STUDY OF THE FEASIBILITY OF AMMONIA AS FUEL IN A FLAT BURNER

Miguel Olcina Girona
P46088439

Supervised by Wu, Chih-Yung

Department of Aeronautics and Astronautics Engineering
National Cheng Kung University

Signature ____________________

Date _______ / _______ / _______

Abstract

This master thesis aims to study the feasibility of using a flat flame burner with ammonia as a fuel, for domestic stove applications. This document also gives an brief introduction into some combustion topics, ammonia, and NO_x information in order to ease understanding of the experimental results.

In order to stabilize the atmospheric concentration of CO_2, emissions worldwide would need to be dramatically reduced from their present level. The Kyoto protocol shows that most countries are committed to finding a solution to this problem. Based on different needs, each country will reduce in a percentage the fossil fuel dependency to avoid, as much as possible, CO_2 emissions.

Wind and solar energy are reducing cost and gaining in efficiency, even so, intermittency on energy production is still the main drawback for them. Ammonia seems the most promising carbon-free alternative, for a future without fossil fuels. The low storage and distribution infrastructure investment, the safety in comparison with hydrogen, and its potential as energy carrier are some ammonia advantages.

This research is focused on continue the task of finding a clean gaseous fuel stove for domestic applications highly efficient, and clean. For this purpose, flat flame burner, as it was found in previous research, reduce emissions and maintain the efficiency. However, in order to reduce CO_2 emissions, it was used ammonia as a fuel and some experiments were done to delineate the feasibility of this combination.

NO_x emissions and thermal efficiency distributions were obtained experimentally so that was used to find the optimal operating point, for this kind of burner and ammonia as a fuel. This research is another step in decarbonization of the economy.

Keywords: Ammonia; Carbon-free; Hydrogen; NOx emissions; Thermal Efficiency; Stoves; Flat Flame Burner; Combustion.

Acknowledgements

First of all, I would like to express my very great appreciation to Professor Wu, Chih-Yung, from the Aeronautic and Aerospace Department of NCKU, for instructing me in my research, by giving me advice and responding to all my questions. From December 2019 until August 2020, it has been a great experience and enrichment being among the Combustion and Propulsion Lab members. I am particularly grateful for the assistance during the experiments given by Mr. Chen, Li-Chia.

Finally, my special thanks are extended to my parents and close friends for their support and encouragement throughout my study.

Contents

List of Tables

List of Figures

Chapter 1

Introduction

1.1 Actual situation

Hominids started using fire a million years ago, endorsing the combustion as the first technology of humankind. At present, about 90 % of our worldwide energy support is provided by combustion. In earlier times, the atmosphere was huge enough to digest the products of combustion with a negligible impact on air quality. However, as combustion has increased worldwide, the product of combustion is increasingly (Figure 1.1 [2]), causing changes in the atmosphere.

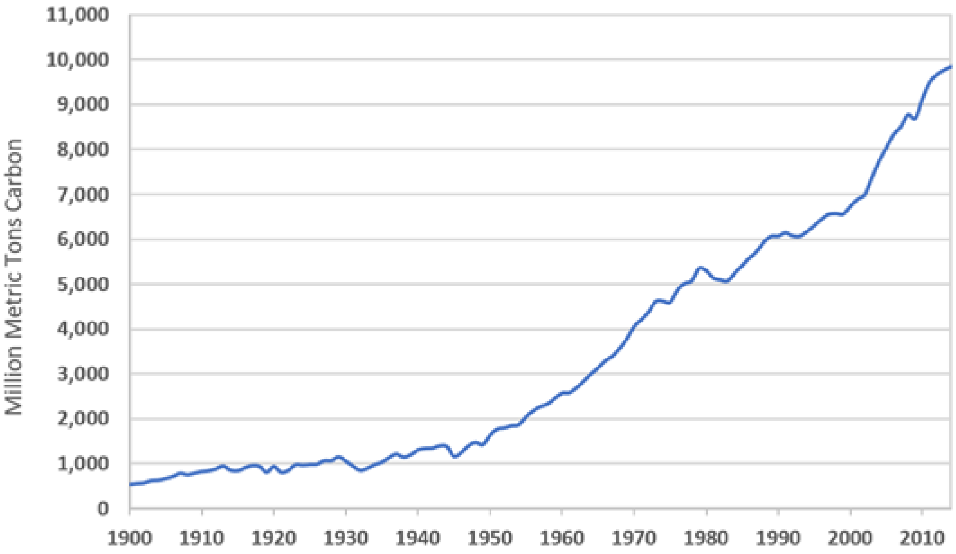


Figure 1.1: Global Carbon Emissions from Fossil Fuels, 1900-2014

The atmosphere can no longer be treated as an infinite reservoir. Combustion products are polluting the air people breathe, and are even changing the climate of the earth.

1.1.1 Evidences of climate change

The Earth's climate was not a constant in time. Small orbital variations created climate changes in the past due to the variation of solar energy that our planet received. Anyhow, more than 95% of probability point the current temperature increasing is result of human activities. Since 1980 the effects on our planet become in a rate that it is not possible to find anything similar over decades to millennia, in the geological strata or permafrost data.

Thanks to the satellites that orbit the Earth, a lot of information about the global climate is collected, these data over decades with other types of information and research reveal the sign of a changing climate. The consensus on this fact at the scientific level is increasingly clear.

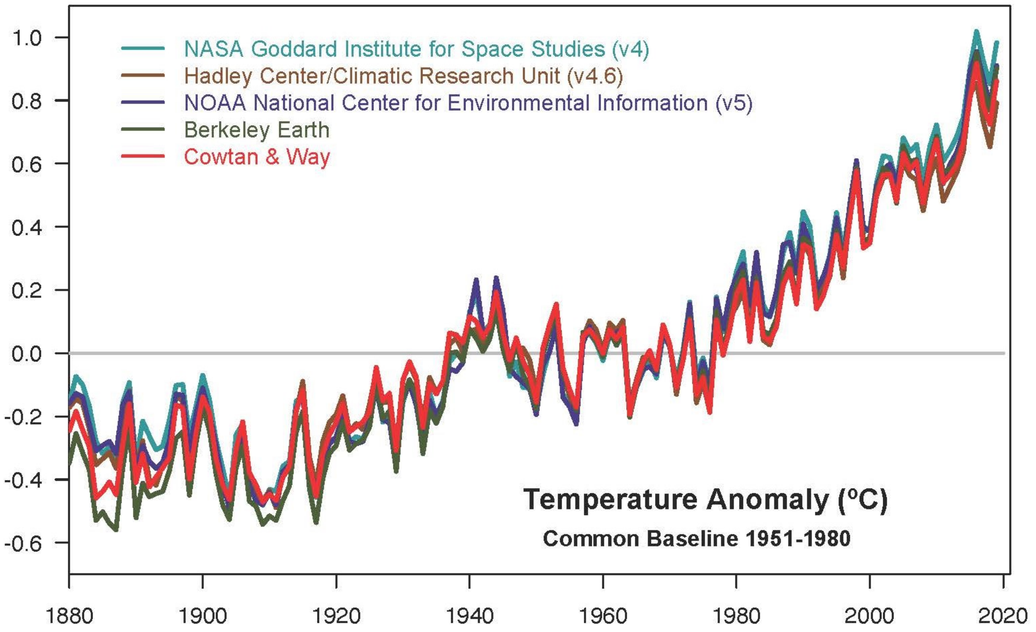


Figure 1.2: Temperature data provided by different researches [22]

Multiple studies published in peer-reviewed scientific journals show that 97 % or more of actively publishing climate scientists agree: Climate-warming trends over the past century (Figure 1.2) are extremely likely due to human activities.

A large part of the heat reflected by Earth is captured by greenhouse gases, this heat goes from space to the atmosphere and then to Earth's surface, so the increased levels of greenhouse gases must cause the Earth temperature rise in response. Because of human activity, there are more greenhouse gasses on the atmosphere and the Earth has been warmed. In the past 35 years, the Earth has warmed more than in other recent times. The five warmest years on record are placed since 2010. 2016 was the warmest year and besides 8 out 12 of its months, from January through September except for June, were the warmest on record for those several months.

The main testimony of climate change related to this warming process are:

- Rising global temperatures in the world
- Warming of the oceans
- Ocean acidification
- Diminution in global snow cover
- Shrinkage of ice caps
- Less and less Arctic sea ice, the thickness and the extend of Arctic sea ice as incredibly and rapidly declined.
- Sea level rise
- Extreme meteorological events

The Earth suffered an average loss of 286 billion of tons of ice per year from 1993 and 2016 in Greenland, while Antarctica lost more than 127 billion of tons of ice during the same period. Indeed Antarctica ice mass loss rate has tripled the last decade . The snow is melting early each year and glaciers are losing ice mass in a retreating process. Due to those water sources, the global sea level increased of approximately 8 inches during the previous century. From the last two decades, this rate nearly double from the one of the last century and it continues to accelerate each year.

Oceans are suffering from climate change, indeed, they have absorbed the main part of this increase of heat. Nowadays, the surface water of oceans is 30% more acid than ever. These are the consequences of the augmentation of carbon dioxide, due to human beings into the atmosphere therefore more absorbed by oceans.

High-temperature events all around the globe increased, unlike low-temperature events that decreased on the records. Since 1950 the United States has also suffered an increase in the numbers of extreme rainfall events. This evidence shows us that climate change is a real issue happening.

1.1.2 Causes of Climate Change

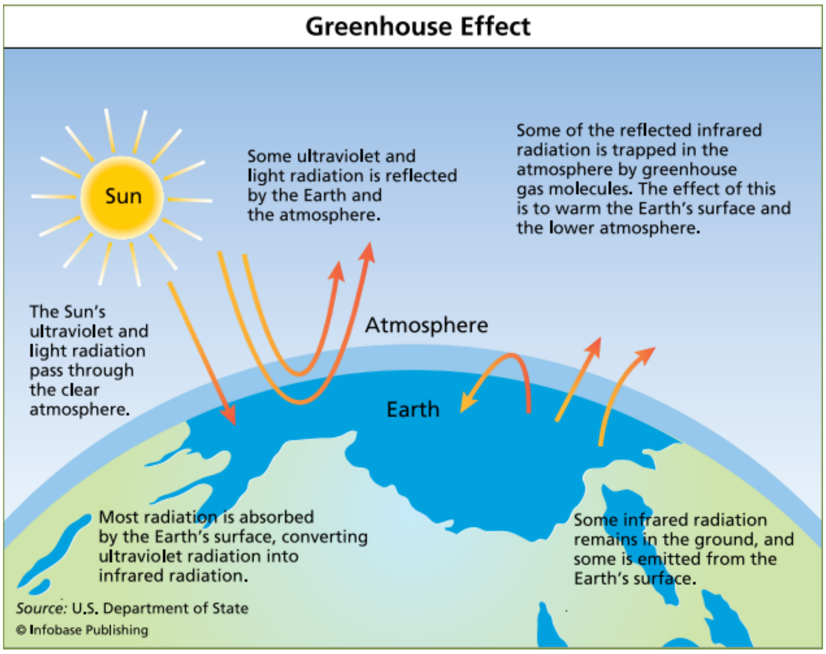


Figure 1.3: Greenhouse gases trap some of the heat that radiates off of the planet, creating the greenhouse effect [6].

A complex process defines the temperature on the Earth, the equilibrium in the energy balance between solar radiation energy and outgoing radiation energy from the Earth's surface and atmosphere. The equilibrium value varies along daily and annual cycles. In addition, Milankovitch cycle produces long-term changes in the climate. This cycle is related with Earth's orbital patterns.It is important to mention that the solar radiation affects only to the atmosphere temperature and then, because heat exchange, ground level temperature is regulated.

Lower UV energy and visible light waves come from Sun passing through the atmosphere unimpeded. When this radiation reaches the Earth's surface, the energy is absorbed by elements on the ground surfaces. The energy is then re-emitted into the atmosphere as infrared waves (heat). Greenhouse gases trap some of this heat in the atmosphere, making the lower atmosphere warmer.

