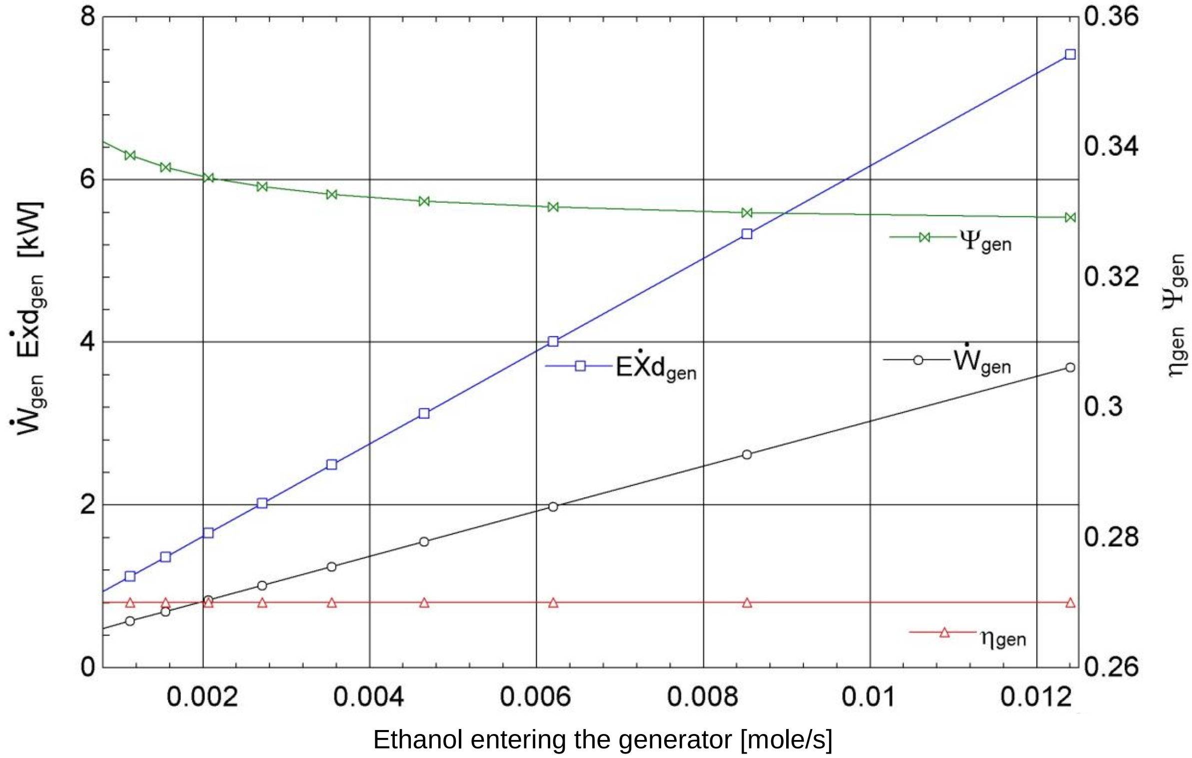

Figure 5.18: Effects of changing amount of ethanol entering engine on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for ethanol and ammonia fuel blend

Secondly for the ammonia ethanol blend another parametric study is performed by changing the molar flow rate of ethanol supplied to engine on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.18. Changing ethanol molar flow rate from 0.0001 mole/s to 0.012 mole/s the results for the overall energy and exergy efficiencies of the generator reduced from 33.06% to 33.02 % and from 27.13% to 27.07%, respectively.

The reduction in the efficiency can be related to the increase in the exergy destruction rate from 0.92 kW to 7.53 kW. The power output of the generator increases from 0.48 kW to 3.68 kW. Which shows the impact of increasing the amount of ammonia fuel entering the power generator setup will be increasing the power output at the same time.

Another parametric study have been performed on the generator by changing the ratio of the ethanol ammonia blend starting from 80% ethanol and 20% ammonia to 20% ethanol and 80% ammonia to plot the changes in the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator.

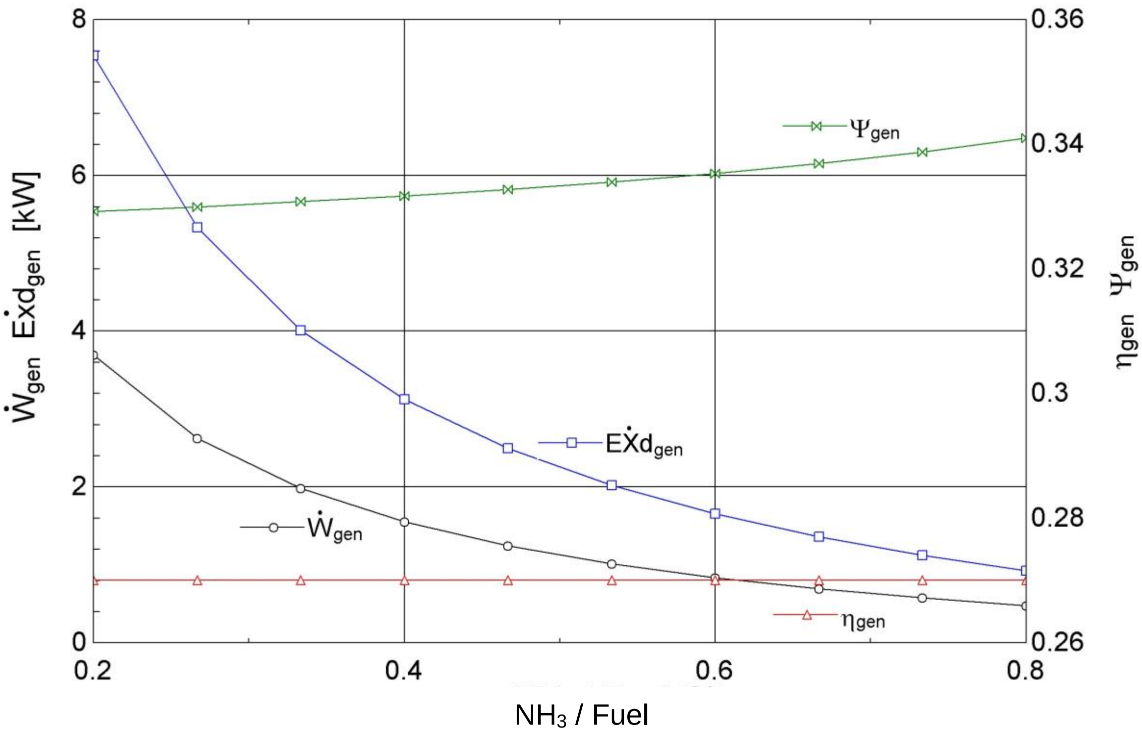

Figure 5.19: Effects of changing the ratio of the ethanol ammonia blend on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for ethanol and ammonia fuel blend

The effect of changing the ratio of the ethanol ammonia blend on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.19. Changing the ratio of the ethanol ammonia blend starting from 80% ethanol and 20%ammonia to 20% ethanol and 80% ammonia increases the power output of the generator from 0.49 kW to 3.70 kW. The same variation of molar variation resulted in an upsurge in the exergy destruction rate of the generator from 0.92 kW to 7.54 kW. Regarding the results for the overall energy and exergy efficiencies of the generator reduced from 27.13% to 27.04% and from 34.1% to 32.9% respectively. This reduction in the efficiency can be interpreted by the increase in the exergy destruction rate.

Lastly another parametric study was performed on the generator model to see the influence of changing the ratio of the ethanol ammonia on CO_2 and NO_x emissions. During the studies once again the mass ratio of the ethanol ammonia blend was changes starting from 80% ethanol and 20% ammonia to 20% ethanol and 80% ammonia.

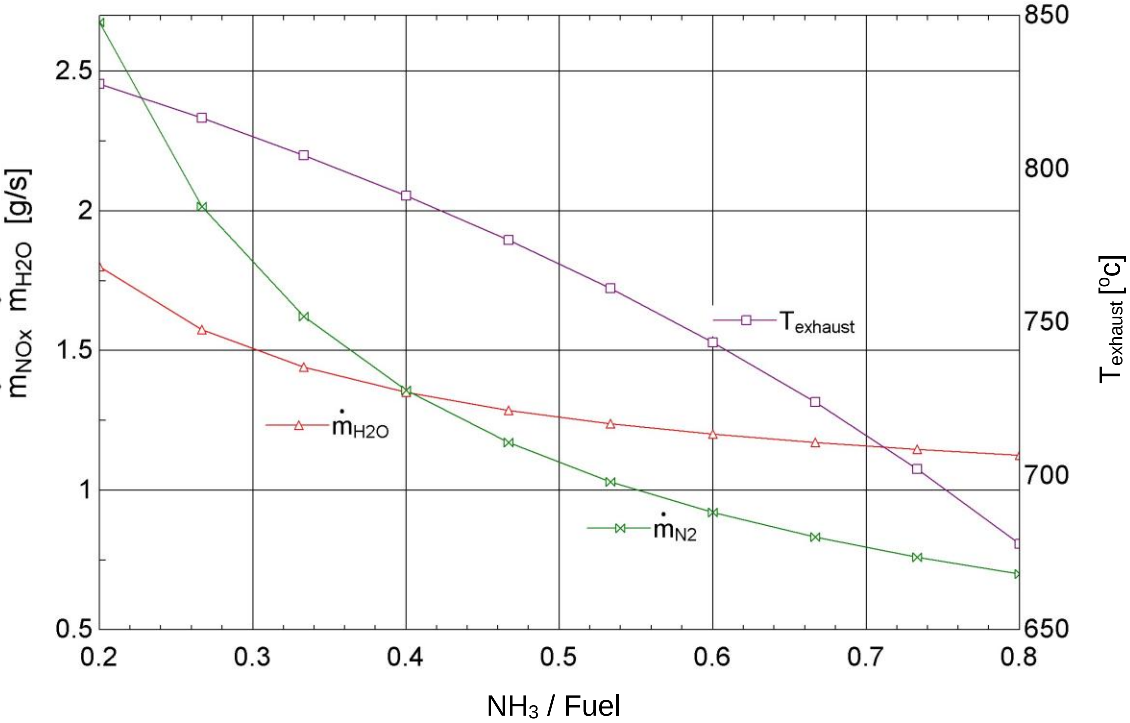

Figure 5.20: Effects of changing the ratio of the ethanol ammonia blend on CO_2 and NO_x emissions

The effect of changing the mass ratio of the ethanol ammonia blend on the exhaust emissions are plotted in Figure 5.20. Changing the mass ratio of the ethanol ammonia blend starting from 80% ethanol and 20% ammonia to 20% ethanol and 80% ammonia decreases the CO_2 emissions starting from 1.60 g/s to 1.24 g/s. The same variation of molar variation resulted in an decrease in NO_x emissions starting from 2.56 g/s to 0.41 g/s, respectively. The reduction in CO_2 occurs with the increase in ammonia ratio as it has no carbon print but at the same time the NO_x emissions were effected in a negative way with the increase in ammonia ratio as it contains nitrogen elements in the fuel. Eventhough the occurrence of NO_x emissions have increased the reduction in CO_2 emissions highly benefits the environment in comparison with the fossil fuel combustion emissions.

5.6. Ammonia based methanol blend

A parametric study is performed on the generator using methanol and ammonia blend to assess the system performance with changing operating conditions such as changing the ammonia and methanol molar flow rate entering the generator, varying the mass flow rate of ammonia entering the generator. The influence of changing the molar flow rate of ammonia supplied to engine on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.21. Changing ammonia molar flow rate from 0.001 mole/s to 0.01 mole/s increases the power output of the generator from 2.85 kW to 3.58 kW. The same variation of molar variation resulted in an upsurge in the exergy destruction rate of the generator from 5.98 kW to 7.42 kW. Regarding the results for the overall energy and exergy efficiencies of the generator slightly increases from 25.81% to 25.84% and from 32.3% to 32.5% respectively.

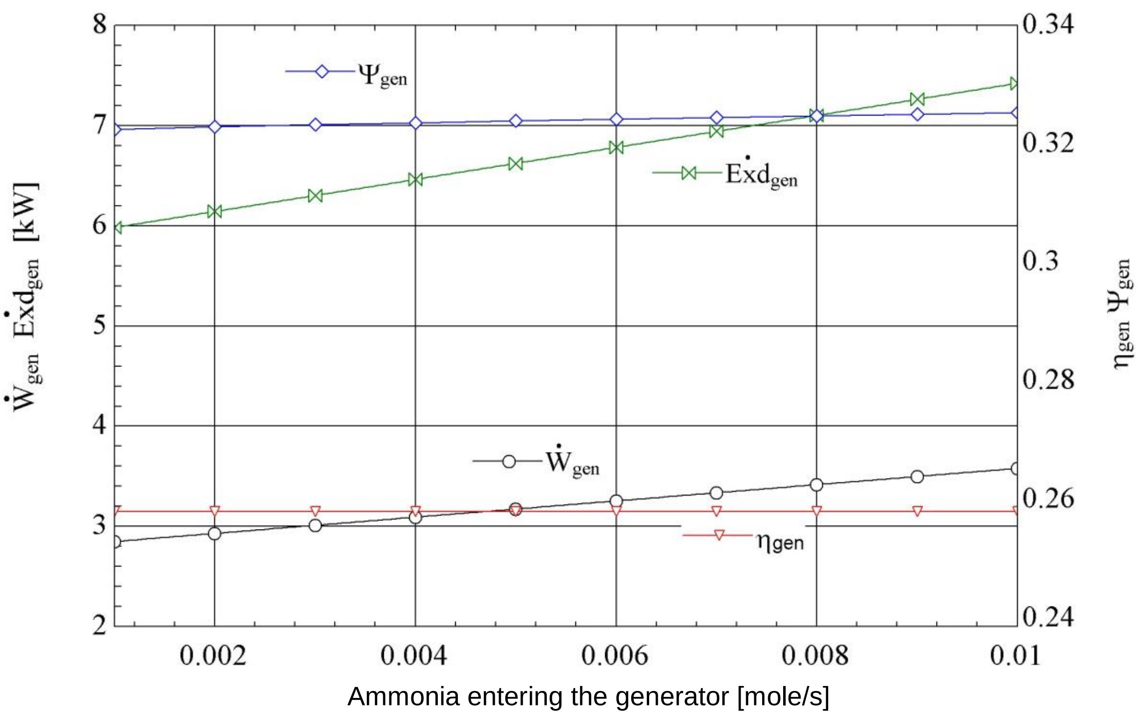

Figure 5.21: Effects of changing amount of ammonia entering engine on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for methanol and ammonia fuel blend