Greenhouse gases in the atmosphere block heat from escaping. Some gases are Long-lived gases, in other words they remain a long time, almost permanently in the atmosphere and do not change with temperature variations, these gases contributing to climate change. Gases, such as water vapour, which respond physically or chemically to changes in temperature, are seen as feedbacks. In the following lines, there is a brief description of each greenhouse gas:

- **Water vapor** (H_2O).

  It is the most common greenhouse gas, at the same time, water vapor behave as feedback to the climate. As Water vapor concentration on atmosphere increases warmer this will be, however, it is a short-lived gas, just raining or snowing can reduce the amount of this component on the atmosphere, this is the most relevant greenhouse feedback mechanism.

- **Carbon dioxide** (CO_2).

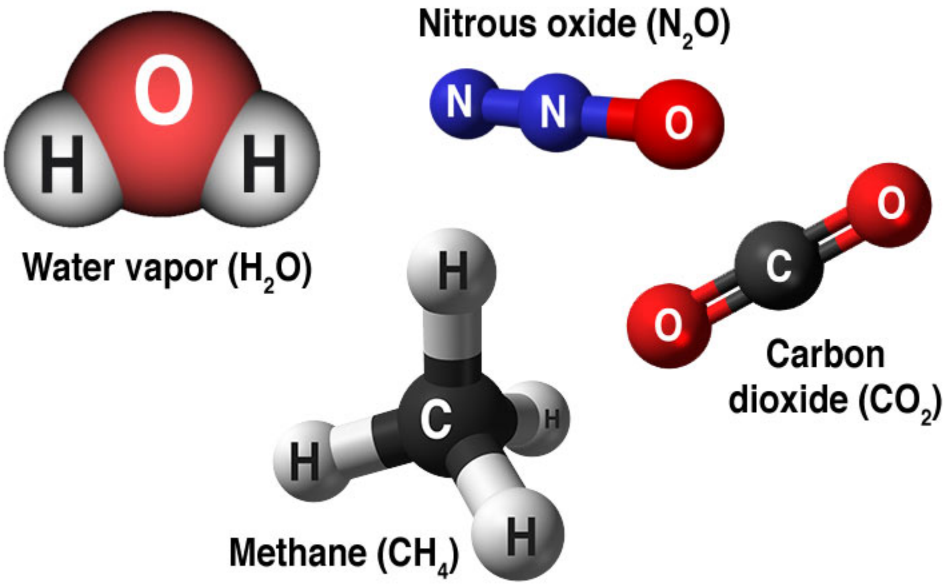


Figure 1.4: Gases that contribute to the greenhouse effect

The 0,04 % of the atmosphere is carbon dioxide, animals respiration, combustion, volcano eruptions or deforestation are activities that release carbon dioxide to the atmosphere, some of them are coming from human activities and other are natural processes caused. CO_2 is a long-lived gas on the atmosphere and since the Industrial Revolution its concentration approximately multiplied by three.

- **Methane** (CH_4). Comparing methane with other gases, this is a far more active greenhouse gas than carbon dioxide, but also one which is much less abundant in the atmosphere. Natural sources and human activities produce this gas, including the decomposition of wastes in landfills, agriculture, and especially rice cultivation, as well as ruminant digestion and manure management associated with domestic livestock. Large amounts of this gas are now trapped in the poles, a temperature increased could liberate this reservoirs and accelerate in this way the climate changing irreversibly.

- **Nitrous oxide** (N_2O).

  Soil cultivation practices, in particular the use of fertilizers (commercial and organic), nitric acid production, fossil fuel and biomass combustion produce this potent greenhouse gas.

- **Chlorofluorocarbons** ($CFCs$). Major cause of the hole in the ozone layer. From industrial origin used in several applications, nevertheless now these gases made from synthetic compounds is mainly regulated by international agreements in production and release to the atmosphere due to the damage on the environment they produce, also they contribute to greenhouse effect [17].

Some of these gases mentioned are produced as a consequence of human activities (Figure 1.5) and they are changing the natural greenhouse.

In the past 100 years, the consumption of oil and coal has increased the percentage of carbon dioxide (CO_2) on the atmosphere. This is happening because during combustion process, carbon and oxygen react to create CO_2. The combustion of any hydrocarbon is a chemical reaction which products are carbon dioxide, heat , vapor water and other chemicals depend on the composition of the particular fuel or burning conditions.

$$\text{Hydrocarbon} + \mathrm{O_2} \longrightarrow \mathrm{H_2O} + \mathrm{CO_2}$$

To a lesser extent, the clearing of land for agriculture, industry, and other human activities has increased concentrations of greenhouse gases. As it is possible to observe in the Figure 1.6 there is a significant percentage for the Buildings.

1.1.3 Effects and possible solutions

Global temperatures are expected to follow the rising current trend for decades to come, scientists assure that this is mainly due to gas emissions produced by human being activities. The Intergovernmental Panel on Climate Change (IPCC), which includes more than 1300 scientists, predicts a temperature rise over the next century of 3 to 6 Celsius

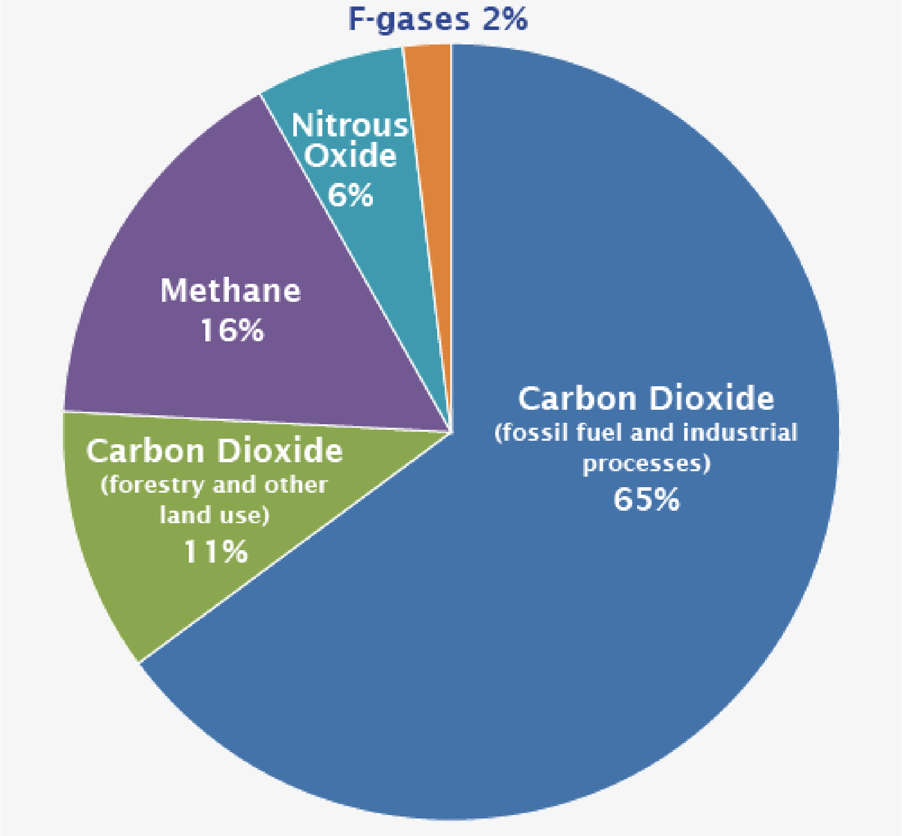


Figure 1.5: Global emissions of gas based on global emissions from 2010 [2]

degrees.

According to the IPCC, the adverse effects of climate change on individual regions will vary over time and with the ability of different societal and environmental systems to mitigate or adapt to change.

The IPCC predicts that increases in global mean temperature of less than 1 to 3 degrees Celsius above 1990 levels will produce beneficial impacts in some regions and harmful ones in others. Costs will increase over time as global temperatures rise [22].

To stop increasing the levels of climate change, it is necessary to research on new energy sources free of carbon emissions. There will be to reduce petrol consumption and change the way humans live on Earth. This master thesis is framed in that thought.

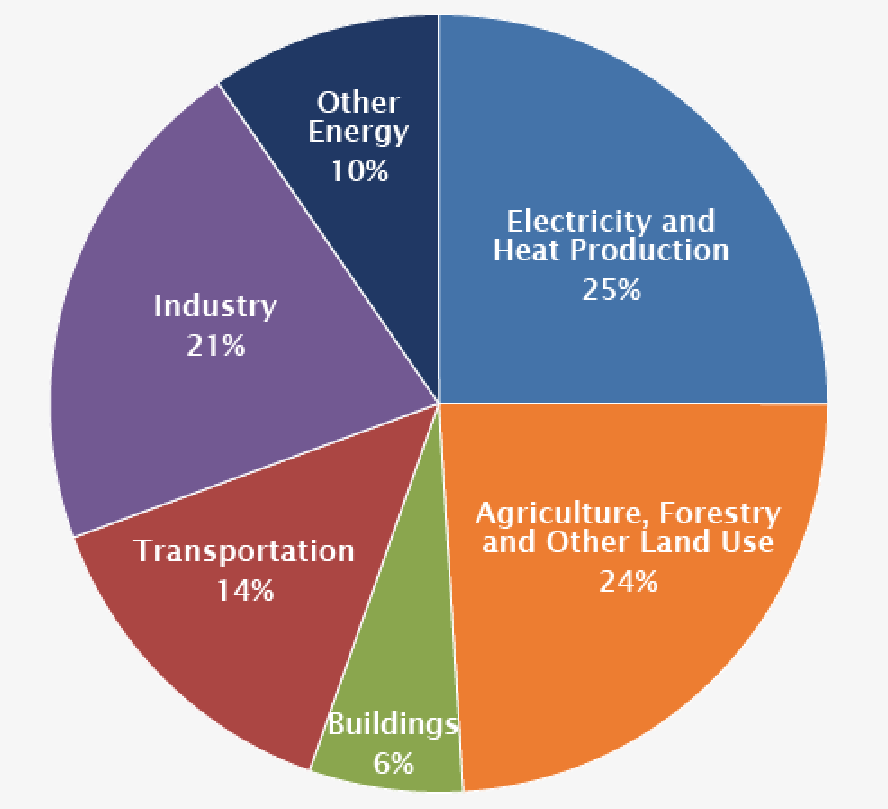


Figure 1.6: Data from global emissions by economic sector at 2010 [2]

1.2 Motivation, aims and objectives

Flat-Flame burners could be used as gaseous domestic burners, to be operated for cooking and water heating. Gaseous fuel stoves are highly convenient, cause a low level of soot, and hence are widely used in modern houses. Nevertheless, they also emit carbon dioxide and toxic gases into the environment. The emission of carbon dioxide is one of the leading factors contributing to global warming.

The fact that air pollution is increasing, becomes a significant issue. The emission of greenhouse gases coming from human activities increase global warming and due to the release of gases from burning some fuels, chemicals compounds are mixing with vapor water creating acid rain. These three negative issues are considered dangerous and harmful for public health. Hence, searching for alternatives to fossil fuels has extended in all directions. Toxic emission also are produced while using domestic stoves, these emit CO_2 and other toxic gases. The long exposition to these gases could lead in several diseases.

Due to this, finding a clean and efficient domestic stove become crucial. This enhancement could also significant decrease in overall emissions of toxic pollutants and greenhouse gases.

In recent years, ammonia has been used as a chemical for hydrogen storage that can be easily dissociated and used as a sustainable fuel for transport fuel cells and power generation. Cost, higher density and the low invest needed for storage and distribution NH_3 offers, show that ammonia present advantages compared with hydrogen. This chemical is easier to produce, handle, store and distribute with an existent, well-developed infrastructure and has promising commercial viability. So this is why it is considered as a fuel in this master thesis. The present study aims to demonstrate the feasibility and operating characteristic of the flat flame burner for domestic applications, using ammonia mixed with hydrogen as a fuel. Anyway, some disadvantages are presented in the using of ammonia as a fuel, one of them is the high NO_x emissions [10].

The main objective of this master thesis, as it was said before, is finding the feasibility of using ammonia as a fuel, comparing the drawbacks and benefits of this, it has also been studied the effects of the different parameters on the process, to obtain the operating characteristic of this burner with ammonia.

This research is also a little step in the big process of achieving an economy with net-zero carbon dioxide emissions. For this goal, there are two ways to proceed, balancing carbon emissions with carbon removal or eliminating carbon emissions. Using Ammonia and hydrogen as a fuel is classified in a second way.

This master thesis is collecting data, about the thermal efficiency in this type of burners using ammonia as a fuel. With this data, it is possible to improve the combustion using flat-flame burners.

1.3 Description of the work

This section is explained briefly what this project is meant to achieve and how it is going to be realized .

This master thesis is going to delineate the feasibility of ammonia as a fuel, ammonia was mixed with hydrogen (H_2) to sustain the flame of the primary fuel the ammonia (NH_3). The results of this work are meant to find out the drawbacks and the benefits of burning this mixed fuel in a flat burner. Which points in the operating range are better than others and also compare NO_x emissions in this range.

Thermal efficiency and emissions were measured and tested the effects of different parameters in these variables, as equivalence ratio, output power and the amount of hydrogen added to the mixture. For measuring these variables, the flowmeters to control the flow of every reactant were needed, the heat exchanger was used to measure the heat produced by the flame and a gas analyzer was applied to measure the combustion products.

In the chapter 4, the further explanation for the measurement system and the experiments developed for this master thesis is delineated.

Chapter 2

Background

2.1 Introduction

In the present research work is detailed thermal efficiency of NH_3 enriched H_2/air fuel mixtures and NO_x emissions for the operating range of a flat flame burner. Some combustion concepts are used and therefore need to be understood. Thus this chapter provides a brief background on the types of flames and associated emissions, primarily focusing on NO_x.

2.2 Type of flame

The combustion characterization of a fuel and its detailed chemistry is often performed under two possible extremes, which are present to some degree in most practical combustion systems: premixed flames and non-premixed or diffusion flames (Figure 2.1).

2.2.1 Premixed flame

The main advantages of premixed flames is that much control of the combustion. It can be reduce the NO_x production, or soot produce by the flame just changing equivalence ratio. It is not widely used due to the fact that for large amounts of fuel and air mixture

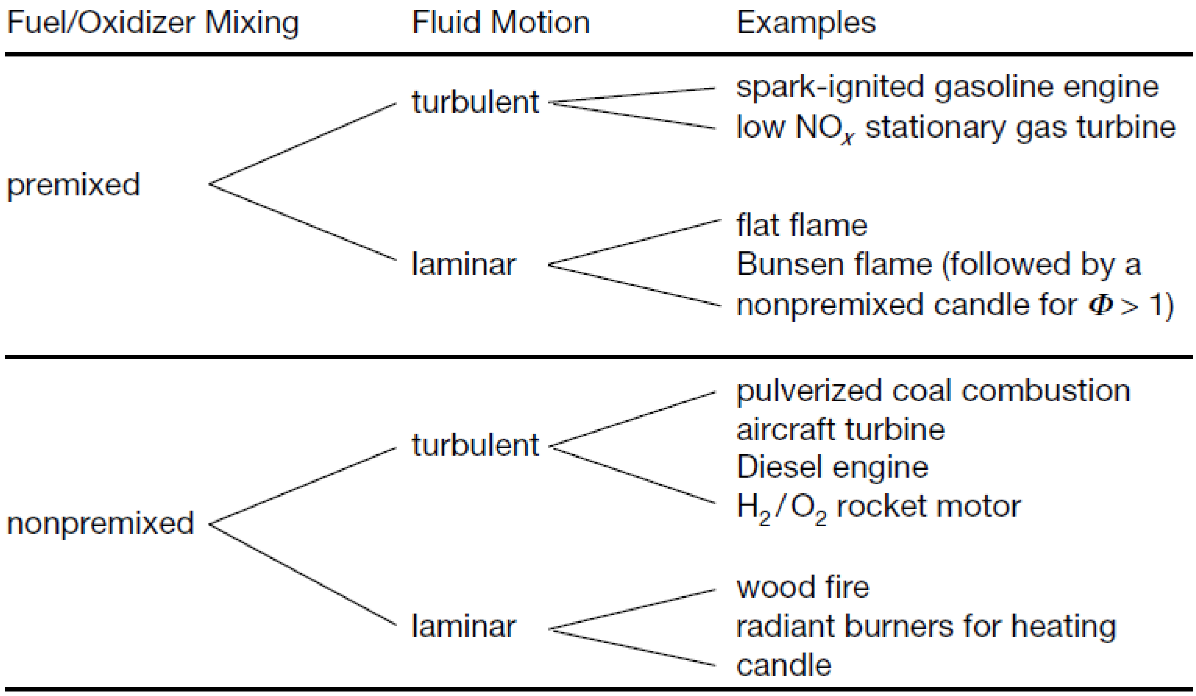


Figure 2.1: Basic flame types and examples [11]

there is high probabilities of accidental ignition and producing an uncontrolled explosion.

Laminar premixed flames, fuel and oxidizer are mixed before going outside from the burner. For this purpose it is usually that gases are premixed in a chamber o simply mixture is produced by connecting pipes. The majority of the chemical transformation in such a combustion process occurs primarily in a thin surface which separates the reactants and the combustion products or burned gases.

In this master thesis it is experimented with laminar premixed flat flame, same type as it is possible to observe in Figure 2.2.

Turbulent premixed flames are produced in a turbulent flow. High turbulence intensity could curved laminar premixed fronts, if i not the case turbulent flame can then be defined as an ensemble of many little laminar premixed flames. This type of flame is used in Otto engine.

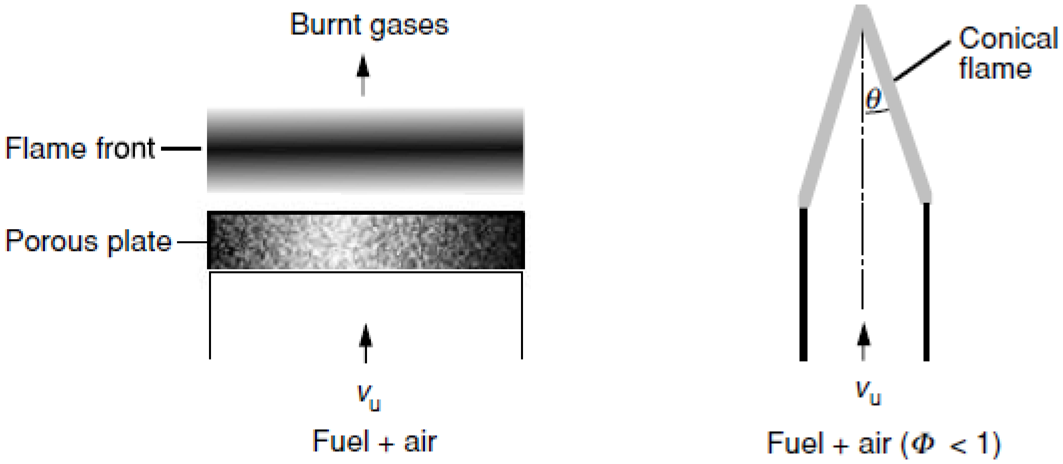
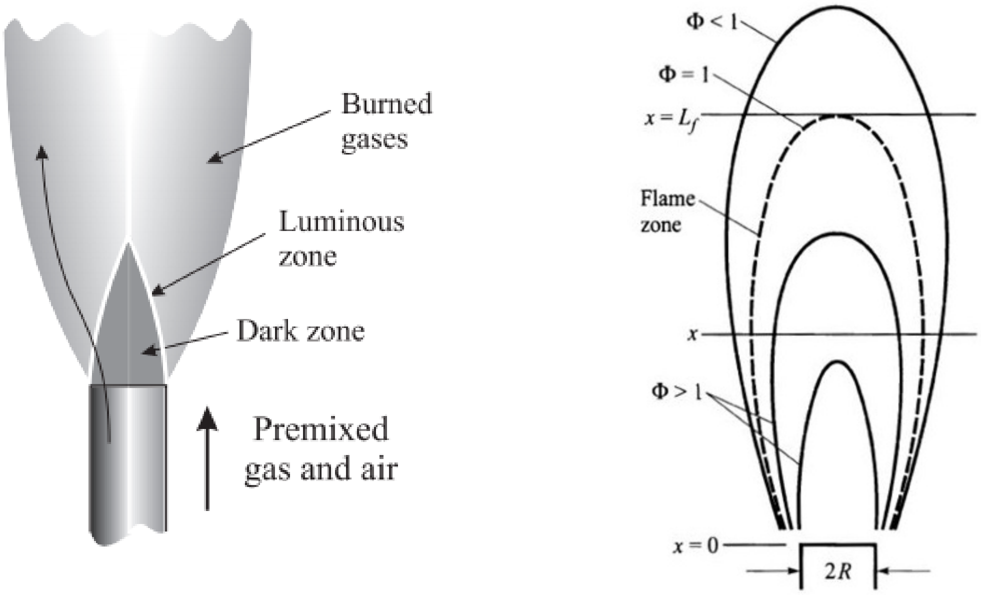


Figure 2.2: Laminar flat flame (left) and Bunsen flame (right), both laminar premixed flames



(a) Premixed flame

(b) Non-premixed flame

Figure 2.3: Schematic of (a) premixed and (b) non-premixed flames [24] [21]

2.2.2 Non-premixed flame

In non-premixed flame, fuel and oxidizer mixing process and combustion happen at the same time.

In a laminar non-premixed flame, combustion occurs at the interface between the fuel and the oxidant, and he burning depends more on reactants rate of diffusion than other parameters or chemical process involved. It can not be characterized by a laminar flame speed like premixed flame. In this kind of flame, equivalence ratio (Φ) covers all the range from 0 (air) and ∞ (fuel).

Turbulence non-premixed flame improved using the turbulence intensity to mixed better and faster fuel and air than laminar case. There is a lot of research made on this topic because this type of flame occurs in Diesel engines, which are presented in cars, boats and some industries.

2.2.3 Flat flame burner compared with Bunsen burner

The paper ”Experimental study of porous metal burners for domestic stove applications” [25] compare the flat flame burner with Bunsen burner, in order to find a highly efficiency and clean domestic stove. The research says that Flat Flame Burner has a better performance considering:

- Flame appearance
- Temperature distribution
- Thermal efficiency
- Pollution emissions (EICO and EINOx)

The results show emissions and thermal efficiency in flat flame burner are not strongly affected by the distance between the cool boundary and the burner exit. This is really relevant issue in domestic applications due to different sized pots and pans change the distance between the burner and the cool boundary, in this case, the pot or pan. Due to this fact, Flat Flame Burner is a better option to avoid emissions, to protect health of people who are cooking with domestic gaseous fuel stoves.

High levels of CO and NO_x emissions in Bunsen burner flames are produced due to flame extinction, quenching the flame and distorting the flame plume at the cool boundary of the pot or pan. This pollutants are radicals in the combustion process of the fuel depending on the composition, in ammonia case CO will not appear.

Finally, it is also important to mention that thermal efficiency is similar under some operating points between both burners..