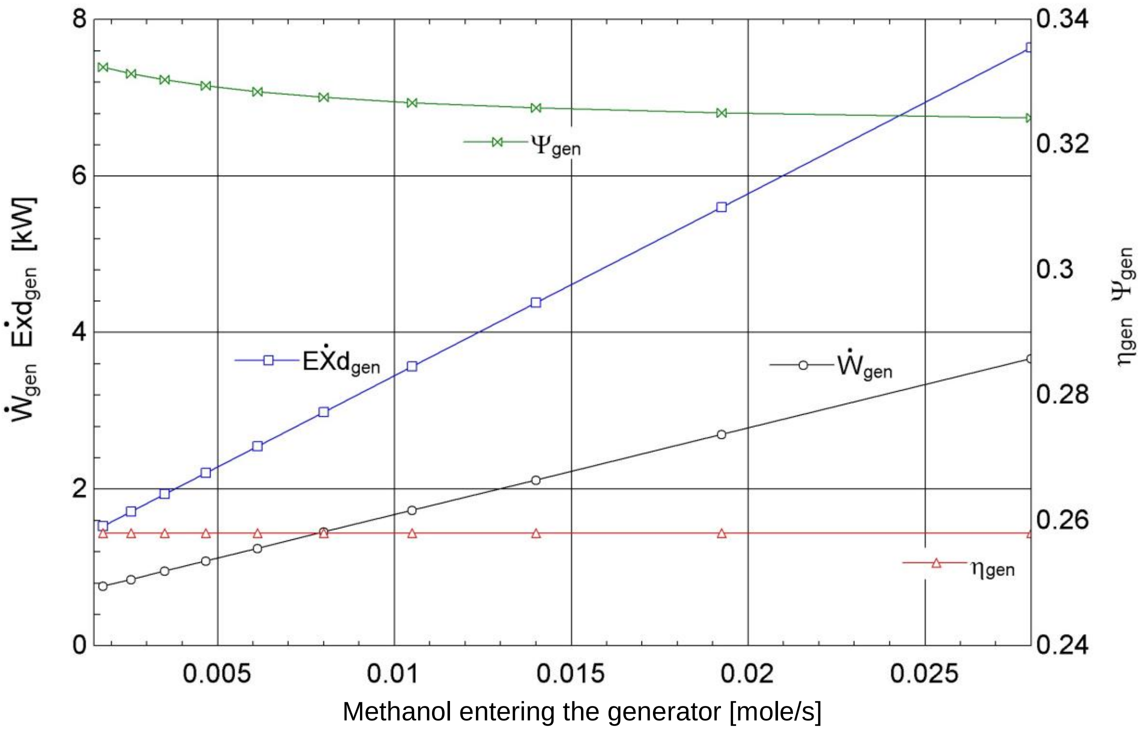

Figure 5.22: Effects of changing amount of methanol entering engine on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for methanol and ammonia fuel blend

Secondly for the ammonia methanol blend another parametric study is performed by changing the molar flow rate of methanol supplied to engine on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.22. Changing methanol molar flow rate from 0.002 mole/s to 0.03 mole/s the results for the overall energy and exergy efficiencies of the generator increases from 25.83% to 25.85% and from 32.4% to 33.2%.

The increase in the efficiency can be related to the reduction in the exergy destruction rate from 7.61 kW to 1.53 kW. The power output of the generator it increases from 0.67 kW to 3.67 kW. Which shows the impact of increasing the amount of ammonia fuel entering the power generator setup will be increasing the power output at the same time.

Another parametric study have been performed on the generator by changing the ratio of the methanol ammonia blend starting from 80% methanol and 20% ammonia to 20% methanol and 80% ammonia to plot the changes in the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator.

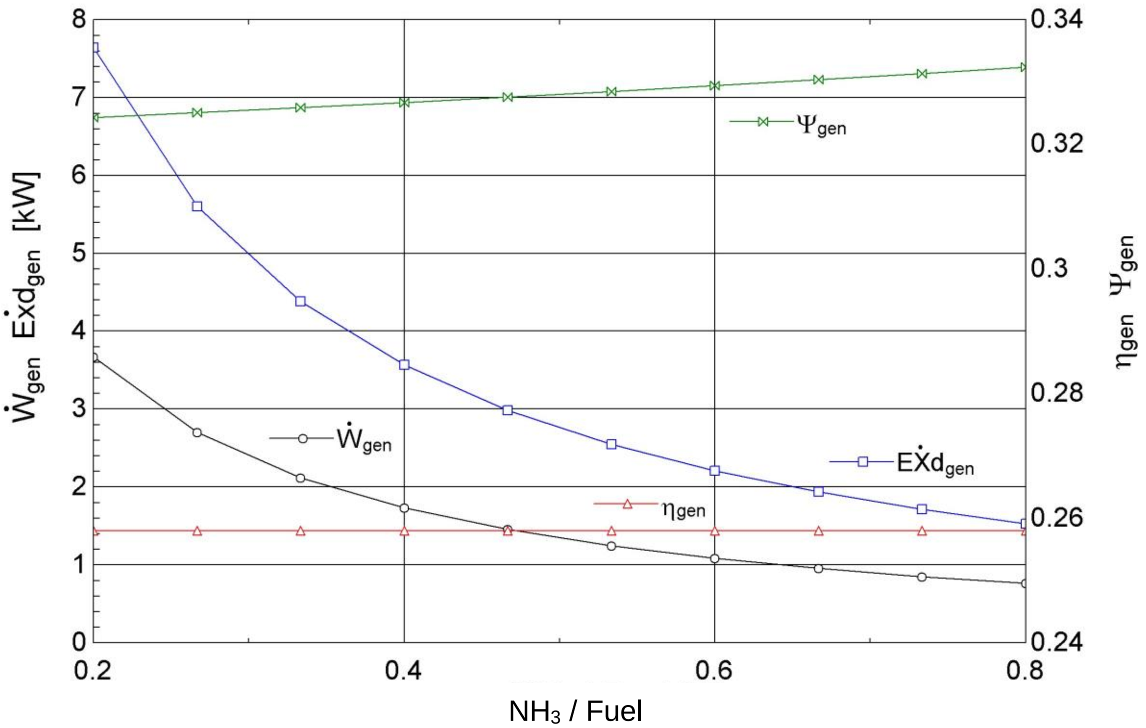

Figure 5.23: Effects of changing the ratio of the methanol ammonia blend on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for methanol and ammonia fuel blend

The effect of changing the mass ratio of the methanol ammonia blend on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.23. Changing the mass ratio of the methanol ammonia blend starting from 80% methanol and 20% ammonia to 20% methanol and 80% ammonia decreases the power output of the generator from 3.66 kW to 0.76 kW. The same variation of molar variation resulted in a reduction in the exergy destruction rate of the generator from 7.59 kW to 1.47 kW. The results for the overall energy and exergy efficiencies of the generator increased from 25.81% to 25.84% and from 32.4% to 33.02% respectively. This reduction in the efficiency can be interpreted by the increase in the exergy destruction rate of the generator.

Lastly another parametric study was performed on the generator model to see the influence of changing the ratio of the methanol ammonia to CO_2 and NO_x emissions. During the studies once again the ratio of the methanol ammonia blend was changes starting from 80% methanol and 20% ammonia to 20% methanol and 80% ammonia.

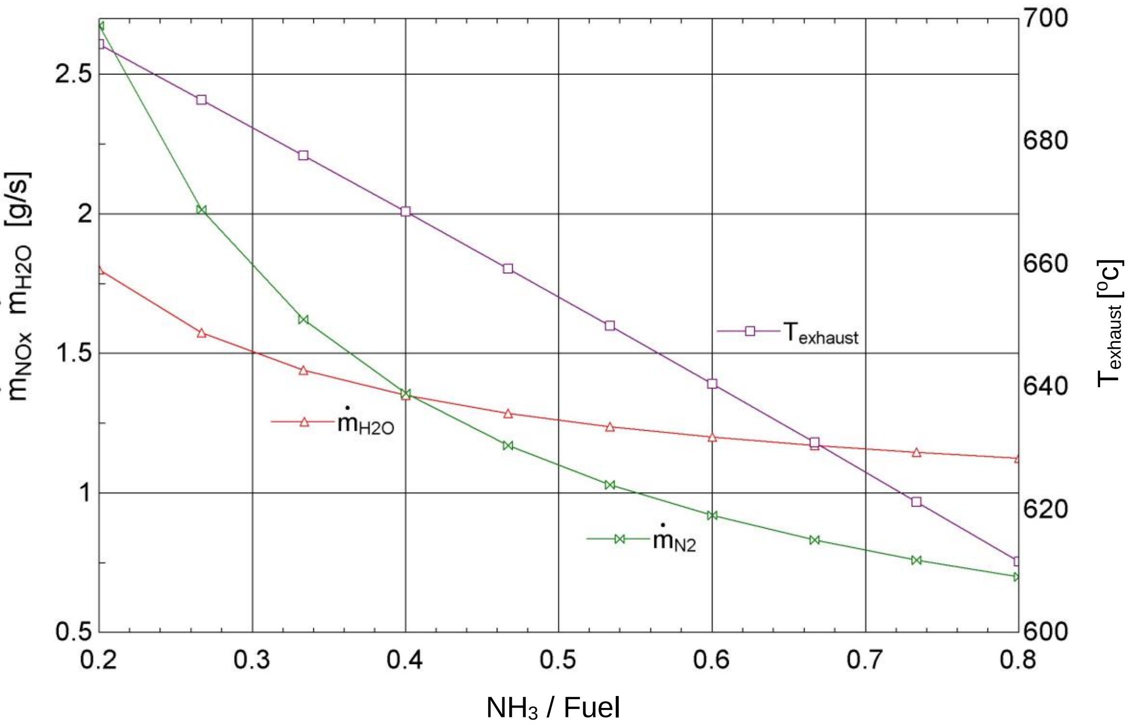

Figure 5.24: Effects of changing the ratio of the methanol ammonia blend on CO_2 and NO_x emissions

The effect of changing the mass ratio of the methanol ammonia blend on the exhaust emissions are plotted in Figure 5.24. Changing the mass ratio of the methanol ammonia blend starting from starting from 80% methanol and 20% ammonia to 20% methanol and 80% ammonia reduces the CO_2 emissions starting from 1.6 g/s to 1.22 g/s. The same variation of molar variation resulted in a change in NO_x emissions starting from 2.72 g/s to 0.75 g/s respectively. The reduction in CO_2 occurs with the increase in ammonia ratio as it has no carbon print but at the same time the NO_x emissions were effected in a negative way with the increase in ammonia ratio as it contains nitrogen elements in the fuel.

5.7. Ammonia based propane blend

A parametric study is performed on the generator using propane and ammonia blend to assess the system performance with changing operating conditions such as changing the ammonia and propane molar flow rate entering the generator, varying the mass flow rate of ammonia entering the generator. The influence of changing the molar flow rate of ammonia supplied to engine on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.25. Changing ammonia molar flow rate from 0.001 mole/s to 0.01 mole/s increases the power output of the generator from 2.93 kW to 3.72 kW. The same variation of molar variation resulted in an upsurge in the exergy destruction rate of the generator from 5.49 kW to 6.87 kW. Regarding the results for the overall energy and exergy efficiencies of the generator slightly increases from 27.9% to 27.92% and from 34.8% to 35.1% respectively.

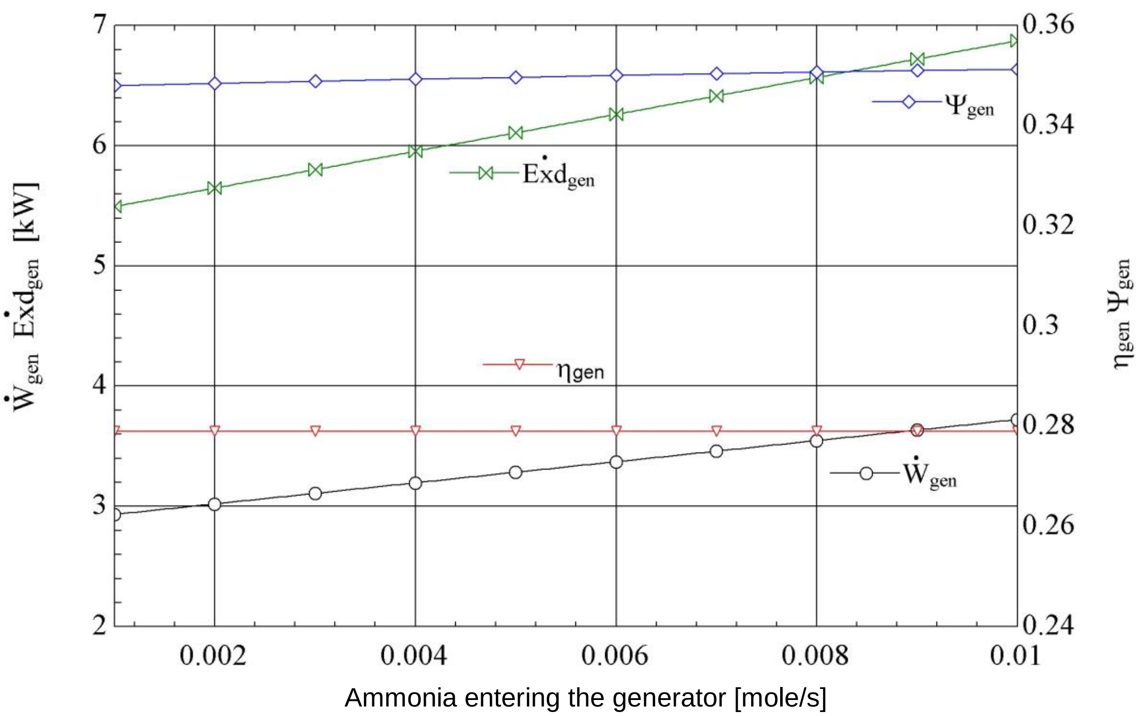

Figure 5.25: Effects of changing amount of ammonia entering engine on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for propane and ammonia fuel blend

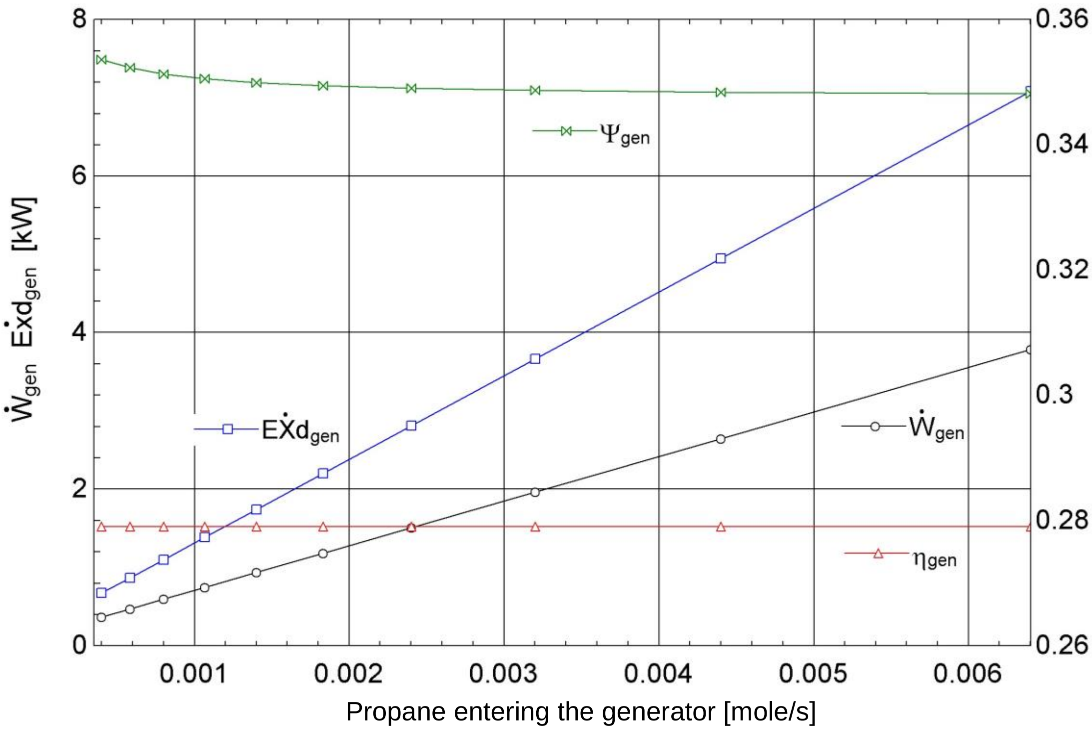

Figure 5.26: Effects of changing amount of propane entering engine on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for propane and ammonia fuel blend

Secondly for the ammonia propane blend another parametric study is performed by changing the molar flow rate of propane supplied to engine on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.26. Changing propane molar flow rate from 0.001 mole/s to 0.007 mole/s the results for the overall energy and exergy efficiencies of the generator increased from 27.9% to 28.03% and from 34.8% to 35.8%.