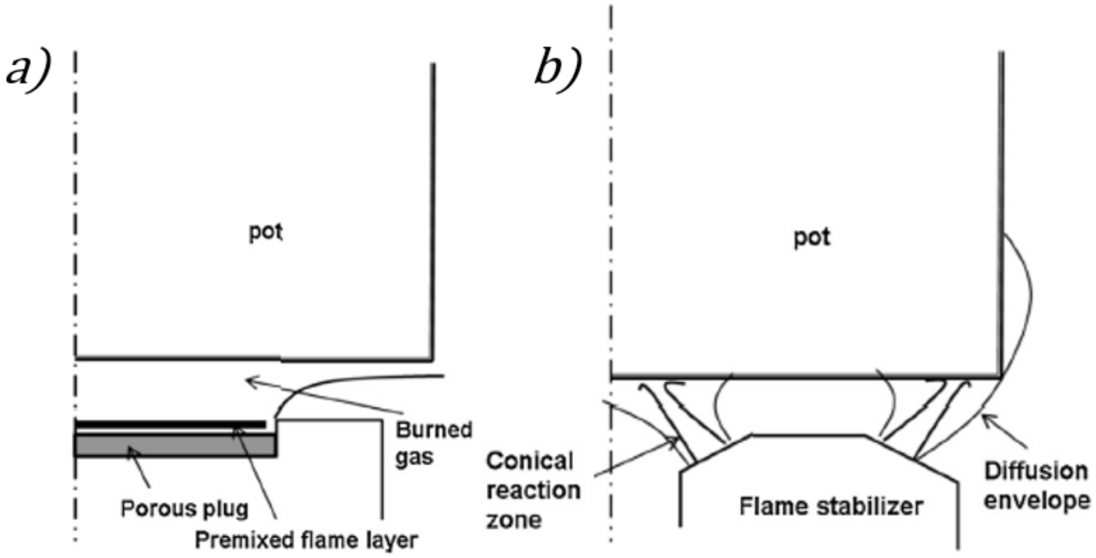


Figure 2.4: Sketch of a) application of Flat Flame Burner for cooking and b) application of traditional cooktop burner

2.3 NO formation mechanisms

One of the major pollutants are the Nitrogen oxides, represented also by NO_x, it is a concern to the environment and are generated by chemical reactions occurring in both premixed and non-premixed flames. Increasingly stringent environmental regulations require increasingly sophisticated approaches for the control of NO_x formation during combustion.

Hence, understanding of the underlying kinetics of NO formation and decomposition in flames is interesting in order to understand NO_x emissions in the different points in this master thesis operating range. NO_x chemistry is usually a strong function of the flame temperature as well as the availability of radical concentrations and are exhibited in the following mechanisms:

2.3.1 Thermal NO

The thermal NO or Zeldovich mechanism includes the oxidation of N2 by O and OH radicals at temperatures greater than 1800 K explaining in the following reactions:

$$N_2 + O \leftrightarrow NO + N \tag{2.1}$$

$$N + O_2 \leftrightarrow NO + O \tag{2.2}$$

$$N + OH \leftrightarrow NO + H \tag{2.3}$$

Equation 2.1 is rate limiting among the three pathways, and due to a slower reaction rate compared to fuel oxidation, the radical concentrations of O and OH species are assumed to be at equilibrium yielding NO formation rate as:

$$\frac{\mathrm{d[NO]}}{\mathrm{dt}} = 2k_{\mathrm{1f}} \cdot \left[\mathrm{O_2}\right]_{\mathrm{eq}} \left[\mathrm{N_2}\right]_{\mathrm{eq}} \tag{2.4}$$

Where $k_{1\mathrm{f}}$ is the forward rate coefficient for Equation 2.1. This mechanism is not contribute much in NO formation in temperature conditions below 1500 K as a result of the high activation energy.

2.3.2 Prompt NO

The prompt NO mechanism (Fennimore mechanism) is related to combustion of hydrocarbons. NO production is rapid (faster even in the low temperature areas, not require high temperature, contrary to those produced via thermal NO mechanism) in a flame front. In this mechanism, the hydrocarbon radicals react with N_2 to form amines and cyano species, which are then further converted to NO via the following pathways:

$$HCN + O \leftrightarrow NCO + H \tag{2.5}$$

$$NCO + H \leftrightarrow NH + CO \tag{2.6}$$

$$NH + H \leftrightarrow N + H_2 \tag{2.7}$$

$$N + OH \leftrightarrow NO + H \tag{2.8}$$

For the prompt NO mechanism, the rate limiting path is the initiation of the N radical from reaction of hydrocarbon radicals with molecular N_2 via:

$$CH + N_2 \leftrightarrow HCN + N \tag{2.9}$$

Comparing Thermal NO and Prompt NO mechanisms it is found that, prompt NO are dominant in premixed flames within an equivalence ratio (Φ) from 0.8 to 1.2 just upstream of the flame front. The thermal NO pathway is most dominant in the post flame regime and has a slower formation rate, it is formed in the hot burned gases with a continuous increase in concentration along with residence time.

2.3.3 Fuel NO

Fuel NO formation route is important for nitrogenous fuel compounds, for instance is relevant for combustion of pulverized coal, anhydrous ammonia and heavy distillate fuels. Unlikely premixed combustion of natural gas and gasoline, in these cases there is not a major concern this way. The conversion of fuel nitrogen to NO depends on the local flame temperature, stoichiometry and nitrogen content in the fuel.

Experimentally, it is shown fuel nitrogen is converted in the intermediate species HCN and NH_3 easily, and this leads in the process of generating more NO or N_2, this is cause by interactions with free radicals and it is depending on the local combustion conditions [14].

2.3.4 N_2O pathway

The N_2O mechanism is used to explain NO_x formation[15] in lean flames and moderate temperature conditions. The reactions to form N_2O are:

$$\mathrm{NCO} + \mathrm{NO} \leftrightarrow \mathrm{N_2O} + \mathrm{CO} \tag{2.10}$$

$$\mathrm{NH} + \mathrm{NO} \leftrightarrow \mathrm{N_2O} + \mathrm{H} \tag{2.11}$$

NO formation reactions using N_2O are the following ones:

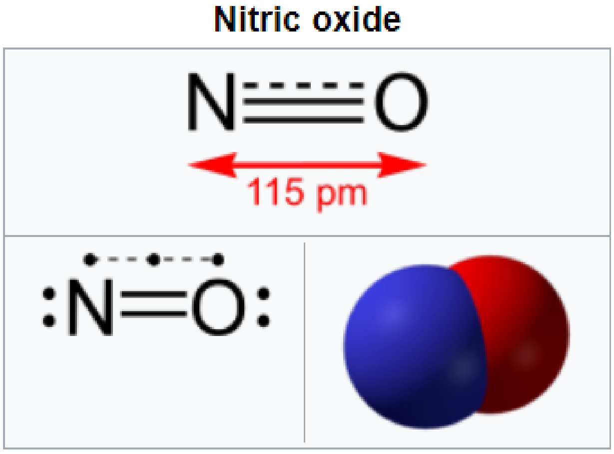


Figure 2.5: Nitric oxide, NO

$$\mathrm{N_2O + CO \leftrightarrow NCO + NO} \tag{2.12}$$

$$\mathrm{N_2O + H \leftrightarrow NH + NO} \tag{2.13}$$

$$\mathrm{N_2O + O \leftrightarrow NO + NO} \tag{2.14}$$

2.3.5 NO_2 pathway

The following equation shows how NO_2 formation mechanism works:

$$\mathrm{NO + HO_2 \leftrightarrow NO_2 + OH} \tag{2.15}$$

There are five NO formation reactions using NO_2 these ways interact with radicals like CN, OH, H and O and it have been written in the following lines:

$$\mathrm{NO_2 + CN \leftrightarrow NCO + NO} \tag{2.16}$$

$$\mathrm{NO_2 + OH \leftrightarrow HO_2 + NO} \tag{2.17}$$

$$\mathrm{NO_2 + H \leftrightarrow NH + NO} \tag{2.18}$$

$$\mathrm{NO_2 + O \leftrightarrow O_2 + NO} \tag{2.19}$$

$$\mathrm{NO_2 + M \leftrightarrow O + M + NO} \tag{2.20}$$

NO_2 mechanisms in NO formation are mainly dependent on the local flame temperature and availability of radicals concentrations, mostly in lean fuel-air areas[5].

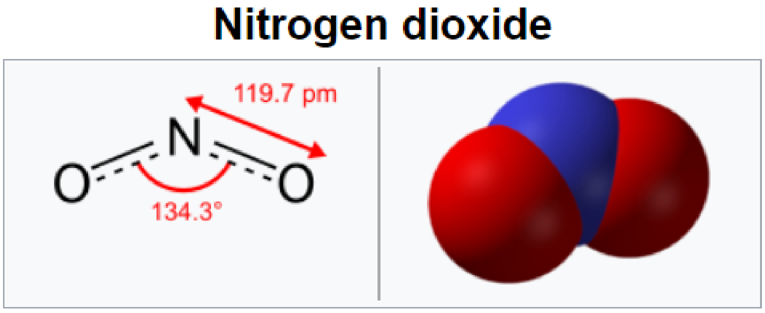


Figure 2.6: Nitrogen dioxide, NO_2

2.3.6 NNH pathway

The NNH mechanism for forming NO consist of the following reaction sequence:

$$\mathrm{N_2 + H \leftrightarrow NNH} \tag{2.21}$$

$$NNH + O \leftrightarrow NH + NO \tag{2.22}$$

$$NH + \mathrm{O}_x \leftrightarrow NO + ... \tag{2.23}$$

The main key parameters for NNH mechanism are the lifetime of NHH, the heat of formation of NHH and the rate constant k_{37} for $NNH + O$ [12]. If there is a sufficient flux through this reaction, the amount of NO produced by this pathway become significance.

There are indications that NNH pathway is relevant in diffusion flame, where it can react with O inside the flame sheet. This mechanism is also important at lower temperatures or at short residence times and reducing conditions at higher temperatures.

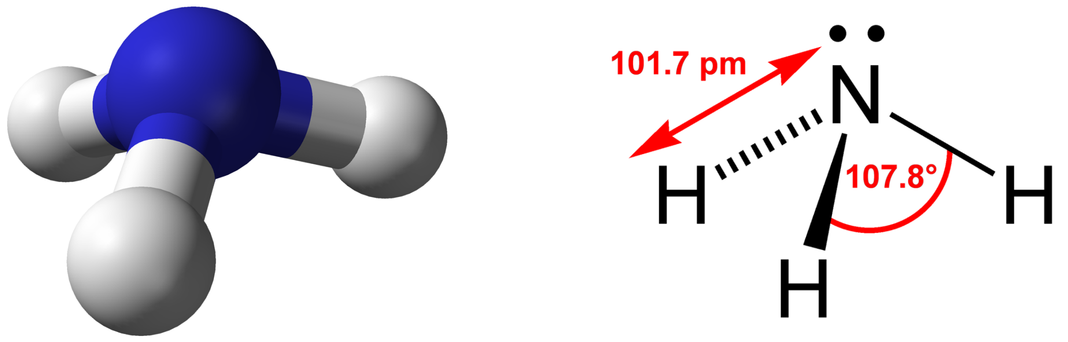
Chapter 3

Ammonia For Power

In this chapter, different topics related to ammonia to explained. Beginning with a brief introduction about the general characteristics of the chemical substance, following by why ammonia is interesting for power and drawbacks of using it, and finishing the chapter, some concepts about the ammonia combustion process.

3.1 Ammonia General Characteristics

Ammonia is a colorless gas with a sharp, penetrating odour. Its molecules have a trigonal pyramidal (as predicted by the valence shell electron pair repulsion theory, VSEPR theory) shape with the three hydrogen atoms and an unshared pair of electrons attached to the nitrogen atom (Figure 6.21b).



(a) Ammonia tridimensional structure

(b) Ammonia chemical structure

Figure 3.1: Plots of structure of ammonia

To finish the introduction about ammonia, there is a table (Table 3.1) with essential data of ammonia properties.

General Characteristics	
Boiling point	239.8 K
Freezing point	195.5 K
Critical point (T, P)	405.5 K, 111.3 atm
Density	0.73 kg/m^2 (1.013 bar at 288,15 K)
Auto-ignition temperature	930 K
Molar mass	17.031 g/mol
Octane number	130
Vaporizarion heat	1371 kJ/kg
Vapor pressure	857.3 kPa
Std molar entropy	193 $Jmol^{-1}K^{-1}$
Std enthalpy of formation	-46 kJ mol^{-1}

Table 3.1: Some ammonia general characteristic

3.2 Ammonia applications

Haber- Bosch process is the process of manufacturing ammonia. It uses an iron-based catalyst at high pressure and high temperature to combine hydrogen and nitrogen. It was invented about 100 years ago by F. Haber and C. Bosch. Mass production of ammonia was started in 1913 by BASF.