The increse in the efficiency can be related to the reduction in the exergy destruction rate from 7.10 kW to 0.67 kW. The same variation of molar variation resulted in an upsurge in the exergy destruction rate of the generator. The power output of the generator decreases from 3.78 kW to 0.37 kW. Which shows the impact of increasing the amount of ammonia fuel entering the power generator setup will be increasing the power output at the same time.

Another parametric study have been performed on the generator by changing the ratio of the propane ammonia blend starting from 80% propane and 20% ammonia to 20% propane and 80% ammonia to plot the changes in the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator.

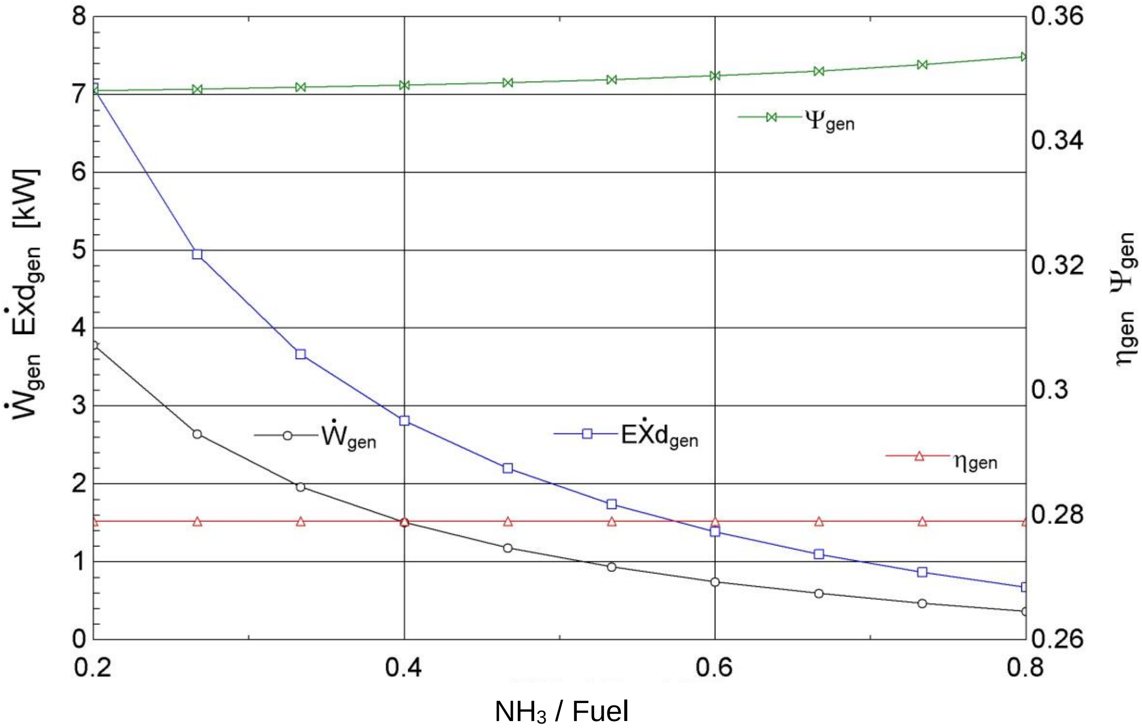

Figure 5.27: Effects of changing the ratio of the propane ammonia blend on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for propane and ammonia fuel blend

The effect of changing the mass ratio of the propane ammonia blend on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.27. Changing the ratio of the propane ammonia blend starting from 80% propane and 20% ammonia to 20% propane and 80% ammonia decreases the power output of the generator from 3.78 kW to 0.37 kW as the molar flow rates of the fuels are low. The same variation of molar variation resulted in a reduction in the exergy destruction rate of the generator from 7.80 kW to 0.673 kW. Regarding the results for the overall energy and exergy efficiencies of the generator increased from 27.9% to 29.97% and from 34.8% to 35.36% respectively. This increase in the efficiency can be interpreted by the decrease in the exergy destruction rate of the generator.

Lastly another parametric study was performed on the generator model to see the influence of changing the mass ratio of the propane ammonia on CO_2 and NO_x emissions. During the studies once again the mass ratio of the propane ammonia blend was changes starting from 80% propane and 20% ammonia to 20% propane and 80% ammonia.

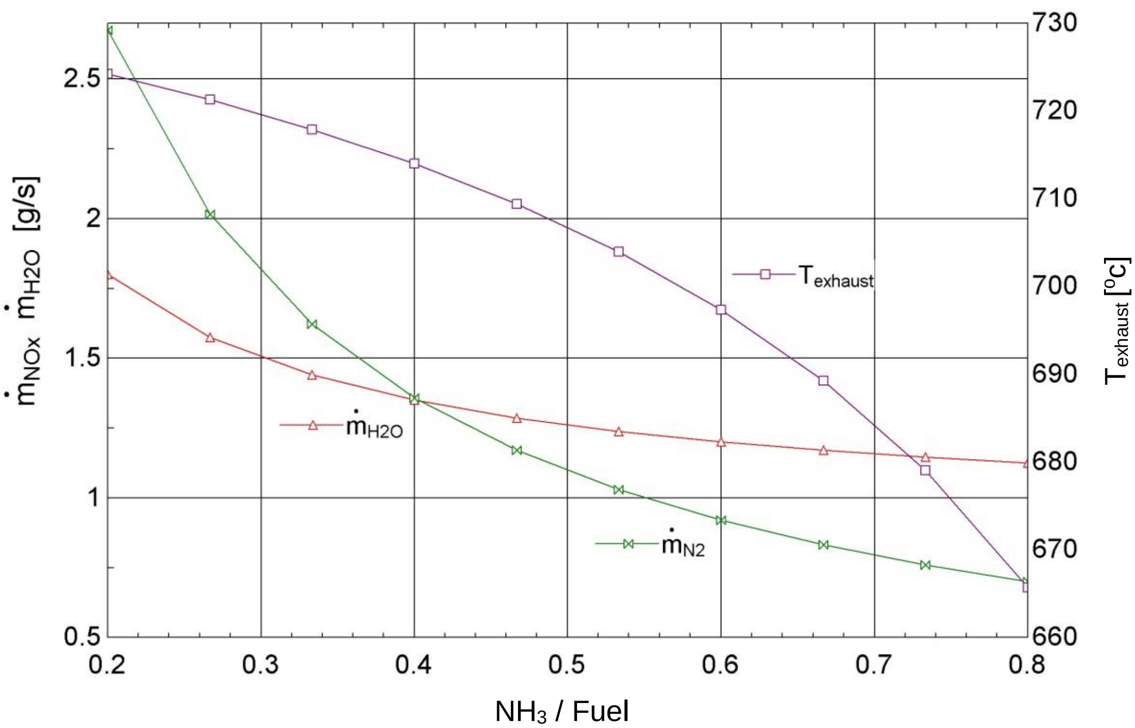

Figure 5.28: Effects of changing the ratio of the propane ammonia blend on CO_2 and NO_x emissions

The effect of changing the mass ratio of the propane ammonia blend on the exhaust emissions are plotted in Figure 5.28. Changing the mass ratio of the propane ammonia blend starting from 80% propane and 20% ammonia to 20% propane and 80% ammonia decreases the CO_2 emissions starting from 1.59 g/s to 1.18 g/s. The same variation of molar variation resulted in an decrease in NO_x emissions starting from 2.7 g/s to 0.74 g/s respectively. The reduction in CO_2 occurs with the increase in ammonia ratio as it has no carbon print but at the same time the NO_x emissions were effected in a negative way with the increase in ammonia ratio as it contains nitrogen elements in the fuel. Eventhough the occurrence of NO_x emissions have increased the reduction in CO_2 emissions highly benefits the environment in comparison with the fossil fuel combustion emissions.

5.8. Ammonia based butane blend

A parametric study is performed on the generator using butane and ammonia blend to assess the system performance with changing operating conditions such as changing the ammonia and propane molar flow rate entering the generator, varying the mass flow rate of ammonia entering the generator. The influence of changing the molar flow rate of ammonia supplied to engine on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.29. Changing ammonia molar flow rate from 0.001 to 0.01 mole/s increases the power output of the generator from 2.97 kW to 3.69 kW. The same variation of molar variation resulted in an upsurge in the exergy destruction rate of the generator from 5.97 kW to 7.32 kW. The results for the overall energy and exergy efficiencies of the generator slightly increases from 26.22% to 26.29% and from 31.8% to 34.5% respectively.

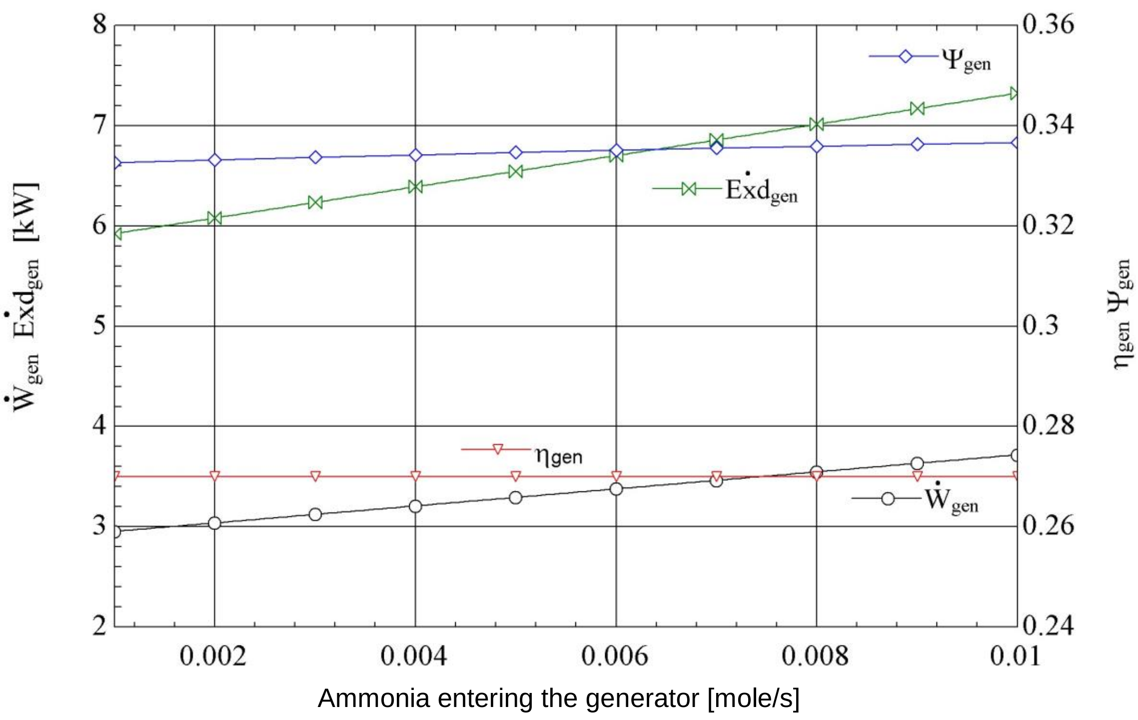

Figure 5.29: Effects of changing amount of ammonia entering engine on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for butane and ammonia fuel blend

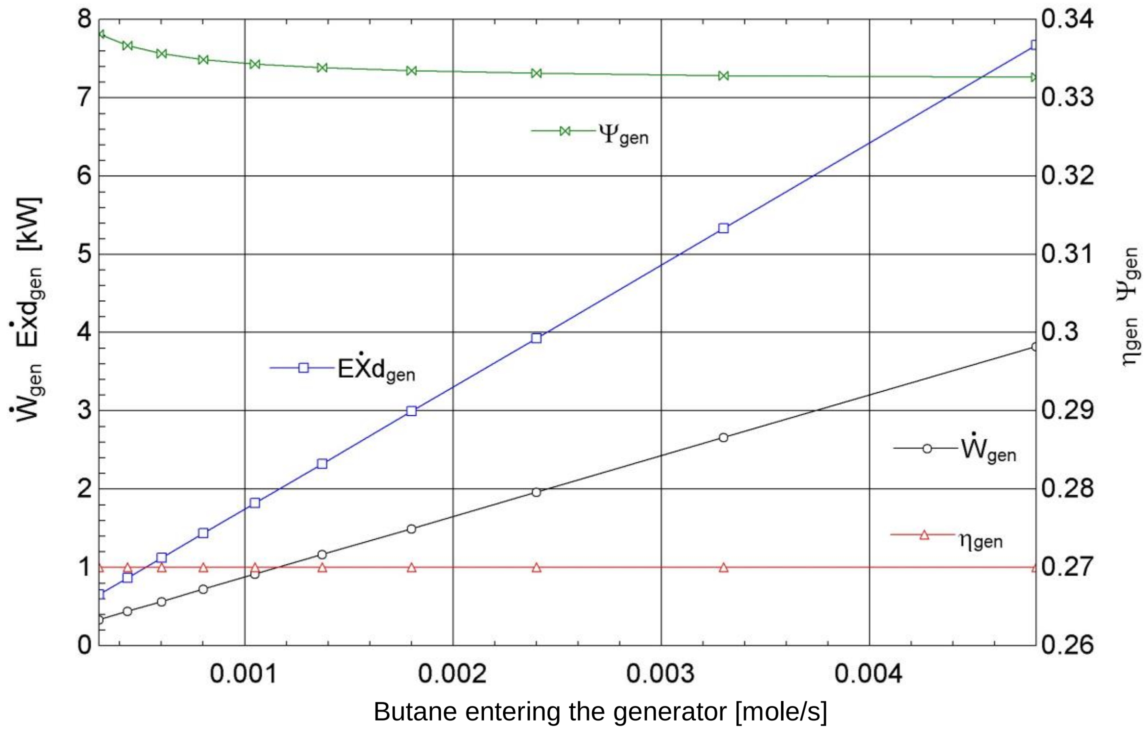

Figure 5.30: Effects of changing amount of butane entering engine on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for butane and ammonia fuel blend

Secondly for the ammonia butane blend another parametric study is performed by changing the molar flow rate of butane supplied to engine on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.30. Changing butane molar flow rate from 0.001 mole/s to 0.007 mole/s the results for the overall energy and exergy efficiencies of the generator decreased from 26.9% to 26.86% and from 33.98% to 33.8%.

The reduction in the efficiency can be related to the increase in the exergy destruction rate from 0.73 kW to 7.82 kW. The same variation of molar variation resulted in an upsurge the power output of the generator from 0.78 kW to 3.75 kW. Which shows the impact of increasing the amount of ammonia fuel entering the generator will be increasing the power output at the same time.

Another parametric study have been performed on the generator by changing the ratio of the butane ammonia blend starting from 80% butane and 20% ammonia to 20% butane and 80% ammonia to plot the changes in the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator.

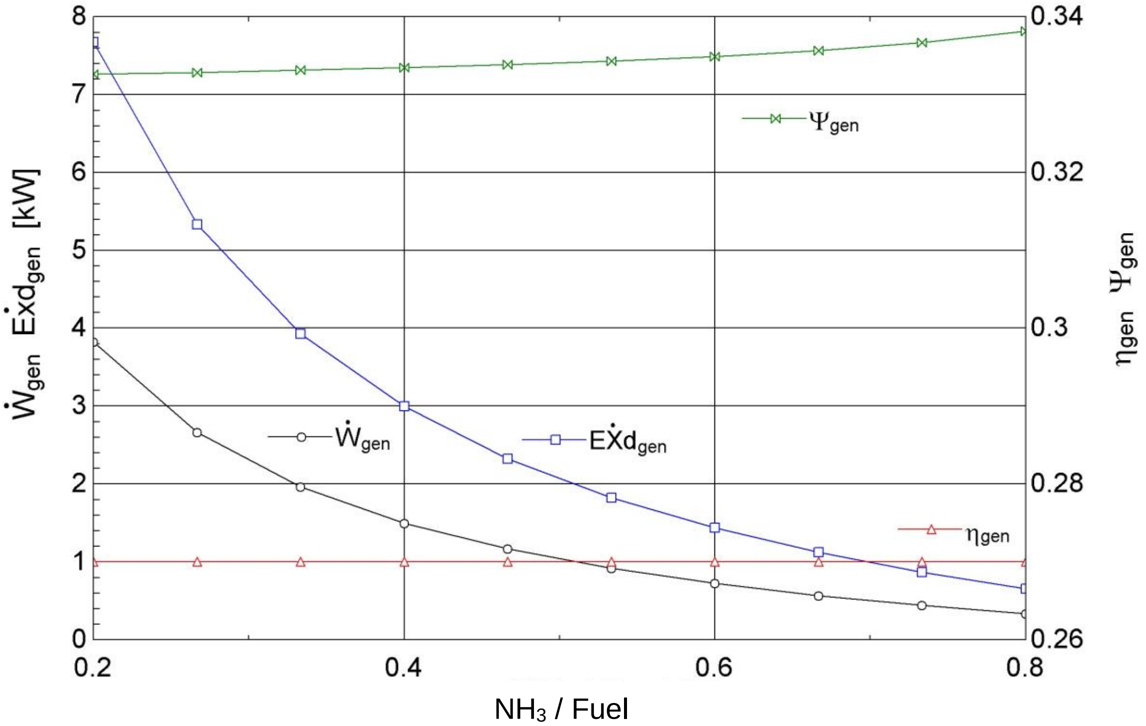

Figure 5.31: Effects of changing the ratio of the butane ammonia blend on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for butane and ammonia fuel blend

The effect of changing the mass ratio of the butane ammonia blend on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.31. Changing the ratio of the butane ammonia blend starting from 80% butane and 20% ammonia to 20% butane and 80% ammonia decreases the power output of the generator from 3.74 kW to 0.35 kW. The same variation of molar variation resulted in a reduction in the exergy destruction rate of the generator from 7.81 kW to 0.665 kW. Regarding the results for the overall energy and exergy efficiencies of the generator increased from 26.9% to 27.17% and from 33.2% to 33.96% respectively. This increase in the efficiency can be interpreted by the decrease in the exergy destruction rate of the generator.

Lastly another parametric study was performed on the generator model to see the influence of changing the mass ratio of the butane ammonia on CO_2 and NO_x emissions. During the studies once again the mass ratio of the propane ammonia blend was changes starting from 80% butane and 20% ammonia to 20% butane and 80% ammonia.

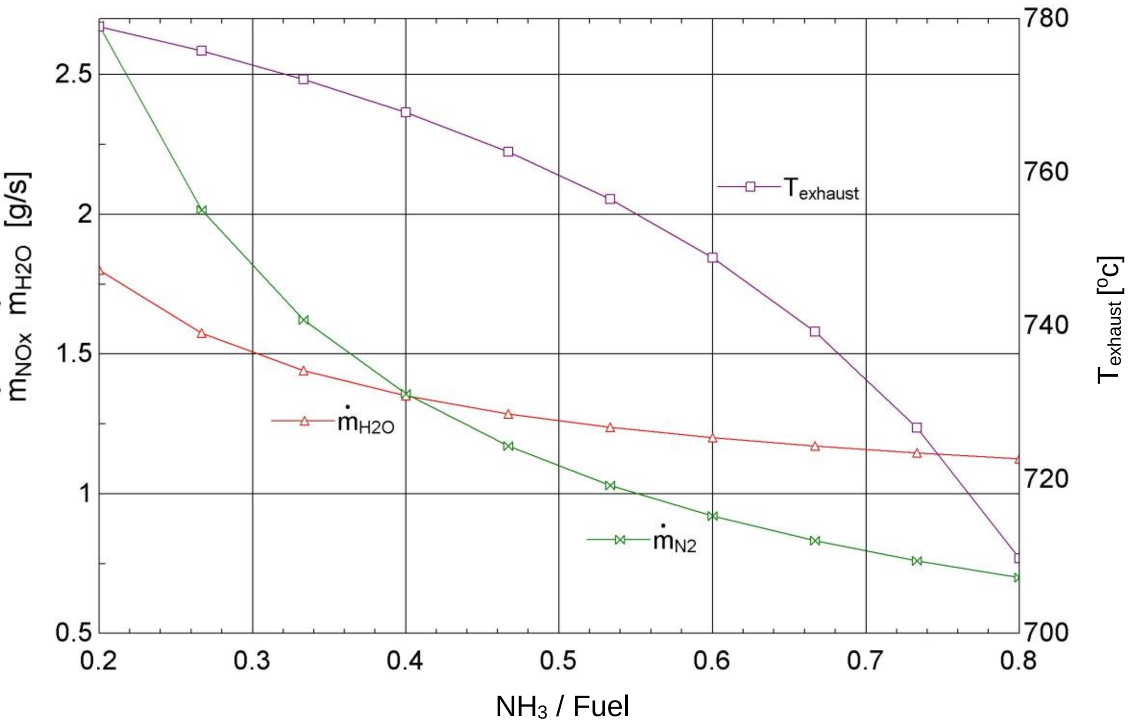

Figure 5.32: Effects of changing the ratio of the butane ammonia blend on CO_2 and NO_x emissions

The effect of changing the mass ratio of the butane ammonia blend on the exhaust emissions are plotted in Figure 5.32. Changing the mass ratio of the butane ammonia blend starting from 80% butane and 20% ammonia to 20% butane and 80% ammonia reduces the CO_2 emissions starting from 1.61 g/s to 1.25 g/s. The same variation of molar variation resulted in an deccrease in NO_x emissions starting from 2.6 g/s to 0.41 g/s respectively. The reduction in CO_2 occurs with the increase in ammonia ratio as it has no carbon print but at the same time the NO_x emissions were effected in a negative way with the increase in ammonia ratio as it contains nitrogen elements in the fuel. Eventhough the occurrence of NO_x emissions have increased the reduction in CO_2 emissions highly benefits the environment in comparison with the fossil fuel combustion emissions.

5.9. Ammonia based natural gas blend

A parametric study is performed on the generator using natural gas and ammonia blend to assess the system performance with changing operating conditions such as changing the ammonia and propane molar flow rate entering the generator, varying the mass flow rate of ammonia entering the generator. The influence of changing the molar flow rate of ammonia supplied to engine on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.33. Changing ammonia molar flow rate from 0.001 to 0.01 mole/s increases the power output of the generator from 3.03 kW to 3.74 kW. The same variation of molar variation resulted in an upsurge in the exergy destruction rate of the generator from 6.41 kW to 8.86 kW. Regarding the results for the overall energy and exergy efficiencies of the generator slightly increases from 26.71% to 26.73% and from 31.8% to 32.1% respectively.

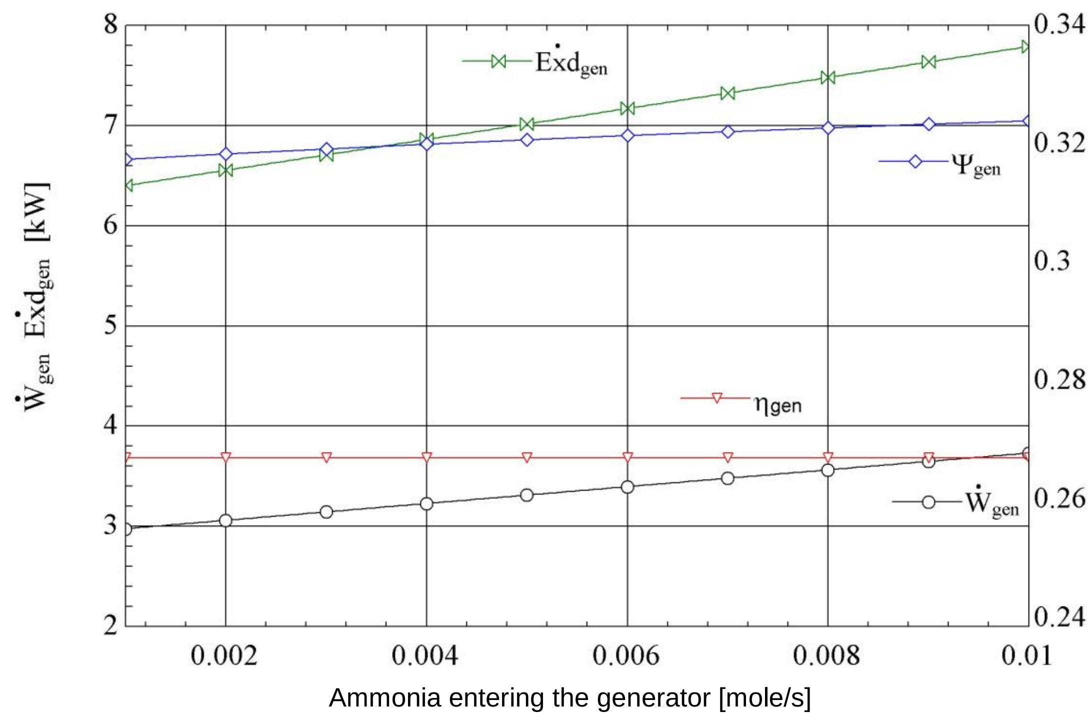

Figure 5.33: Effects of changing amount of ammonia entering engine on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for natural gas and ammonia fuel blend

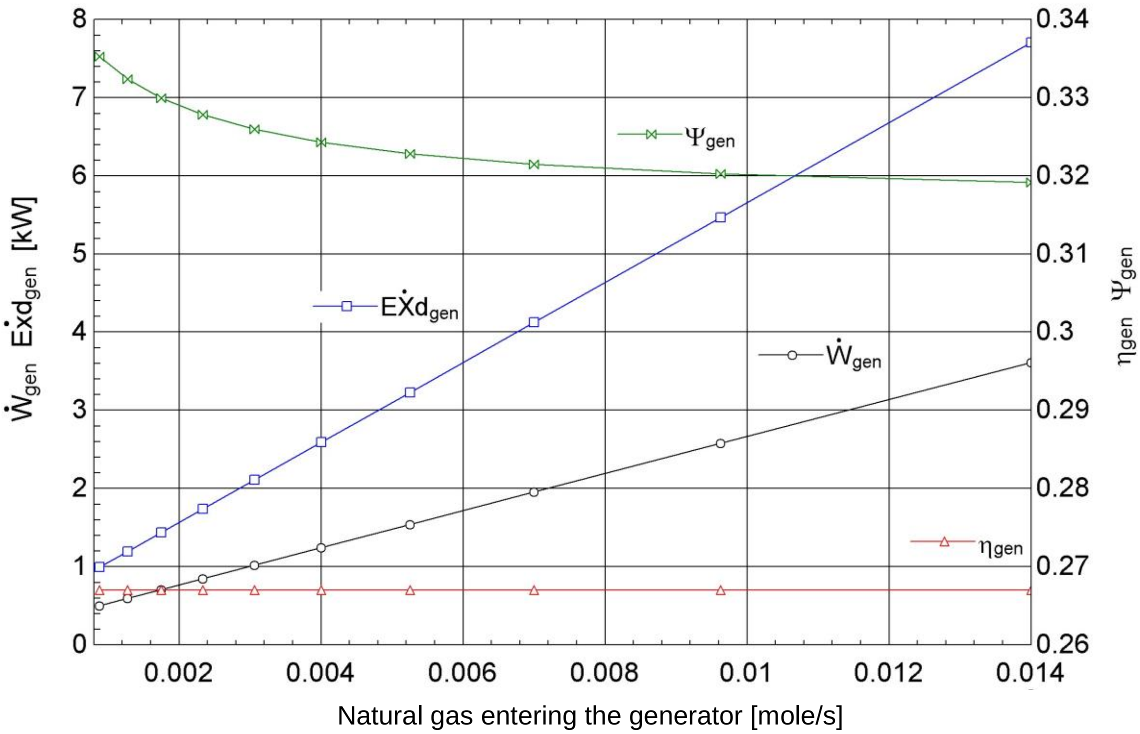

Figure 5.34: Effects of changing amount of natural gas entering engine on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for natural gas and ammonia fuel blend

Secondly for the ammonia natural gas blend another parametric study is performed by changing the molar flow rate of natural gas supplied to engine on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.34. Changing natural gas molar flow rate from 0.001 mole/s to 0.007 mole/s the results for the overall energy and exergy efficiencies of the generator increased from 26.9% to 26.93% and from 31.8% to 33.8%.