The major use of ammonia is for fertilizer in the agricultural sector, it was relevant to increase food production in the world and allow humanity to grow in number. It is also used as a raw material for various industrial products, for example as a refrigerant in large-scale industrial coolers. Furthermore, ammonia is essential as a chemical additive for selective catalytic reduction (SCR) of NO_x in thermal power generation, and most large-scale thermal power stations have installed ammonia tanks for that purpose. This ammonia industry with so much time of research and investment on production, storage, transport and utilization makes it a suitable candidate to replace fossil-based fuels with minimal investment. Indeed, the boiling temperature and condensation pressure of ammonia are similar to propane, ships designed for propane transportation can generally be used for ammonia.

The worldwide production of ammonia each year is around 180 millions tons. Nowadays, the method most used to get ammonia obtain hydrogen from natural gas and nitrogen from the atmosphere, this is the current commercial production of ammonia . It is calculated that the CO_2 emission from these industries is almost 1% of the total CO_2 released globally. Attempts to produce “green ammonia” using renewable hydrogen, as well as it is beginning in Europe and Australia the carbon capture and storage (CCS) for CO_2.

Hydrocarbon fuels still have some benefits when comparing with Ammonia utilization as a fuel. Ammonia has 40% of the heat of combustion expected for typical hydrocarbon fuel and NH_3/air flame maximum laminar burning velocity is around 20% also in compared with a typical hydrocarbon fuel. Even so, these known problems associated with ammonia as a fuel, there were some tries in the past to use ammonia as a fuel that started in the 1940s. Nowadays, the list of uses for ammonia that are being studied is endless, NH_3 for hydrogen storage, for energy carrier or use as a fuel, as it is shown in the Figure 3.2.

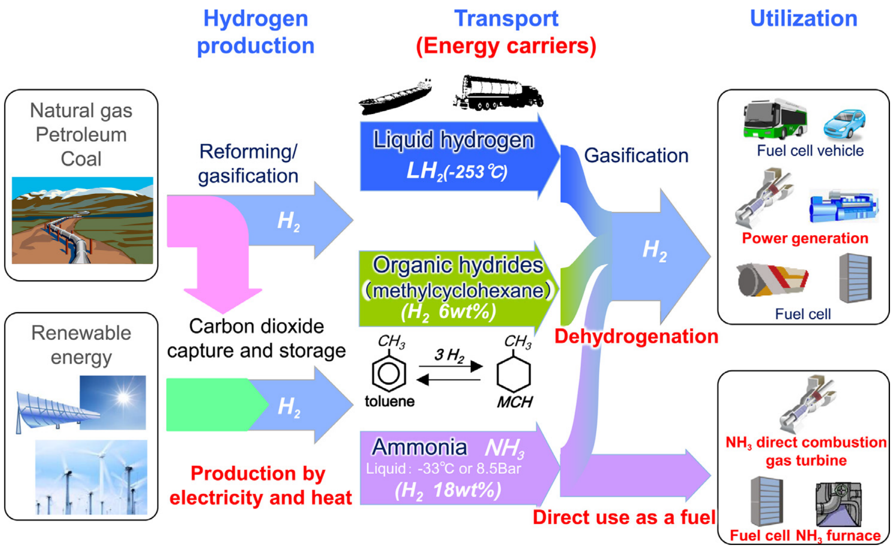


Figure 3.2: Scheme showing hydrogen production, transport, and various uses

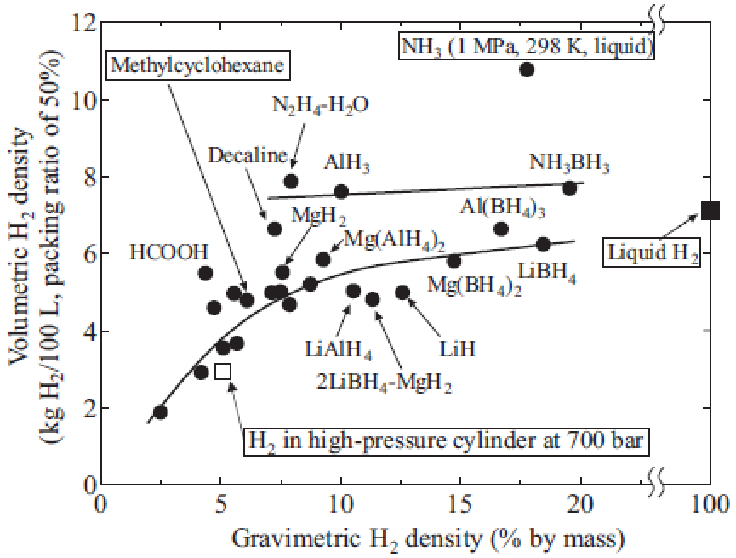


Figure 3.3: Gravimetric and volumetric H_2 density of hydrogen carriers.

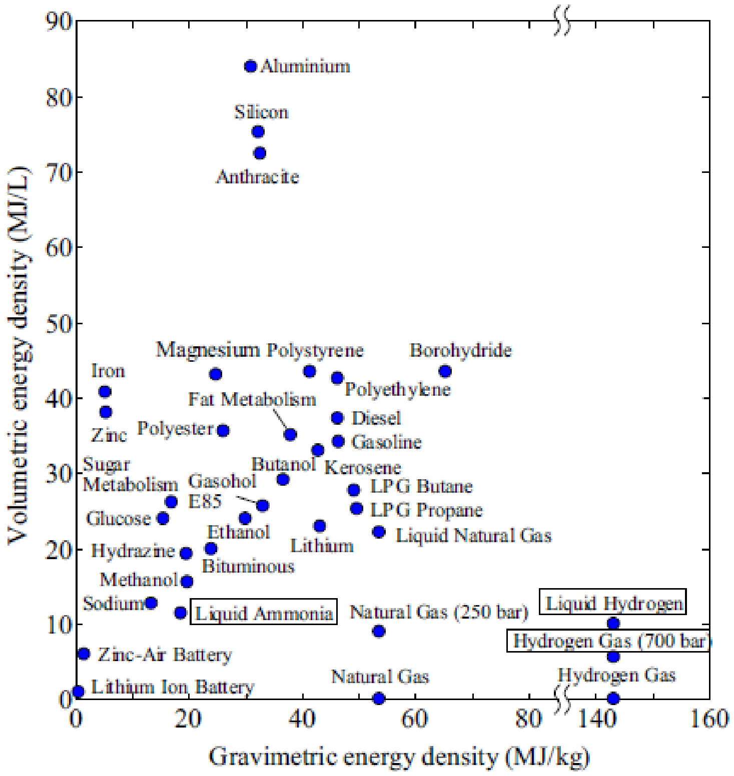


Figure 3.4: Gravimetric and volumetric energy density of combustible materials and batteries. Higher heat value (HHV) for fuels are used because metals are included

In the Figure 3.4, it is compared the energy density of liquid ammonia with hydrogen in the same state. 0.016 MJ/L and 0.010 MJ/L are the volumetric energy density of ammonia and hydrogen respectively.

3.3 Interest in Ammonia For Power

Ammonia is consider on of the most interesting hydrogen carrier as it shown in the Figure 3.3 also good for energy storage as it is possible to observe in Figure 3.4. However, In the process of ammonia becoming a viable energy is necessary ti reach the energy contained to be release at the same power levels required for commercial or large scale applications nowadays. Gas turbines, reciprocating engines, fuel cells and cycles were developed for hydrocarbon fuel, to be competitive ammonia technology need to be developed. Thus, new devices, techniques and industries that can use ammonia coming from clean and renewable sources would have the following advantages:

3.3.1 Reducing emissions

Due to the lack of carbon in its chemistry, ammonia offers the possibility of being burned without direct CO_2 emissions. Using NO_3 in gas turbines, fuel cells and reciprocating engines could be a possible step to obtain a carbon free future.

In addition if all the resources used in these cycles come from renewable and clean sources, it can be entirely sustainable and carbon-free. Even so the transition from current fossil fuels to ammonia technology will still produce carbon, because of the high plan demanding of this process, the idea of combining the use of both fuels, ammonia and fossil fuels, could ease the transition and lead in the near term in a reduction of $CO-2$ emissions, ultimately leading to zero-carbon energy systems.

3.3.2 Improving security of supply

The raw material used for Ammonia synthesising are abundant on Earth, hydrogen, which could be obtained from water and nitrogen around 70% of the atmosphere. A large amount of ammonia is produced currently, 180 Mtonnes/year of ammonia are produced and transported and is therefore a practical and scalable fuel. With the capability of providing grid-scale energy storage, ammonia facilitates the increasing exploitation of renewable energy sources. This technology is comparison with other renewable energy sources present advantages.

3.3.3 Reducing costs of energy

In the close future if the prices of fossil fuels still increase, ammonia could be a competitive free carbon solution. Nonetheless, nowadays fossil fuels are still governing the economy, it is possible for ammonia to open some competitive scenarios due to its characteristics as the already existing industrial production, and the storage and distribution nets created for this chemical.

All of these advantages, reduce the initial investment; it is not the same starting from anon-existing business than invest in re-scale the industrial capacity for a technology. Saving money in developing safe handling procedures, infrastructure and training personal in compare with other alternatives.

As a energy carrier, the cost of ammonia energy storage is similar as pumping water in a pumped-storage hydroelectricity plant, without the necessity of finding adequate geological slope. Other storage technologies like electrical batteries are above the cost of ammonia.

It is required making a plan and consideration about how it is going to be the ammonia economy, it will need to be price competitive and is urgent further research to solve problems that currently this carbon-free technology present . There is nowadays a wide variety of energy storage technologies, mechanical, thermal, electrical and chemical technologies for storing electrical energy adaptable from small to large scale applications [13].

In near term, some hydrocarbons present a viable option for energy storage. But to avoid CO_2 emissions in chemical storage and to find the optimal distribution of large amounts of energy only remain as a valid candidates hydrogen and ammonia.

Finally, hydrogen safty problems due to high flammability need of a more complex system in comparision with ammonia. The already existing centenary developed infrastructure, push ammonia as a strong candidate to support at large scale the concept of flexible energy storage. In order to solve some renewable energies intermittence in production problem .

3.4 Disadvantages

Ammonia presents several drawbacks. It could damage health if no proper actions are taken. Another disadvantage of using ammonia is the corrosion on pipelines and storage system. Fire and explosion could occur with ammonia, so it also must be made into consideration.

3.4.1 Health and safety

Ammonia (NH_3) is one of the most commonly produced industrial chemicals in the United States. It is used in industry and commerce, and also exists naturally in humans and in the environment. Despite these facts, the human exposure of ammonia could carry dangerous consequences depending on exposure concentrations and exposure time. It can find the result in Table 3.2. Besides ammonia is compared in toxicity, flammability, and reactivity with other usual fuels in Figure 3.5, and also in Figure 3.7 the NFPA 704 diamond.