The reduction in the efficiency can be related to the increase in the exergy destruction rate from 1.10 kW to 7.84 kW. Regarding the power output of the generator it increases from 0.67 kW to 3.67 kW. Which shows the impact of increasing the amount of ammonia fuel entering the power generator setup will be increasing the power output at the same time.

Another parametric study have been performed on the generator by changing the ratio of the propane ammonia blend starting from 80% natural gas and 20% ammonia to 20% natural gas and 80% ammonia to plot the changes in the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator.

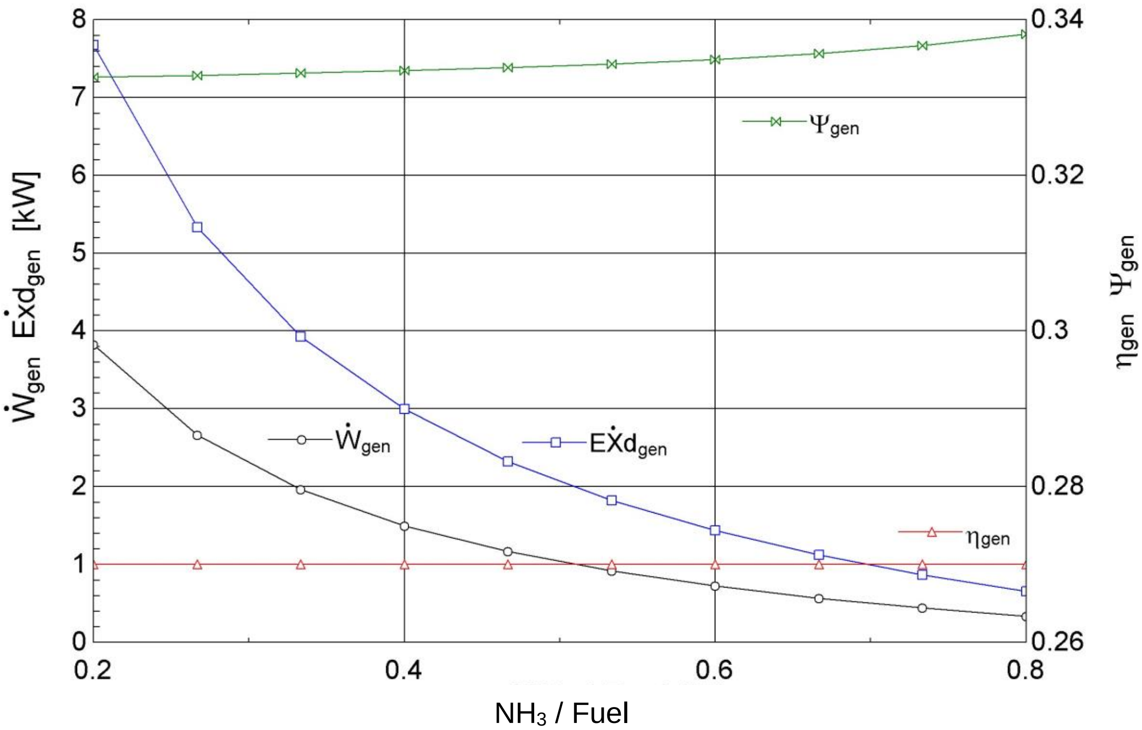

Figure 5.35: Effects of changing the ratio of the propane ammonia blend on the exergy destruction rate, power output, overall energy and exergy efficiencies of the generator for natural gas and ammonia fuel blend

The effect of changing the mass ratio of the propane ammonia blend on the power output, exergy destruction rate, overall energy and exergy efficiencies of the generator is plotted in Figure 5.35. Changing the ratio of the propane ammonia blend starting from 80% natural gas and 20% ammonia to 20% natural gas and 80% ammonia decreases the power output of the generator from 3.81 kW to 0.47 kW. The same variation of molar variation resulted in a reduction in the exergy destruction rate of the generator from 7.81 kW to 0.773 kW. Regarding the results for the overall energy and exergy efficiencies of the generator increased from 27.9% to 27.97% and from 33.8% to 34.16% respectively. This increase in the efficiency can be interpreted by the decrease in the exergy destruction rate of the generator.

Lastly another parametric study was performed on the generator model to see the influence of changing the mass ratio of the natual gas ammonia on CO_2 and NO_x emissions. During the studies once again the mass ratio of the propane ammonia blend was changes starting from 80% natural gas and 20% ammonia to 20% natural gas and 80% ammonia.

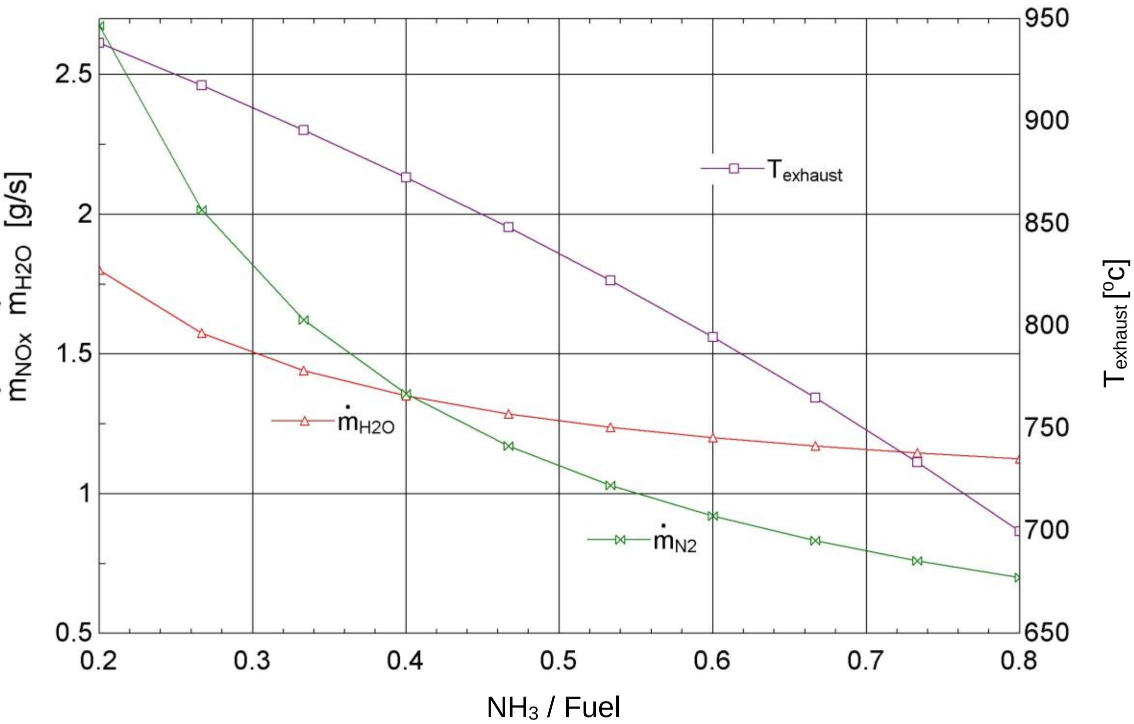

Figure 5.36: Effects of changing the ratio of the natural gas ammonia blend on CO_2 and NO_x emissions

The effect of changing the mass ratio of the natural gas ammonia blend on the exhaust emissions are plotted in Figure 5.36. Changing the mass ratio of the propane ammonia blend starting from 80% natural gas and 20% ammonia to 20% natural gas and 80% ammonia reduces the CO_2 emissions starting from 1.65 g/s to 1.20 g/s. The same variation of molar variation resulted in a decrease in NO_x emissions starting from 0.44 g/s to 2.53 g/s respectively. The reduction in CO_2 occurs with the increase in ammonia ratio as it has no carbon print but at the same time the NO_x emissions were effected in a negative way with the increase in ammonia ratio as it contains nitrogen elements in the fuel. Eventhough the occurrence of NO_x emissions have increased the reduction in CO_2 emissions highly benefits the environment in comparison with the fossil fuel combustion emissions.

5.10. Overall comparison

This part of the chapter will be compiling all of the results gathered from the theoretical analysis and plotting them in graphs where the difference in using a different combustion promoter regarding its thermodynamic properties such as the exhaust temperatures, exergy destruction rates, energy efficiencies, exergy efficiencies, CO_2 emissions and NO_x emissions of each fuel blend.

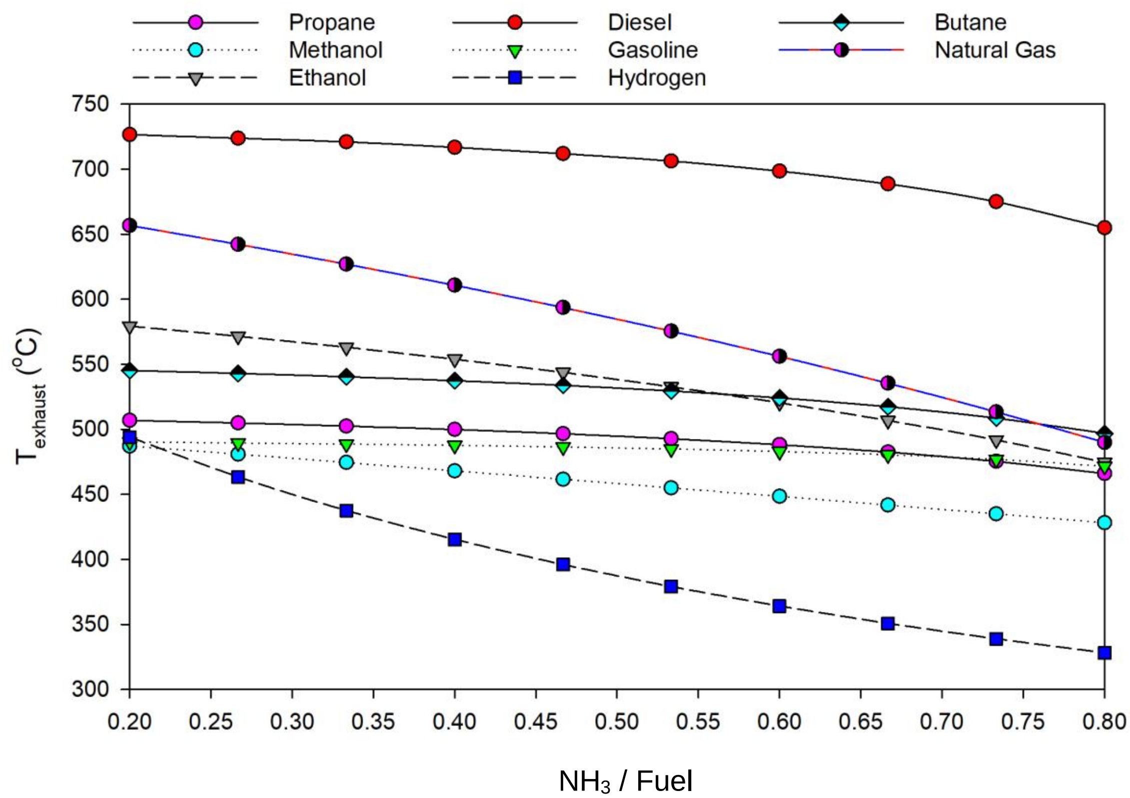

Figure 5.37: The exhaust temperatures of different ammonia fuel blends with respect to the fuel ratio used in the theoretical analysis

One by one all of the exhaust temperatures are plotted on the graph at different fuel ratios of different combustion promoters such as hydrogen, gasoline, diesel, ethanol, methanol, propane, butane and natural gas which resulted in the temperature curves are given in Figure 5.37. The ranges of these values have been discussed separately for each blend previously in this chapter. The lower heating value of the fuel blends profoundly effect the resulting exhaust temperature that comes out of the exhaust system where the piping was assumed to be 0.5 meter long which is approximately the length for the exhaust piping used in the generator used for experimental purposes that resulted in a loss of

28.75% compared to the modelling results where the combustion occurs completely. Then the energy efficiencies of the different fuel blends were plotted on another graph once again with respect to the change in fuel ratio for different blends that can be seen in Figure 5.38. Each line represent a different fuel blend and the average energy efficiency calculated for each one of them, the reason why a bar chart is used lies within the minor changes for the energy efficiencies with respect to different fuel ratios that have resulted as a result of the losses of the system that did not get effected with the changes in the fuel ratio.

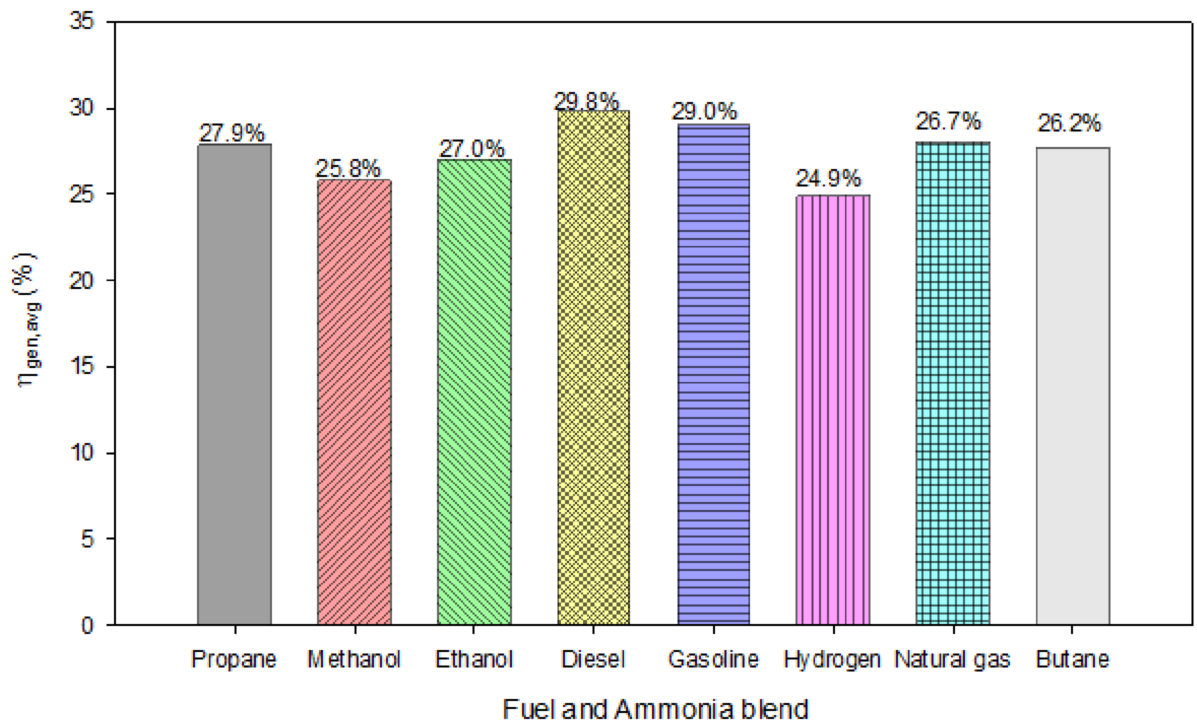

Figure 5.38 : The energy efficiencies of different ammonia fuel blends with respect to the fuel ratio used in the theoretical analysis

As the range and the losses are given for the system is specified the occurrence of the changes are considerably minor for the energy efficiencies of hydrogen, gasoline, diesel, ethanol, methanol, propane, butane and natural gas blends resulted in an average of 24.9%, 29%, 29.8%, 27%, 25.8%, 27.9%, 26.2% and 26.7%, respectively. The energy efficiencies are affected by the change in the losses to the system from the exhaust and surroundings that are changing with the change in temperature occurring from the combustion process of different fuel blends. The difference in the efficiencies are occurring as a result of the different lower heating values that each blend offers. The highest efficiency achieved were 29.8% by the diesel blend as the energy density of this fuel is one of the highest amongst conventional fuels. The optimal ratio that will give out the most efficient combustion in terms of energy analysis can be seen on the figure. The exergy efficiencies of the different fuel blends were plotted with respect to the change in fuel ratio for different blends where each line represent a different fuel blend at a different fuel ratio.

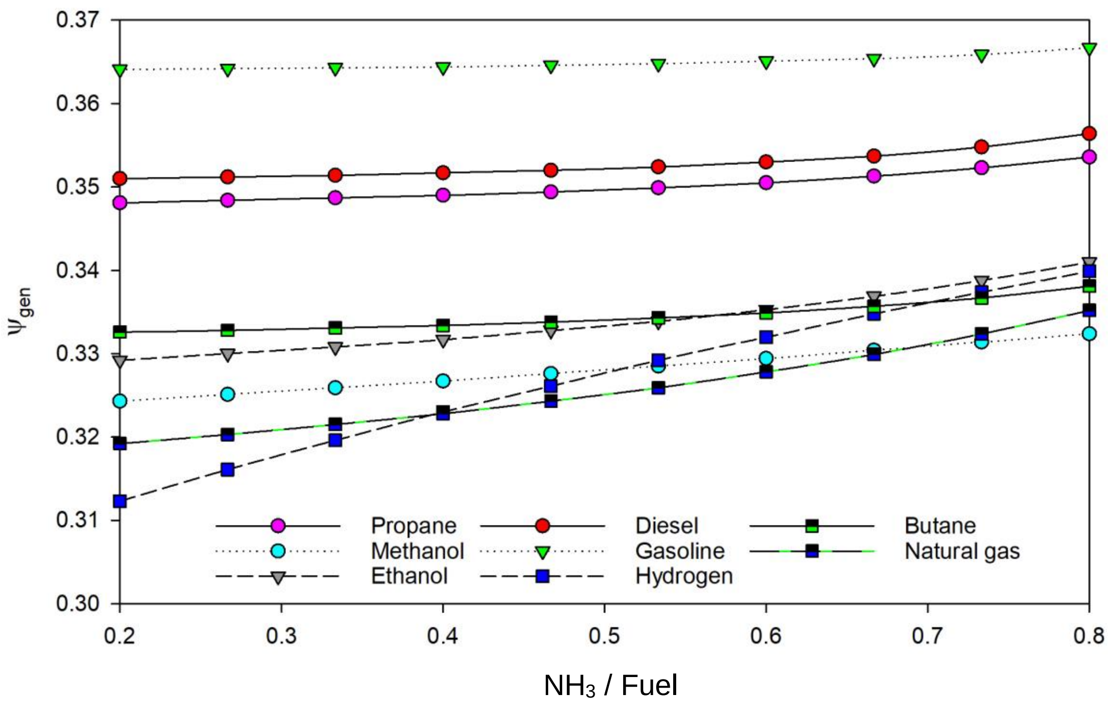

Figure 5.39: The exergy efficiencies of different ammonia fuel blends with respect to the fuel ratio used in the theoretical analysis

The exergy efficiencies of hydrogen, gasoline, diesel, ethanol, methanol, propane, butane and natural gas blends have been compiled in Figure 5.39. The exergy efficiencies are affected with the change in the temperature of the system that is profoundly affected by losses in the exhaust that are also affected with the change in temperature occurring from the combustion process of different fuel blends. The highest efficiency achieved were 36.5% by the gasoline blend at a blend ratio of 80% percent gasoline and 20% ammonia. The difference in the efficiencies are occurring as a result of the different lower heating values that each blend offers, as gasoline blend have achieved the highest and the hydrogen blend have resulted in the lowest exergy efficiency values.

The results and findings from the emission tests is combined on the following figures. Figure 5.40 presents the CO_2 emission analysis for all of the blends except the hydrogen one as there are no occurrence of any types of carbon emissions from combustion hydrogen and ammonia.

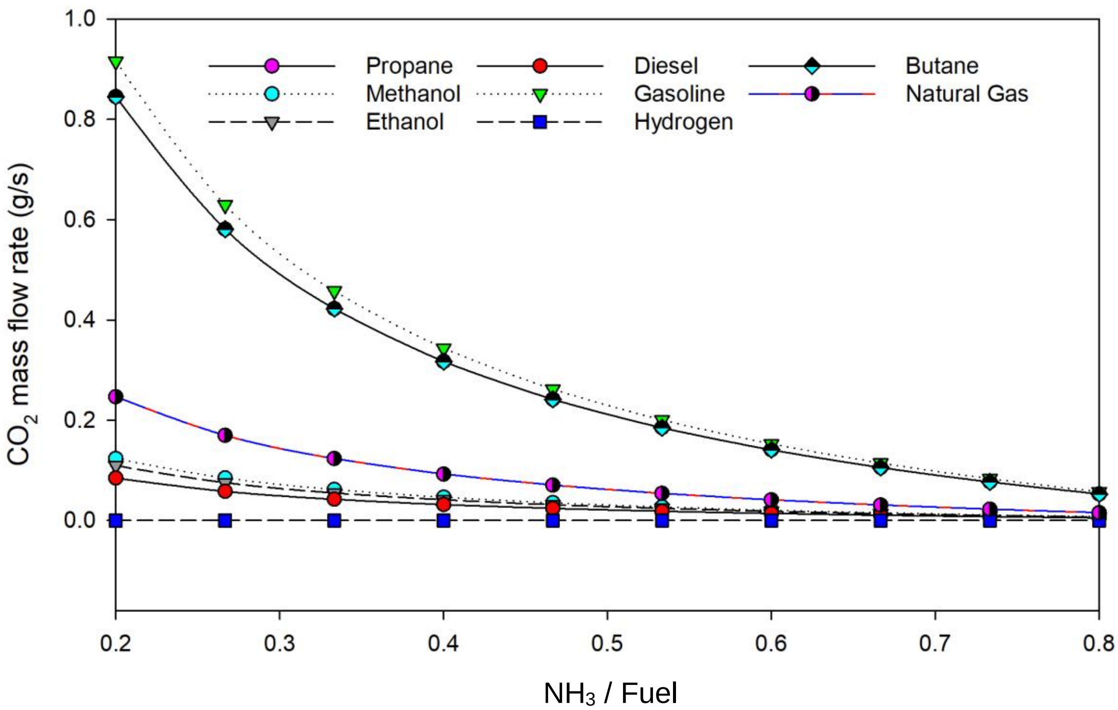

Figure 5.40: The CO_2 emissions of different ammonia fuel blends with respect to the fuel ratio used in the theoretical analysis

In all of the blends the increase in ammonia ratio seems to decrease the amount of CO_2 emitting as a result of the combustion process. For the hydrogen blend there were no CO_2 emissions as both fuels has no carbon print in their chemical structures. Other than hydrogen for all of the fuel blends the lowest emission values were observed at the 80% ammonia and 20% secondary fuel throughout the studies. But when comparatively discussed the lowest emissions amongst all of the blends seems to be occurring for the diesel and ammonia fuel blend. For minimum carbon related emissions the best option would be using fuel sources without any carbon prints such as hydrogen and ammonia that were experimented in the studies.

Regarding the emission analysis in Figure 5.41 the NO_x emissions were compiled for all of the fuel blends modelled and analysed in the to see ammonia's contribution regarding the NO_x emission for the combustion of fossil types. As the occurrence of the NO_x emissions were not considered to be an issue when it comes to combusting a fuel with no nitrogen inclusion in their formulas.

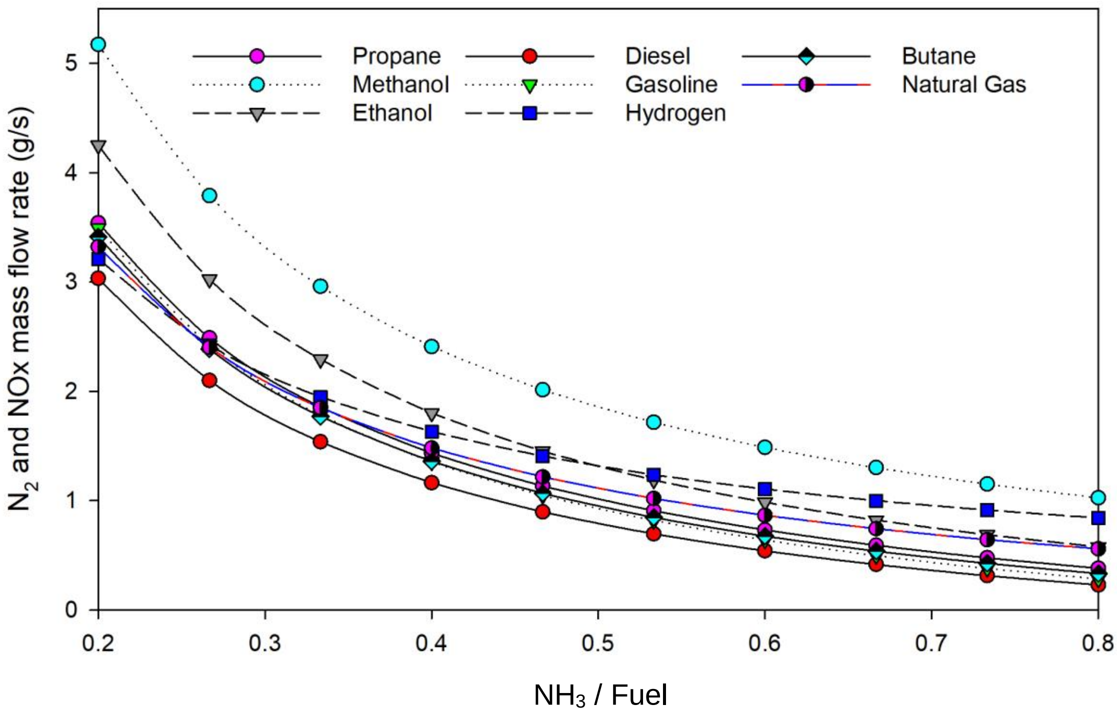

Figure 5.41: The NO_x emissions of different ammonia fuel blends with respect to the fuel ratio used in the theoretical analysis

In all of the blends the increase in ammonia ratio seems to reduce the NO_x emissions occurring in the system before adding ammonia to the combustion process. This is the case for all of the blends this time the highest values were observed at the 80% ammonia when it was at its highest throughout the studies. The highest NO_x emissions amongst all of the blends seems to be occurring for the diesel blend but still the emissions of the hydrogen blends is considerably higher compared to other blends as the only product for this blend is H_2O and NO_x. The reduction occurs with the respect to the amount of air necessary to burn the secondary fuel source which is more than what is needed for ammonia combustion except the hydrogen blend.

Another aspect is to investigate how much each fuel will cost to power the generator and produce 3.65 kW of power for one day. The mass flow rate values used in the analysis to generate this amount of power will be combined with the energy densities and prices of each fuel. The fuel prices are considered regarding the listings in the province of Ontario by the average assessments of their financial values in Canadian dollar's as of 2018 [101].

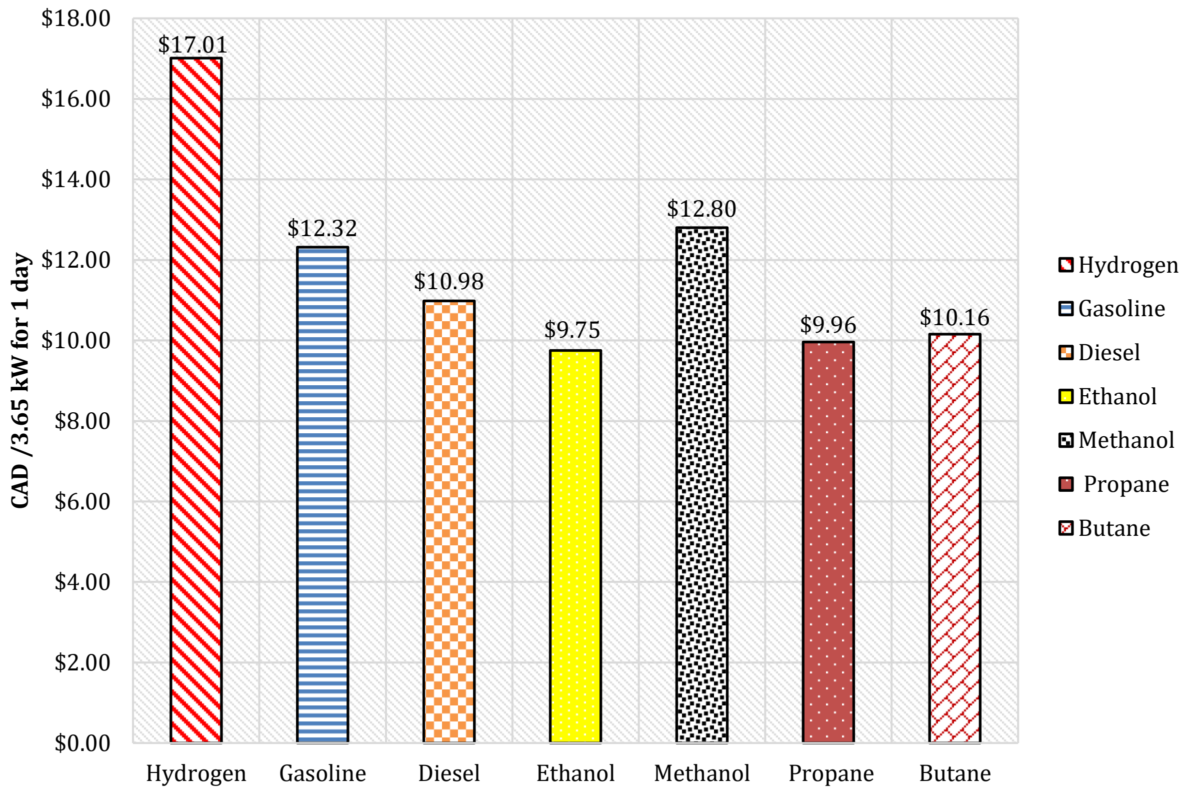

Figure 5.42: The cost of hydrogen, gasoline, diesel, ethanol, methanol, propane and butane fuels to generate 3.65 kW of power for one day with respect to the fuel pricings in Canada

Figure 5.42 represents the price of each fuel used in the modelling of combustion with ammonia based fuel blends to generate 3.65 kW of power for one day, Where hydrogen, gasoline, diesel, ethanol, methanol, propane and butane cost CAD 17.01, CAD 12.31, CAD 10.98, CAD 9.75, CAD 12.8, CAD 9.96 and CAD 10.15, respectively. The results are sorted mostly similar to their fuel densities but the effect of fuel pricing also effects the listings. The most expensive one to generate the same amount of power is hydrogen fuel mostly because of its lower energy density compared to the others fuels and its pricing in Canada.