Substance	Health	Flammability	Reactivity
Ammonia	3	1	0
Hydrogen	0	4	0
Gasoline	1	3	0
LPG	1	4	0
Natural Gas	1	4	0
Methanol	1	3	0

0=No hazard, 4=Severe hazards

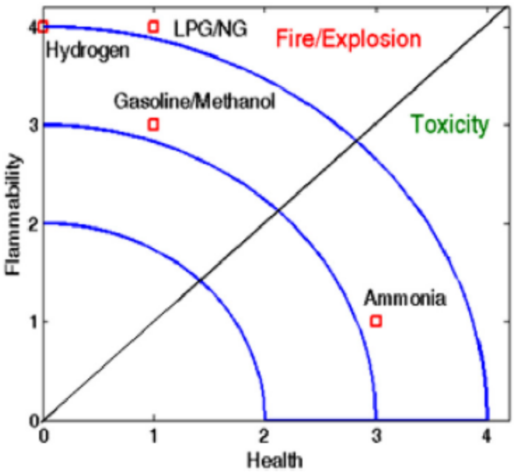


Figure 3.5: Toxicity and Fire/Explosion comparison of different fuels

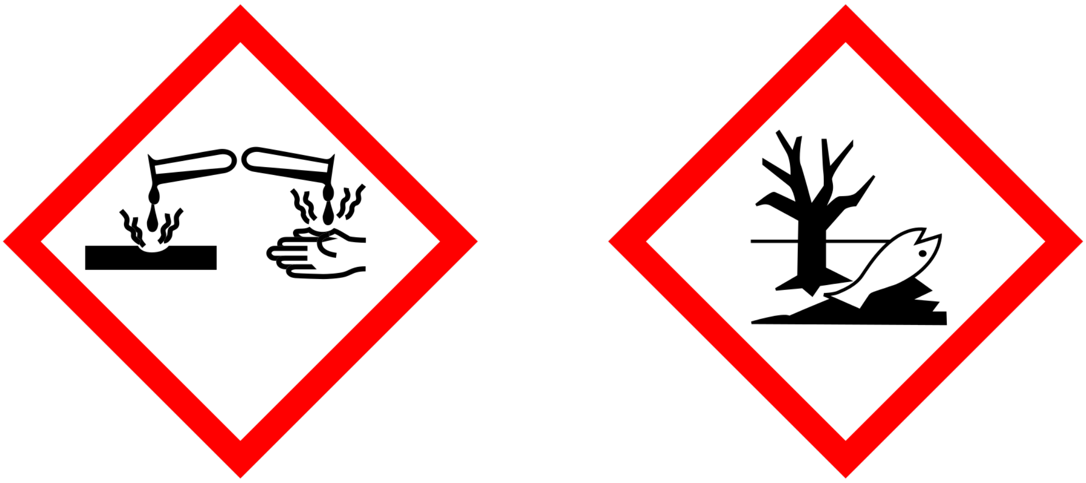
Effect	Ammonia concentration in air (by volume)
Readily detectable odor	20 -50 ppm
No impairment of health for prolonged exposure	50 - 100 ppm
Severe irritation of eyes, ears, nose and throat. No lasting effect on short exposure	400 - 700 ppm
Dangerous, less than hours of exposure may be fatal	2000 - 3000 ppm
Serious edema, strangulation, asphyxia, rapidly fatal	5000 - 10000 ppm

Table 3.2: Effects on human of ammonia exposure depending on concentration in ppm

The main reason why it is bad for health is that it ammonia interacts directly with any moisture present on the human body, such as the skin, respiratory cavities, and especially on the mucous membrane, and forms there the corrosive ammonium hydroxide. This chemical compound causes tissue necrosis by disrupting the lipids present on the membrane cells this process, also known as saponification destroys the cells. When the cellular proteins decompose, due to this cellular destruction, the water present in them is extracted, this generated an inflammatory response causing even more damage.

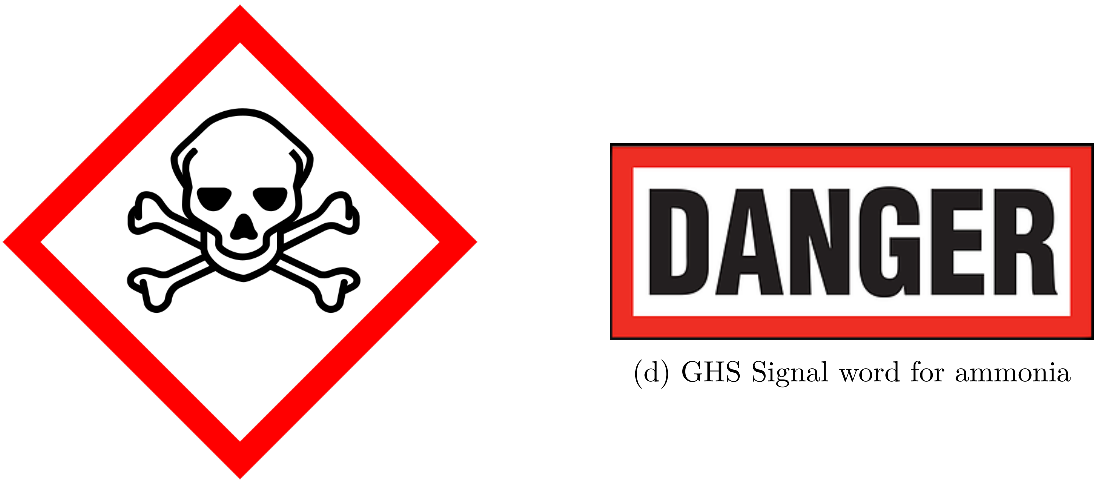
Globally Harmonized System (GHS) required to classify and label chemical components is an internationally recognised standard manage by the Unite Nations. It was designed to replace the different and uncertain sets of classification diagrams used all around the world. For ammonia GHS designed those following pictograms, also the signal word

'Danger' (Figure 3.6).



(a) GHS05: Corrosive

(b) GHS06: Toxic



(d) GHS Signal word for ammonia

(c) GHS09: Environmental hazard

Figure 3.6: GHS hazard pictograms and Signal word for ammonia

To end this subsection it is necessary to explain the four divisions of NFPA, there are coded by their color:

- The red color that you can see on top indicates flammability
- The blue on the left part shows the health-danger level
- The yellow on the right represents the level of chemical reactivity
- The white, on the other hand, contains codes for special risk, for example COR that means highly corrosive

3.4.2 Corrosive nature of ammonia

Using a chemical as a working fluid or fuel could have some impacts on pipelines and structural components depending on its characteristics. This impact is important in the selection process, this increased the complexity in order to find an appropriate candidate for the use that is planned. Corrosion, or other chemical reaction with some constructive materials could be an important drawback.

NH_3 is incompatible with various industrial materials. NH_3 is corrosive to brass, zinc alloys and copper, forming a greenish/blue color corrosion. Ammonia should not be mixed with bromine, hypochlorites, iodine, and chlorine as ammonia is an alkaline reducing agent and reacts with oxidizing agents acids, and halogens.

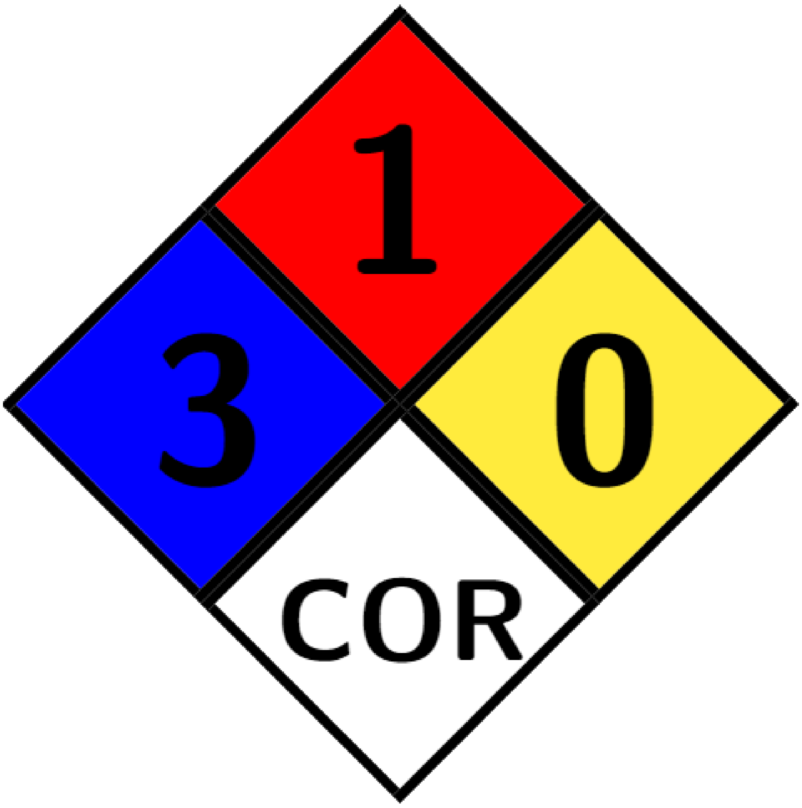
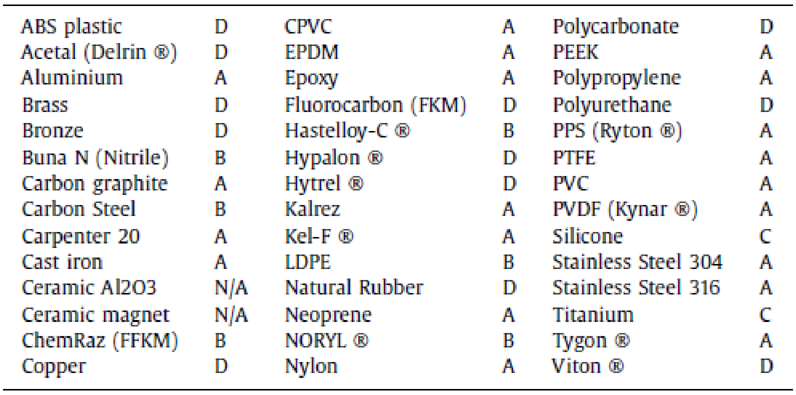


Figure 3.7: NFPA 704 for ammonia

In the following figure, there is a list of compatibility results between ammonia and various industrial materials, Figure 3.8 . Thus, the careful material selection needs to be



ABS plastic	D	CPVC	A	Polycarbonate	D
Acetal (Delrin ®)	D	EPDM	A	PEEK	A
Aluminium	A	Epoxy	A	Polypropylene	A
Brass	D	Fluorocarbon (FKM)	D	Polyurethane	D
Bronze	D	Hastelloy-C ®	B	PPS (Ryton ®)	A
Buna N (Nitrile)	B	Hypalon ®	D	PTFE	A
Carbon graphite	A	Hytrel ®	D	PVC	A
Carbon Steel	B	Kalrez	A	PVDF (Kynar ®)	A
Carpenter 20	A	Kel-F ®	A	Silicone	C
Cast iron	A	LDPE	B	Stainless Steel 304	A
Ceramic Al2O3	N/A	Natural Rubber	D	Stainless Steel 316	A
Ceramic magnet	N/A	Neoprene	A	Titanium	C
ChemRaz (FFKM)	B	NORYL ®	B	Tygon ®	A
Copper	D	Nylon	A	Viton ®	D

Figure 3.8: Material compatibilities with ammonia [3]

Figure 3.9: Explosions and cracks in cylinder by build-up pressure, respectively [19]

performed when considering ammonia for power generation.

Chemical Compatibility Database; A: excellent; B: good- minor effect, slight corrosion or discoloration; C: fair- moderate effect, not recommended for continuous use, with softening or loss of strength, swelling may occur; D: severe- not recommended; N/A: information not available.

3.4.3 Fire and Explosions

There were some explosions in the past, and some of them have been documented, Figure 3.9. The pressurized storage maintain as a liquid the ammonia inside the container, this characteristic could lead in a well-known phenomena called BLEVEs (Boiling Liquid

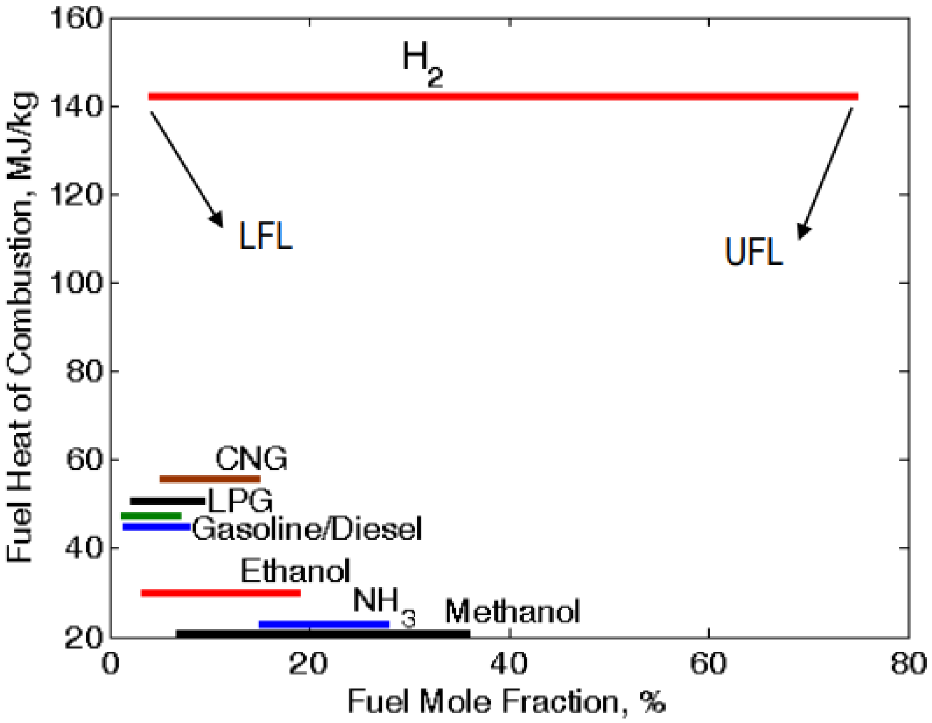


Figure 3.10: Low and upper flammability limits of various fuels [18]

Evaporation Vapor Explosions), an a external heat source close to the container could compromise the structural integrity. The break of this container release ammonia to the environment, if there is fire, an heat source or just a simple spark increase the probability of an explosion [23].