As explained back in Chapter 2 the energy density or the specific energy of a fuel source itself is not enough to measure its contribution to combustion or assess its performance. In order to give a better understanding for the possible contribution that ammonia offers to be used in power generators an alternative graph is represented in Figure 5.43, showing the relation between the shaftwork of the generator with the energy density of each fuel blend trailed in the studies.

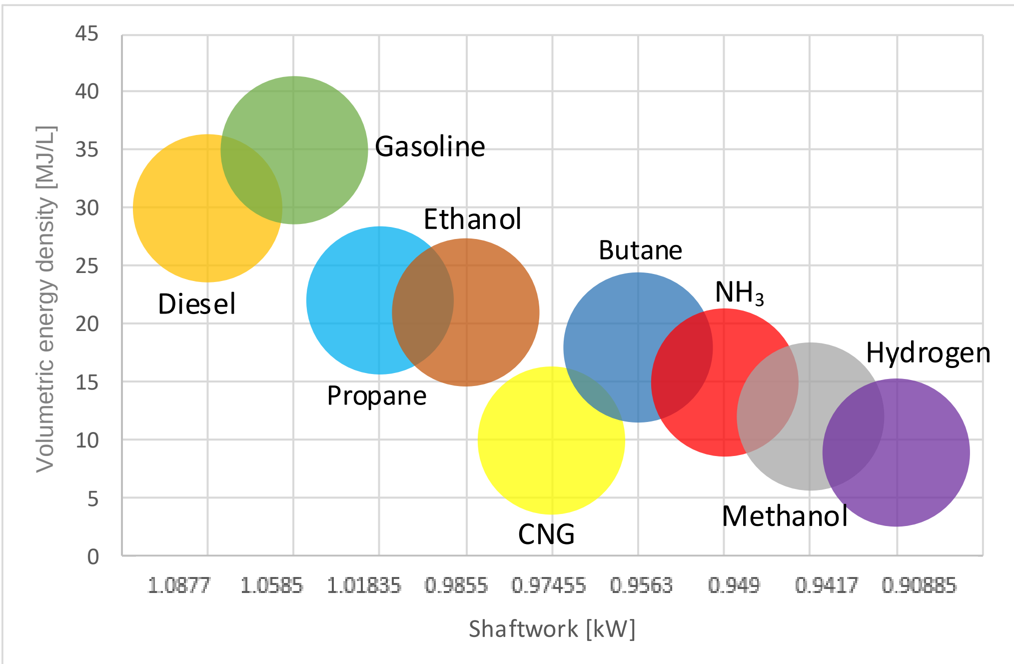

Figure 5.43: Shaftwork versus energy density of each fuel blend used in the studies

The shaftwork is simply calculated by using measured energy efficiencies of each blend and the lower heating value of each fuel source. Figure 5.43 represents a different aspect to assess the performance of ammonia fuel different than Figure 2.7. Where the highest and lowest shaftwork values can be observed for the diesel and hydrogen fuel, respectively. The experimental and theoretical analysis of combustion states the difference that complete combustion offers, as the performance measures seems to be increasing with the increase ammonia addition to the generator in the theoretical modelling of ammonia combustion. This was not the case for the experimental analysis, but the both studies where gasoline and ammonia fuel blend is used validates each other as both findings resulted in similar exhaust temperatures work outputs and emissions eventhough the energy and exergy efficiencies are changing differently as a result of complete combustion that was stated in the assumptions for the thermodynamic analysis.

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

In this chapter the main findings are gathered from the results of the experimental and theoretical analysis of the ammonia based fuel blends, then these findings are followed by conclusions that are derived from these main findings. Lastly some recommendations are suggested for the future researchers that will be working on ammonia power generators in the upcoming years.

6.1. Conclusions

The fossil fuels are labelled as one of the most important sources for transportation, electricity generation and many other applications for many years but with the possibility of their depletion and their negative impact towards the environment there should be some options made available. The fuel sources without any carbon print such as ammonia and hydrogen will be favoured as non-fossil and non-carbon dioxide emitting sources that can be implemented in to devices that were previously designed for fossil fuel sources rather than designing new systems which will be much more cheap and efficient at the same time. The main findings regarding the influence of ammonia for power generators observed in the thesis study are;

- The increase of ammonia ratio to the fuel blend during the experimental studies have resulted in an upserge for the exhaust temperatures starting from 369.9 C^o to 480.1 C^o. The increase in temperature with the addition of ammonia was caused by the higher ignition temperatures of ammonia compared to gasoline fuel. Eventhough the temperatures are seemingly higher, the stainless steel engine block can still withstand this temperatures without the occurrence of any temperature related issues.
- The power output decreases from 3689.2 W to 3572.8 W with the increase in the ammonia percentage in the fuel blend as expected with the lower heating value of gasoline compared to ammonia. Also the engine of the generator stops working under full ammonia content as its flame speed and temperature is not high enough to ignite the fuel with the help of a spark plug. Another reason why the engine did not operate with full ammonia content may also be related to the outside conditions where the experiments took place, the low temperatures might affrected the igniton process for ammonia fuel.

- Regarding the greenhouse emissions, a reduction was observed for CO_2 emissions ranging from 2.535 g/s to 2.4916 g/s, which shows that blending ammonia will result in a decrease for the deleterious emissions occurring after combustion. Eventhough these values are seemingly small when used in generators with bigger capacities it will make a considerable difference to protect the environment.
- The results gathered from the experimental studies then was later on used for the modelling of combustion using ammonia based fuel blends, ammonia seems to be decreasing the CO_2 emissions in all of the fuels used. In these models the maximum power output is set to 3.65 kW as this is the maximum power output for the power generator used in the experiments. The losses in energy efficiency are mostly related to the losses in the exhaust and the losses to the environment in terms of conduction and convection. These losses are correlated to the work done by researchers and then they are used in calculating the efficiencies of different fuel blends with respect to their lower heating values that caused minimal changes.
- The validation of the experimental studies were made with the theoratical findings that resulted in similar exhaust temperatures, work outputs and emissions eventhough the energy and exergy efficiencies are changing differently as a result of complete combustion that was stated in the assumpions for the thermodynamic analysis. The experimental and theoratical analysis of combustion states the difference that complete combustion offers, as the performance measures seems to be increasing with the increase ammonia addition to the generator in the theoratical modelling of ammonia combustion.
- The performance analysis of the dual fueled combustion results for the overall energy and exergy efficiencies of the experimental setup to reduce from 35.7 % to 28.74 % and from 44.85 % to 36.4 %, respectively with the increase of ammonia percentage in the fuel blend. The exergy efficiencies seems to decrease with the upserge in exergy destruction for all fuels with the increase in ammonia percentage. The reduction in the performance measures are caused as a result of the lower energy density and lower heating values that ammonia has in comparison with gasoline but the reduction in CO_2 emissions will be worth using ammonia with a combustion promoter.

6.2. Recommendations for future work

Regarding the future development of ammonia generators there are still some challenges to overcome, especially the high autoigniton temperatures of ammonia combustion. This can be considered as the primary challenge for the possible usage of ammonia as a fuel source for generators in the upcoming future. One of the most significant advantages ammonia fuel offers is yielding no carbon related emissions when it combusts. There are many ongoing studies on the field concerning the problems related to the implementation of ammonia to daily life usage. The recommendations for the future researchers regarding the usage of ammonia for power generators can be listed as

- A possible research subject regarding the combustion of ammonia might be utilizing the usage of fuels like hydrogen that has no carbon print as a combustion promoter for ammonia to yield no CO_2 emissions.
- The life cycle assessment of the ammonia fuel may be conveyed concerning its usage for power generators to assess the environmental impacts associated with all the stages starting from raw material extraction through materials processing, manufacture, distribution, use, repair and maintenance, and disposal or recycling.
- The economic analysis of the possible usage of ammonia for power generators can be conveyed extensively to see the contribution it offers from a financial aspect other than its effects concerning the thermodynamic properties and emissions that was studied in the thesis research.

REFERENCES

[1] Withagen C. Pollution and exhaustibility of fossil fuels. Resour Energy Econ 1994;16:235–42. doi:10.1016/0928-7655(94)90007-8.

[2] Zamfirescu C, Dincer I. Using ammonia as a sustainable fuel. J Power Sources 2008;185:459–65. doi:10.1016/j.jpowsour.2008.02.097.

[3] World Energy Council. World Energy Scenarios 2016. World Energy Counc 2016:1–138. doi:ISBN: 978 0 946121 57 1.

[4] World Energy Council. World Energy Resources 2016. World Energy Resour 2016 2016:1–33. doi:http://www.worldenergy.org/wp-content/uploads/2013/09/Complete_WER_2013_Survey.pdf.

[5] Crolius S. “Major Development for Ammonia Energy in Japan Ammonia Energy” - The Global Information Portal for Ammonia as an Energy Vector Avaliable from: http://www.ammoniaenergy.org/major-development-for-ammonia-energy-in-japan/ n.d.

[6] Sims REH, Rogner HH, Gregory K. Carbon emission and mitigation cost comparisons between fossil fuel, nuclear and renewable energy resources for electricity generation. Energy Policy 2003;31:1315–26. doi:10.1016/S0301-4215(02)00192-1.

[7] Ammonia | Industrial Efficiency Technology Database; Measures, [5 February 2018]. Available from http://yara.com/investor_relations/reports_presentations/.

[8] Cobble MH. Calculations of Generator Performance. CRC Handb Thermoelectr 1995;2:489–92. doi:doi:10.1201/9781420049718.ch39.

[9] Sahoo BB, Sahoo N, Saha UK. Effect of engine parameters and type of gaseous fuel on the performance of dual-fuel gas diesel engines-A critical review. Renew Sustain Energy Rev 2009;13:1151–84. doi:10.1016/j.rser.2008.08.003.

[10] Huang W. Impact of Rising Natural Gas Prices on U . S . Ammonia Supply. Management 2007;WRS-0702:WRS-0702.

[11] Pereira EG, Da Silva JN, De Oliveira JL, MacHado CS. Sustainable energy: A review of gasification technologies. Renew Sustain Energy Rev 2012;16:4753–62. doi:10.1016/j.rser.2012.04.023.

[12] Matar S, Hatch LF. Ammonia Production (Haber Process). Chem. Petrochemical Process., 2001, p. 145. doi:10.1016/B978-088415315-3/50002-X.

[13] Erisman JW, Sutton MA, Galloway J, Klimont Z, Winiwarter W. How a century of ammonia synthesis changed the world. Nat Geosci 2008;1:636–9. doi:10.1038/ngeo325.

[14] Bicer Y. Investigation of Novel Ammonia Production Options Using Photoelectrochemical Hydrogen. University of Ontario Institute of Technology, 2017.

[15] Chakraborty D, Petersen HN, Elkjær C, Cagulada A, Johannessen T. Solid ammonia as energy carrier: Current status and future prospects. Fuel Cells Bull 2009;2009:12–5. doi:10.1016/S1464-2859(09)70336-0.

[16] Giddey S, Badwal SPS, Kulkarni A. Review of electrochemical ammonia production technologies and materials. Int J Hydrogen Energy 2013;38:14576–94. doi:10.1016/j.ijhydene.2013.09.054.

[17] Frattini D, Cinti G, Bidini G, Desideri U, Cioffi R, Jannelli E. A system approach in energy evaluation of different renewable energies sources integration in ammonia production plants. Renew Energy 2016;99:472–82. doi:10.1016/j.renene.2016.07.040.

[18] Dunn R, Lovegrove K, Burgess G. A review of ammonia-based thermochemical energy storage for concentrating solar power. Proc. IEEE, vol. 100, 2012, p. 391–400. doi:10.1109/JPROC.2011.2166529.

[19] Makhlouf A, Serradj T, Cheniti H. Life cycle impact assessment of ammonia production in Algeria: A comparison with previous studies. Environ Impact Assess Rev 2015;50:35–41. doi:10.1016/j.eiar.2014.08.003.

[20] Hasler K, Bröring S, Omta SWF, Olfs HW. Life cycle assessment (LCA) of different fertilizer product types. Eur J Agron 2015;69:41–51. doi:10.1016/j.eja.2015.06.001.

[21] Duynslaegher C, Jeanmart H, Vandooren J. Ammonia combustion at elevated pressure and temperature conditions. Fuel 2010;89:3540–5. doi:10.1016/j.fuel.2010.06.008.

[22] Klerke A, Christensen CH, Nørskov JK, Vegge T. Ammonia for hydrogen storage: challenges and opportunities. J Mater Chem 2008;18:2304. doi:10.1039/b720020j.

[23] Bradley D, Lawes M, Sheppard CGW, Woolley R, Inst Mech E. Ammonia as an engine fuel. Using Nat Gas Engines 1996;1996:9–15. doi:10.4271/650052.

[24] Lan R, Irvine JTS, Tao S. Synthesis of ammonia directly from air and water at ambient temperature and pressure. Sci Rep 2013;3. doi:10.1038/srep01145.

[25] Kyriakou V, Garagounis I, Vasileiou E, Vourros A, Stoukides M. Progress in the Electrochemical Synthesis of Ammonia. Catal Today 2017;286:2–13. doi:10.1016/j.cattod.2016.06.014.

[26] Langhus DL. Modern Electrochemistry, Volume 1: Ionics (Bockris, John O’M.; Reddy, Amulya K. N.). J Chem Educ 1999;76:1069. doi:10.1021/ed076p1069.2.

[27] Li FF, Licht S. Advances in understanding the mechanism and improved stability of the synthesis of ammonia from air and water in hydroxide suspensions of nanoscale Fe2O3. Inorg Chem 2014;53:10042–4. doi:10.1021/ic5020048.

[28] Lan R, Alkhazmi KA, Amar IA, Tao S. Synthesis of ammonia directly from wet air at intermediate temperature. Appl Catal B Environ 2014;152–153:212–7. doi:10.1016/j.apcatb.2014.01.037.

[29] Zhang L, Yang W. Direct ammonia solid oxide fuel cell based on thin proton-conducting electrolyte. J Power Sources 2008;179:92–5. doi:10.1016/j.jpowsour.2007.12.061.

[30] Lan R, Irvine JTS, Tao S. Ammonia and related chemicals as potential indirect hydrogen storage materials. Int J Hydrogen Energy 2012;37:1482–94. doi:10.1016/j.ijhydene.2011.10.004.

[31] Meng G, Ma G, Ma Q, Peng R, Liu X. Ceramic membrane fuel cells based on solid proton electrolytes. Solid State Ionics 2007;178:697–703. doi:10.1016/j.ssi.2007.02.018.

[32] Licht S, Cui B, Wang B, Li FF, Lau J, Liu S. Ammonia synthesis by N2and steam electrolysis in molten hydroxide suspensions of nanoscale Fe2O3. Science (80-) 2014;345:637–40. doi:10.1126/science.1254234.

[33] Fujiwara S, Inaba M, Tasaka A. New molten salt systems for high-temperature molten salt batteries: LiF-LiCl-LiBr-based quaternary systems. J Power Sources 2010;195:7691–700. doi:10.1016/j.jpowsour.2010.05.032.

[34] Garagounis I, Kyriakou V, Skodra A, Vasileiou E, Stoukides M. Electrochemical Synthesis of Ammonia in Solid Electrolyte Cells. Front Energy Res 2014;2. doi:10.3389/fenrg.2014.00001.

[35] Zhang X, Pasaogullari U, Molter T. Influence of ammonia on membrane-electrode assemblies in polymer electrolyte fuel cells. Int J Hydrogen Energy 2009;34:9188–94. doi:10.1016/j.ijhydene.2009.08.099.

[36] Skodra A, Stoukides M. Electrocatalytic synthesis of ammonia from steam and nitrogen at atmospheric pressure. Solid State Ionics 2009;180:1332–6. doi:10.1016/j.ssi.2009.08.001.

[37] Serizawa N, Miyashiro H, Takei K, Ikezumi T, Nishikiori T, Ito Y. Dissolution Behavior of Ammonia Electrosynthesized in Molten LiCl–KCl–CsCl System. J Electrochem Soc 2012;159:E87. doi:10.1149/2.099204jes.

[38] Shipman MA, Symes MD. Recent progress towards the electrosynthesis of ammonia from sustainable resources. Catal Today 2017;286:57–68. doi:10.1016/j.cattod.2016.05.008.

[39] Kim K, Yoo CY, Kim JN, Yoon HC, Han JI. Electrochemical synthesis of ammonia from water and nitrogen catalyzed by nano-Fe2O3 and CoFe2O4 suspended in a molten LiCl-KCl-CsCl electrolyte. Korean J Chem Eng 2016;33:1777–80. doi:10.1007/s11814-016-0086-6.

[40] Di J, Chen M, Wang C, Zheng J, Fan L, Zhu B. Samarium doped ceria-(Li/Na)2CO3 composite electrolyte and its electrochemical properties in low temperature solid oxide fuel cell. J Power Sources 2010;195:4695–9. doi:10.1016/j.jpowsour.2010.02.066.

[41] Nowick AS, Du Y, Liang KC. Some factors that determine proton conductivity in nonstoichiometric complex perovskites. Solid State Ionics 1999;125:303–11. doi:10.1016/S0167-2738(99)00189-7.

[42] Skodra A, Ouzounidou M, Stoukides M. NH3 decomposition in a single-chamber proton conducting cell. Solid State Ionics 2006;177:2217–20. doi:10.1016/j.ssi.2006.03.051.

[43] Kordali V, Kyriacou G, Lambrou C. Electrochemical synthesis of ammonia at atmospheric pressure and low temperature in a solid polymer electrolyte cell. Chem Commun 2000:1673–4. doi:10.1039/b004885m.

[44] Tillement O. Solid state ionics electrochemical devices. Solid State Ionics 1994;68:9–33. doi:10.1016/0167-2738(94)90231-3.

[45] Bicer Y, Dincer I. Assessment of a Sustainable Electrochemical Ammonia Production System Using Photoelectrochemically Produced Hydrogen under Concentrated Sunlight. ACS Sustain Chem Eng 2017;5:8035–43. doi:10.1021/acssuschemeng.7b01638.

[46] Murakami T, Nishikiori T, Nohira T, Ito Y. Electrolytic synthesis of ammonia in molten salts under atmospheric pressure. J Am Chem Soc 2003;125:334–5. doi:10.1021/ja028891t.

[47] Daly H. Fossil fuels. Appl Energy 1994;47:101–21. doi:10.1016/0306-2619(94)90074-4.

[48] Davis SJ, Peters GP, Caldeira K. The supply chain of CO2 emissions. Pnas 2011;108:18554–9. doi:10.1073/pnas.1107409108/-/DCSupplemental.www.pnas.org/cgi/doi/10.1073/pnas.1107409108.

[49] Lackner KS. Comparative Impacts of Fossil Fuels and Alternative Energy Sources. Issues Environ Sci Technol 2010:1–41. doi:10.1039/9781847559715-00001.

[50] Dijkman TJ, Benders RMJ. Comparison of renewable fuels based on their land use using energy densities. Renew Sustain Energy Rev 2010;14:3148–55. doi:10.1016/j.rser.2010.07.029.

[51] Fulkerson W, Judkins RR, Sanghvi MK. Energy from fossil fuels. Sci Am 1990;263:128–35. doi:10.1038/scientificamerican0990-128.

[52] Dincer I, Zamfirescu C. Methods and apparatus for using ammonia as sustainable fuel, refrigerant and nox reduction agent, 2011. doi:CA2654823A1, CA2654823C, US20110011354.

[53] The future of fossil fuels. Energy Process 2016;48:28–9.

[54] Han WQ, Yao C De. Research on high cetane and high octane number fuels and the mechanism for their common oxidation and auto-ignition. Fuel 2015;150:29–40. doi:10.1016/j.fuel.2015.01.090.

[55] Bureau of Ocean Energy Management Regulation and Enforcement. "Fossil Fuels: A Legacy of Disaster", [5 February 2018]. Avaibale from https://ihsmarkit.com/products/boemre-standards.html. n.d.

[56] Allcott H, Wozny N. Gasoline Prices, Fuel Economy, and the Energy Paradox. Rev Econ Stat 2014;96:779–95. doi:10.1162/REST_a_00419.

[57] Höök M, Tang X. Depletion of fossil fuels and anthropogenic climate change-A review. Energy Policy 2013;52:797–809. doi:10.1016/j.enpol.2012.10.046.

[58] Bacha J, Freel J, Gibbs A, Gibbs L, Hemighaus G, Hoekman K, et al. Diesel Fuels Technical Review. Chevron Glob Mark 2007:1–116. doi:10.1063/1.3575169.

[59] Ickes AM, Bohac S V., Assanis DN. Effect of fuel cetane number on a premixed diesel combustion mode. Int J Engine Res 2009;10:251–63. doi:10.1243/14680874JER03809.

[60] Hackbarth A, Madlener R. Consumer preferences for alternative fuel vehicles: A discrete choice analysis. Transp Res Part D Transp Environ 2013;25:5–17. doi:10.1016/j.trd.2013.07.002.

[61] International Energy Agency. CO2 Emissions from fuel Combustion. IEA Stat 2012:138. doi:10.1787/co2-table-2011-1-en.

[62] Aurell J, Hubble D, Gullett BK, Holder A, Washburn E, Tabor D. Characterization of Emissions from Liquid Fuel and Propane Open Burns. Fire Technol 2017;53:2023–38. doi:10.1007/s10694-017-0670-2.

[63] Ledjeff-Hey K, Kalk T, Mahlendorf F, Niemzig O, Trautmann A, Roes J. Portable PEFC generator with propane as fuel. J Power Sources 2000;86:166–72. doi:10.1016/S0378-7753(99)00424-3.

[64] Schnoor JL. Biofuels and the environment. Environ Sci Technol 2006;40:4042. doi:10.1021/es0627141.

[65] Agency IE. Biofuels for transport. 2004. doi:10.1787/9789264015135-en.

[66] Lee CS, Park SW, Kwon S Il. An experimental study on the atomization and combustion characteristics of biodiesel-blended fuels. Energy and Fuels 2005;19:2201–8. doi:10.1021/ef050026h.

[67] Shahid EM, Jamal Y. A review of biodiesel as vehicular fuel. Renew Sustain Energy Rev 2008;12:2477–87. doi:10.1016/j.rser.2007.06.001.

[68] Basha SA, Gopal KR, Jebaraj S. A review on biodiesel production, combustion, emissions and performance. Renew Sustain Energy Rev 2009;13:1628–34. doi:10.1016/j.rser.2008.09.031.

[69] Hoekman SK, Robbins C. Review of the effects of biodiesel on NOx emissions. Fuel Process Technol 2012;96:237–49. doi:10.1016/j.fuproc.2011.12.036.

[70] IEA. World Energy Outlook 2016. Int Energy Agency Paris, Fr 2016:28. doi:http://www.iea.org/publications/freepublications/publication/WEB_WorldEnergyOutlook2015ExecutiveSummaryEnglishFinal.pdf.

[71] ASTM. Specification for Biodiesel (B100) – Astm D6751-08. Filtration 2008:9000–9000.

[72] Agency IE. IEA - Biofuels. Gov Fuel Blending Mandates 2013. http://www.iea.org/etp/tracking/biofuels/.

[73] Costa RC, Sodré JR. Hydrous ethanol vs. gasoline-ethanol blend: Engine performance and emissions. Fuel 2010;89:287–93. doi:10.1016/j.fuel.2009.06.017.

[74] Fang Q, Fang J, Zhuang J, Huang Z. Effects of ethanol-diesel-biodiesel blends on combustion and emissions in premixed low temperature combustion. Appl Therm Eng 2013;54:541–8. doi:10.1016/j.applthermaleng.2013.01.042.

[75] Gross CW, Kong SC. Performance characteristics of a compression-ignition engine using direct-injection ammonia-DME mixtures. Fuel, vol. 103, 2013, p. 1069–79. doi:10.1016/j.fuel.2012.08.026.

[76] Reiter AJ, Kong SC. Combustion and emissions characteristics of compression-ignition engine using dual ammonia-diesel fuel. Fuel 2011;90:87–97. doi:10.1016/j.fuel.2010.07.055.

[77] Ryu K, Zacharakis-Jutz GE, Kong SC. Effects of gaseous ammonia direct injection on performance characteristics of a spark-ignition engine. Appl Energy 2014;116:206–15. doi:10.1016/j.apenergy.2013.11.067.

[78] Grannell SM, Assanis DN, Bohac S V., Gillespie DE. The Fuel Mix Limits and Efficiency of a Stoichiometric, Ammonia, and Gasoline Dual Fueled Spark Ignition Engine. J Eng Gas Turbines Power 2008. doi:10.1115/1.2898837.

[79] Grannell SM. Exhaust Emissions from a stochiometric, ammonia and gasoline dual fueled spark ignition engine. ASME 2009 Intern. Combust. ENgine Div. Spring Tech. Conf., 2009, p. 135–41.

[80] Mørch CS, Bjerre A, Gøttrup MP, Sorenson SC, Schramm J. Ammonia/hydrogen mixtures in an SI-engine: Engine performance and analysis of a proposed fuel system. Fuel 2011;90:854–64. doi:10.1016/j.fuel.2010.09.042.

[81] Duynslaegher C, Contino F, Vandooren J, Jeanmart H. Modeling of ammonia combustion at low pressure. Combust Flame 2012;159:2799–805. doi:10.1016/j.combustflame.2012.06.003.

[82] Parod RJ. Ammonia. Encycl. Toxicol., 2014, p. 206–8. doi:10.1016/B978-0-12-386454-3.00468-1.

[83] Basic Materials Used in an Electrical Generator | Sciencing [5 February 2018]. Available from https://sciencing.com/basic-materials-used-electrical-generator-7615888.html" . n.d. https://sciencing.com/basic-materials-used-electrical-generator-7615888.html (accessed February 6, 2018).

[84] "Updated Parts List of Diesel Engine Generator - Atima [5 February 2018]. Available from http://www.maquirent.com/Portals/0/Manuales/generadores/updated-parts-list-of-diesel-engine-generator-set.pdf." . n.d.

[85] Berman D, Erdemir A, Sumant A V. Graphene: A new emerging lubricant. Mater Today 2014;17:31–42. doi:10.1016/j.mattod.2013.12.003.

[86] Pang HH, Brace CJ. Review of engine cooling technologies for modern engines. Proc Inst Mech Eng Part D J Automob Eng 2004;218:1209–15. doi:10.1243/0954407042580110.

[87] Nakahira T, Tsujimura K, Kakegawa T, Aika K-I, Takiguchi M, Ikeda M, et al. Catalytic engine NOx reduction of diesel engines with new concept onboard ammonia synthesis system. SAE Tech Pap 1992. doi:10.4271/920469.

[88] Forzatti P, Lietti L, Tronconi E. Catalytic Removal of NOx Under Lean Conditions from Stationary and Mobile Sources. Catal. Sustain. Energy Prod., 2009, p. 393–438. doi:10.1002/9783527625413.ch13.

[89] Zukerman R, Vradman L, Herskowitz M, Liverts E, Liverts M, Massner A, et al. Modeling and simulation of a smart catalytic converter combining NOx storage, ammonia production and SCR. Chem Eng J 2009;155:419–26. doi:10.1016/j.cej.2009.08.015.

[90] Forzatti P. Present status and perspectives in de-NOx SCR catalysis. Appl Catal A Gen 2001;222:221–36. doi:10.1016/S0926-860X(01)00832-8.

[91] FIRMAN Owner's Manual Portable Generator Model Number: P03602. n.d.

[92] OM-CP-QUADTEMP-A and OM-CP-QUADTEMP2000 Spec Sheet, Available from: https://www.omega.com/das/pdf/OM-CP-QUADTEMP-A.pdf. n.d.

[93] Data Sheet for Agilent Technologies 54600-Series Oscilloscopes, Available from: https://literature.cdn.keysight.com/litweb/pdf/5968-8152EN.pdf?id=1000034159:epsg:dow. n.d.

[94] Dinçer İ, Rosen M (Marc A. EXERGY : Energy, Environment and Sustainable Development. Elsevier Science; 2012.

[95] Cengel YA, Boles MA. Thermodynamics An Engineering Approach. vol. 53. 2013. doi:10.1017/CBO9781107415324.004.

[96] Eriksson L. Modeling and control of turbocharged SI and DI engines. Oil Gas Sci. Technol., vol. 62, 2007, p. 523–38. doi:10.2516/ogst:2007042.

[97] Bartok JW. Approximate Heating Value of Common Fuels. Engineer 2004:6269–6269.

[98] Vukadinovic V, Habisreuther P, Zarzalis N. Experimental Study on Combustion Characteristics of Conventional and Alternative Liquid Fuels. J Eng Gas Turbines Power 2012;134:121504. doi:10.1115/1.4007333.

[99] Morris DR, Szargut J. Standard chemical exergy of some elements and compounds on the planet earth. Energy 1986;11:733–55. doi:10.1016/0360-5442(86)90013-7.

[100] Dincer I, Rosen M. Exergy Analysis of Renewable Energy Systems. 2013. doi:10.1016/b978-0-08-097089-9.00011-5.

[101] National Energy Board of Canada. Canada's Energy Future 2016: Province and Territory Outlooks. 2016. doi:ISSN 2369-1479.