Taking care while experimenting with ammonia is really important even if there were documented accidents only for large containers in industrial facilities. Range from 18% to 28% fuel mole fraction (Figure 3.10) is the flammability limits for this chemical. Hence, some extra protection as a dilution system is needed to avoid this range when combustion devices or external heat source are in use near by. NH_3 ignition energy is at least two or three orders of magnitude higher than for common hydrocarbons ignition energy, and low laminar burning rate help to prevent the severity of ammonia combustion hazards.

According to some key points in the Compendium of Chemical Hazards of ammonia from the Health Protection Agency (UK) [1], incident about fire-related to ammonia has the following characteristics:

- Ammonia vapor in the air is flammable and may explode when ignited
- Chemically stable when it is under normal conditions
- Poisonous fumes are emitted by ammonia when it is heated to decomposition
- It is important to use fine water spray and liquid-tight protective clothing with breathing apparatus

3.5 Ammonia Combustion

Ammonia is a potential carbon-free fuel and one possible step in the decarbonization of energy generation. It has been used during the past 100 years as a fertilizer, chemical raw material, and refrigerant. However as fuel presents several challenges, such as low flammability, high NO_X emission, and low radiation intensity.

The low burning velocity of NH_3/Air flames makes flame enhancement important for the success in this application of ammonia. Also, its low reactivity makes ammonia combustion challenging.

$$NH_3 + \frac{3}{4} \cdot O_2 \longrightarrow \frac{1}{2} \cdot N_2 + \frac{3}{2} \cdot H_2O \tag{3.1}$$

Hydrogen addition is a reasonable approach for simultaneously achieving carbon-free combustion and flame enhancement. The experiments made for this report it is used a mix of ammonia and hydrogen as a fuel, the chemical equation used for calculation is the following one:

$$\begin{multline}(a \cdot H_2 + b \cdot NH_3) + \left(\frac{1}{2} \cdot a + \frac{3}{4} \cdot b\right)(3.77 \cdot N_2 + O_2) \longrightarrow \\ \left(\frac{6}{4} \cdot b + a\right) \cdot H_2O + \left(\frac{1}{2} \cdot 3.77 \cdot a + \frac{3}{4} \cdot (3.77 + 2/3)\right) \cdot N_2 \tag{3.2}\end{multline}$$

Where a is the number of hydrogen moles and b ammonia moles, the air is simplified by this expression $(3.77 \cdot N_2 + O_2)$. It was found necessary for the understanding of experiments the explication of several concepts related with NO_x and ammonia.

3.5.1 Chemical kinetics of ammonia oxidation and fuel NO_x

Ammonia oxidation chemistry has been extensively studied over the past several decades mainly because of its relevance to fuel NO_x formation and selective non-catalytic reduction of NO_x (SNCR) using ammonia as a reducing agent.

There are some important early efforts to describe ammonia oxidation with detailed kinetics, for instance the work of J. Miller and his team. The understanding of ammonia oxidation has improved since then and the kinetics models have improved in comprehensiveness and accuracy over the years. Nevertheless, the reaction pathway which is shown in the Figure 3.11, remains relevant to understanding the chemistry of NH_3 oxidation.

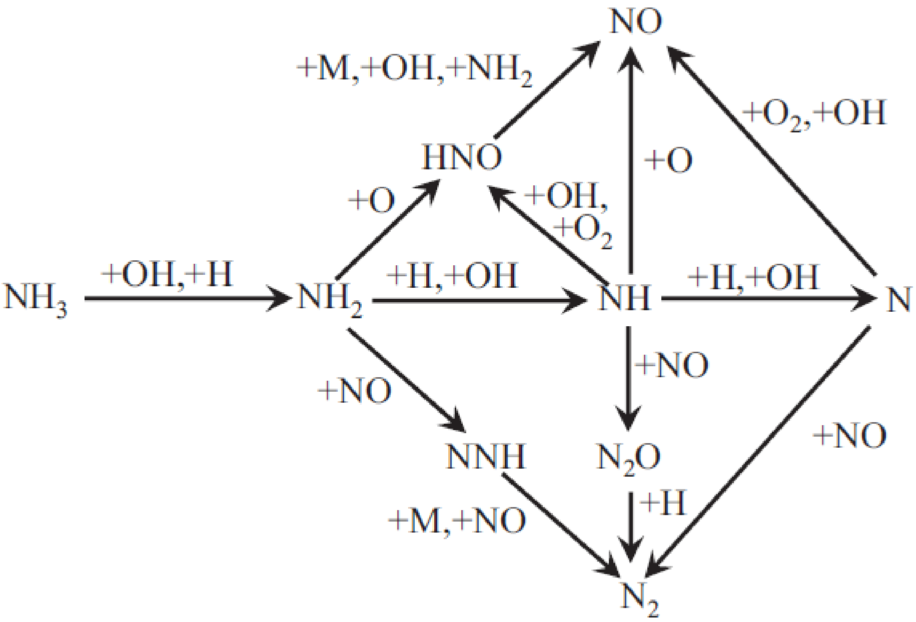


Figure 3.11: NH_3 oxidation pathway by Miller et al. [16]

Chapter 4

Equipment

4.1 Introduction

In this chapter, the equipment used in the experiments is described. Since this thesis is based on experimental research, it is quite important the material used. This chapter contains a comprehensive description of the material is chosen, how it addresses the problem, and why.

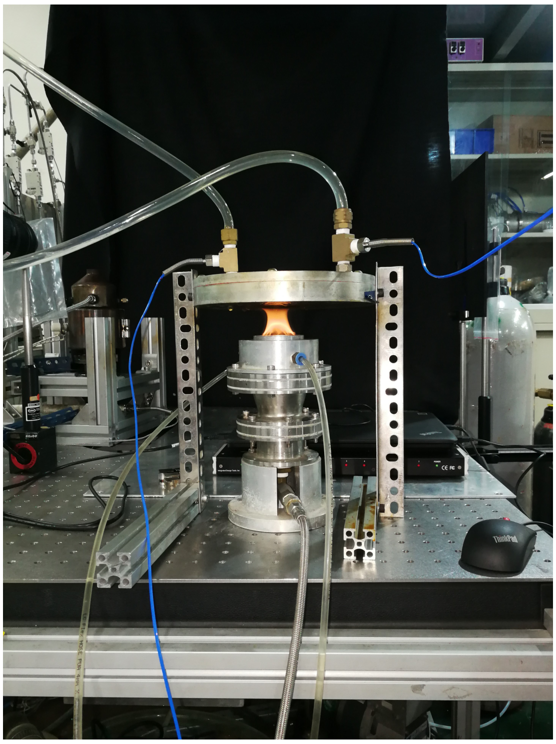


Figure 4.1: Operating the equipment during experiments

4.2 Flat Flame Burner and Cooling System

Flat flame burner with a porous media refrigerated with a water system is the burner used in this master thesis. It was designed in the Combustion and Propulsion Laboratory in NCKU.

The model BL-710D Figure 4.2b was used for the cooling system. There was a PID controlled speed and temperature with LED digital display. There was temperature accuracy of ±0.1°C.

(a) Flat Flame Burner

(b) Cooling System

Figure 4.2: Burner and Cooling System used for the experiments

4.3 Measurement System

Three flowmeters were used to measure the flow of ammonia, hydrogen and air. The BROOKS flowmeters used in the experiments were necessary to calibrate in order to make accurate measurements, unlike DPC that not need to calibrate.

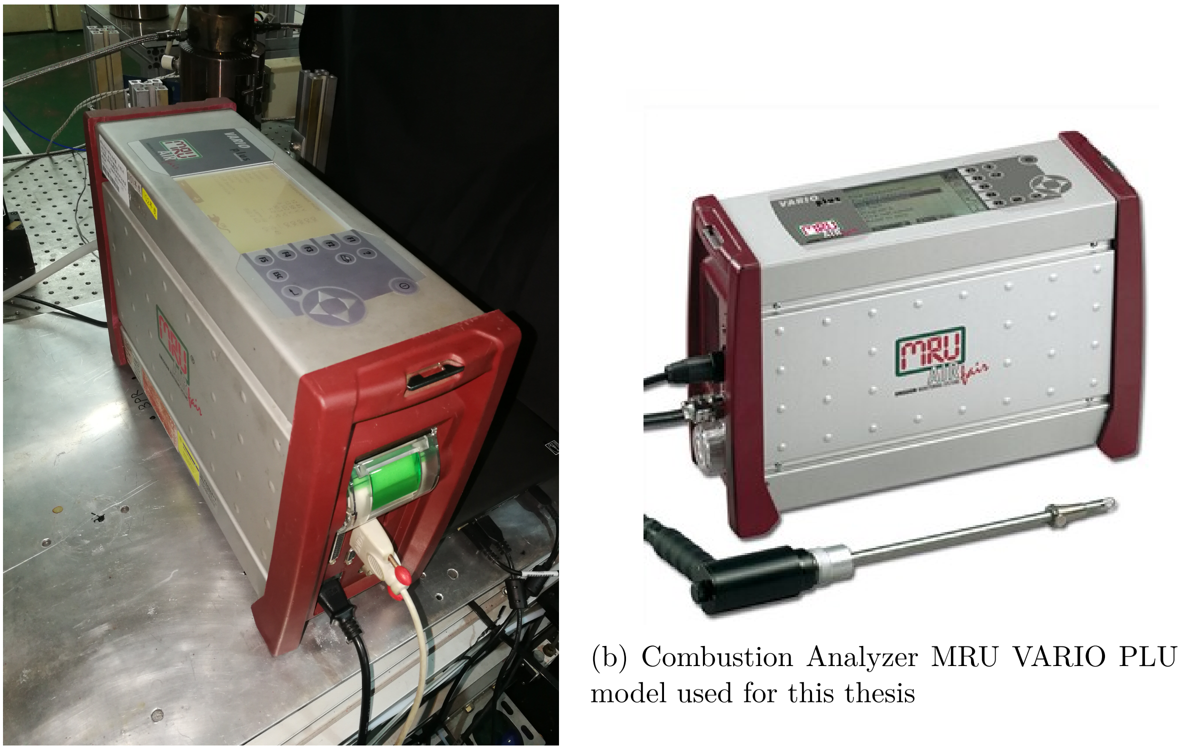
(a) BROOKS INSTRUMENTS Flowmeter: Thermal Mass Flow 5800E Series

(b) AALBORG Flowmeter: DPC Intelligent Mass Flow Controller

Figure 4.3: Gas Flowmeters used for the experiments

4.4 Gas Analyzer

The gas analyzer model MRU VarioPlus was used in these experiments. This equipment were able to detect: O_2%, CO_2%, CO ppm, NO ppm, NO_2 ppm, SO_2 ppm, H_2S ppm and CH_4%.



(a) Gas analyzer during the experiments

(b) Combustion Analyzer MRU VARIO PLUS model used for this thesis

Figure 4.4: Gas analyzer

4.5 Protection

Corrosion is one of the main drawbacks of ammonia, as it is explained in the chapter 3. Due to this fact it is recommended to wear protection while it is operating ammonia. Thanks to the ammonia odor it is easily recognizable when there is some gas leak from this gas during the experiments. It is also essential to have safety glasses for protecting eyes from ammonia irritation.

Figure 4.5: Mask used during the experiments

Protection is not related only with mask and glasses, the experiments were taken place under a gas exhaust installed in the laboratory to absorb the combustion products and other gases.

4.6 Bottled gas

Chemical substances that are gaseous at standard temperature and pressure (which is expressed usually with STP) are usually stored using Bottled gas. For this purpose, the gas has been compressed, so the material which is made off the bottle required to be the strength to resist. Carbon steel, stainless steel, aluminum, or composite are some examples or materials used to make this kind of storage. For the thesis experiments, it was needed ammonia, hydrogen bottled gas (Figure 4.6a and Figure 4.6b).

(a) Ammonia Bottled (b) Hydrogen Bottled

Figure 4.6: Laboratory gas bottled used in the experiments

4.7 Heat exchanger and Thermocouple System

The heat exchanger used for the experiments is a circular piece of metal with two connections, for the water cooling system, in this connections there are thermocouples K-type to measure temperature in and out of the heater in order to calculate the heat provided from the combustion. In Figure 4.8 the thermocouples are connected to the computer by the blue cables. The water from the cooling system is measured with a water flowmeter (Figure 4.7).

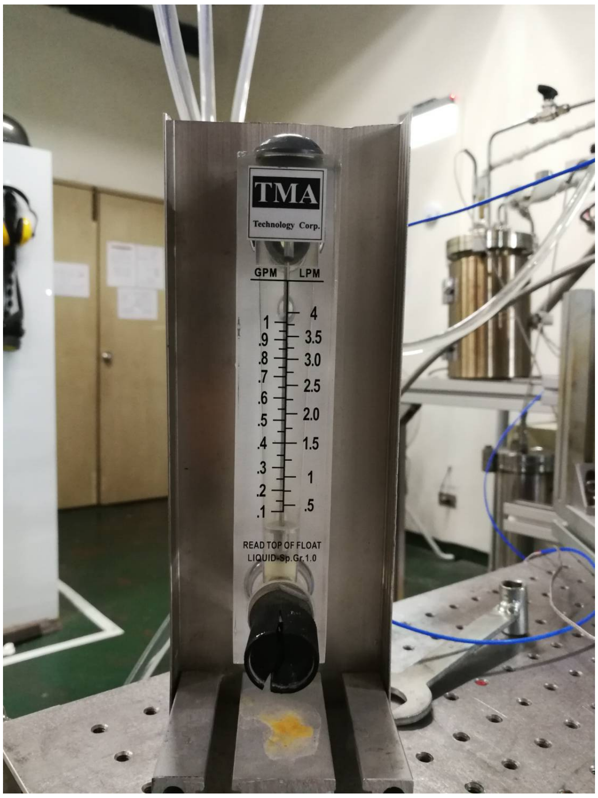


Figure 4.7: Water Flowmeter for Heat Exchanger

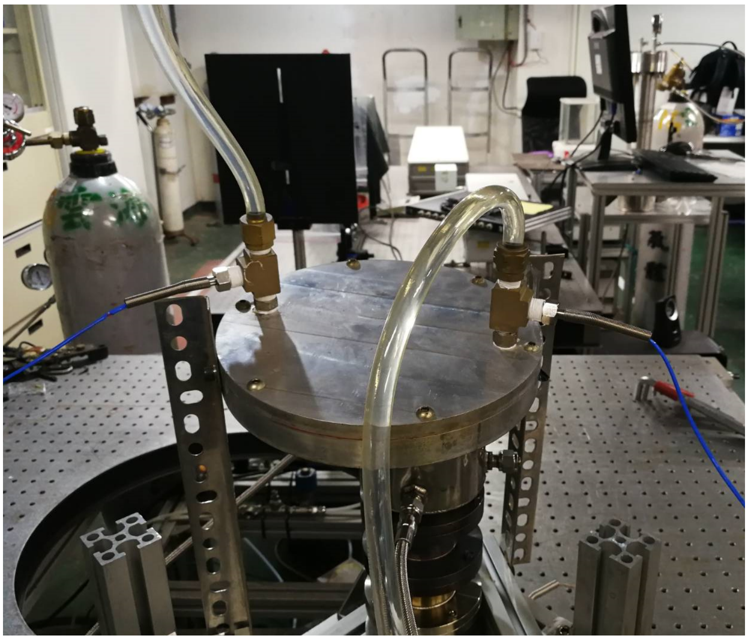


Figure 4.8: Heat Exchanger, Water System Heater and Thermocouple System

Chapter 5

Experiment 1: Thermal Efficiency

5.1 Introduction

In this chapter, the equivalence ratio, output power and hydrogen percentage in the fuel mix affect the thermal efficiency, η_{th}, and were delineated. It was necessary to establish the distribution of points, time and flame limits were taken in consideration. With this information, it will be possible to know in which points the burner is operating in higher efficiency performance and why.

In the next section it will be explained the approach to the experiment, and in the following sections, it is presented the results with some comments about trends that appear. The conclusions of the studies are presented in the last chapter of this master thesis.

5.2 Approach to the experiment

The following operating parameters have been considered: equivalence ratio (Φ, measured in relation with the stoichiometric relation with fuel and air, 0.6 lean fuel flame and 2.0 a very rich fuel flame), hydrogen percentage in the fuel mix (the amount of hydrogen is varied from 20% to 50%) and the output power (which is related with the amount of fuel that will be burned in each point). These parameters will vary in order to be able to completely represent all the possible operating states of the burner and to be able to have a record of the effect on the thermal efficiency of these parameters throughout their range of variation. The values of these parameters are shown below:

- **Equivalence ratio, Φ:** 0.6, 0.8, 1.0, 1.2, 1.5, 1.7 and 2.0
- **Amount of hydrogen, $\%H_2$:** 20%, 25%, 30%, 35%, 40%, 45% and 50%
- **Output Power:** 500 W, 1000 W and 1500 W

The number of points for each output power case is 49. The sum of all cases for this experiment reach 147 points.

It needs to be mentioned that fuel will be composed only by hydrogen and ammonia, and when it is expressed the amount of hydrogen in the fuel mix, for instance, $\%H_2$ is 20 %, the amount of ammonia will be the rest, in this case 80 %. This percentage of hydrogen is related to the fuel amount, and it will not be taken into consideration the amount of air.

5.2.1 Calculations

To do the experiments, it is necessary to calculate the volume per second required for each reactant (H_2,NH_3 and Air). This data will be controlled by the flowmeters. The initial parameters will be equivalence ratio, amount of hydrogen, and output power.

The first step is to know the chemical expression for the combustion process, this expression is already in chapter 3, but it will be shown again (Equation 5.1).

$$(a \cdot H_2 + b \cdot NH_3) + \left(\frac{1}{2} \cdot a + \frac{3}{4} \cdot b\right)(3.77 \cdot N_2 + O_2) \longrightarrow \left(\frac{6}{4} \cdot b + a\right) \cdot H_2O + \left(\frac{1}{2} \cdot 3.77 \cdot a + \frac{3}{4} \cdot (3.77 + 2/3)\right) \cdot N_2 \quad (5.1)$$

This is a simplified expression for the real combustion process. Using this expression it is possible to know the mole relation in each stoichiometric case between fuel and air. Changing the values of a and b (always following this Equation 5.2, in other words, there will be one mole of fuel in every case, a will be the coefficient for hydrogen H_2 and b for ammonia NH_3) it can adjust the chemical expression for different percentage of hydrogen in the mix.

$$a + b = 1 \tag{5.2}$$

Each different fuel mix have different lower heating value (LHV), this concept is the amount of heat released during the combustion of a specified amount of it, the values found for the chemicals are expressed in energy/mass of fuel. For knowing the energy that is each fuel mix used in this experiment it is needed to use the following expression Equation 5.3, because LHV is expressed related with mass it is used molar mass (M_{H_2} and M_{NH_3}) of each chemical in the fuel to calculated the averaged LHV for the fuel mix.

$$\begin{aligned} LHV_{fuel} &= \frac{Fuel\ mix\ energy}{Fuel\ mix\ mass} = \frac{m_{H_2} \cdot LHV_{H_2} + m_{NH_3} \cdot LHV_{NH_3}}{m_{fuel}} \\ &= \frac{a \cdot M_{H_2} \cdot LHV_{H_2} + b \cdot M_{NH_3} \cdot LHV_{NH_3}}{a \cdot M_{H_2} + b \cdot M_{NH_3}} \end{aligned} \tag{5.3}$$

Due to Equation 5.2, the number of moles are equal to the mole fractions in the fuel mix. As a result, fuel mix average molar mass M_{fuel} is equal directly to fuel mix mass.

$$M_{fuel} = M_{NH_3} \cdot b + M_{H_2} \cdot a \tag{5.4}$$

Fuel mass flow $\dot{m}_{fuel}$ is calculated using the output power defined in each point as an input variable, and the LHV_{fuel} is calculated as is expressed in Equation 5.3.

$$\dot{m}_{fuel} = \frac{OutputPower}{LHV_{fuel}} \tag{5.5}$$

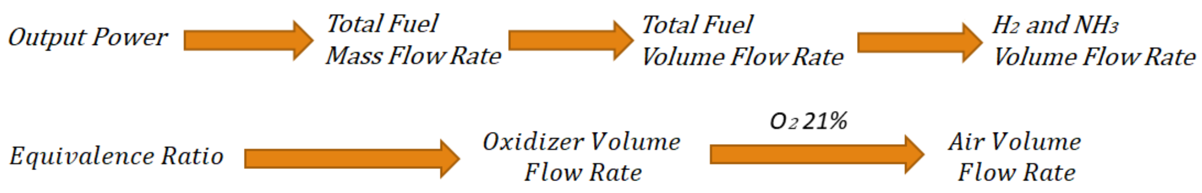


Figure 5.1: Calculation process

$$\dot{V}_{fuel} = \frac{\dot{m}_{fuel}}{PM_{fuel}/RT} \tag{5.6}$$

Then fuel mix volume is calculated using the ideal gas law Equation 5.6, and each volume for each fuel component follows the same proportion as moles proportion, thus multiplying the coefficient a and b and total fuel volume is obtained each fuel flow volume.

$$\dot{V}_{H_2} = \dot{V}_{fuel} \cdot a \tag{5.7}$$

$$\dot{V}_{NH_3} = \dot{V}_{fuel} \cdot b \tag{5.8}$$

The next step is to calculate the amount of air. For this, it will be necessary to use the equivalence ratio (Equation 5.9).

$$\varPhi = \frac{n_{fuel}/n_{ox}}{(n_{fuel}/n_{ox})_{st}} = \frac{a+b}{\frac{1}{2} \cdot a + \frac{5}{4} \cdot b} \tag{5.9}$$

This relation it is also valid for volumes, so applying this equation it is possible to obtain oxygen volume and also air volume because air composition is around 21% oxygen.

$$\dot{V}_{O_2} = \frac{\dot{V}_{fuel}}{\varPhi \cdot (n_{fuel}/n_{ox})_{st}} \tag{5.10}$$

$$\dot{V}_{air} = \dot{V}_{O_2}/0.21 \tag{5.11}$$

Following this process, it is obtained beginning with 3 parameters that define each case ($\%H_2$, Φ and Output Power) it is possible to obtain the inputs for the flowmeters: $\dot{V}_{H_2}$,$\dot{V}_{NH_3}$ and $\dot{V}_{air}$.

5.2.2 Designing process

The process to obtain the final points for the experiment was started using the flat flame burner for burning at first propane, hydrogen, and finally burning hydrogen plus ammonia. Propane was an easy gas to be burned and to get introduced in the use of this burner and in the combustion experiments. Also delightful in order to know how to manage with laboratory equipment.

The next step in the designing process was to discover limits for the amount of hydrogen used for the study points. For this purpose the first experiment was taken place, this experiment consists in finding out the limits of the amount of hydrogen to sustain a stable flame using as fuel hydrogen and ammonia mix, starting at the amount of $30\%H_2$ and then reducing the percentage of hydrogen in the mix until seeing flames instabilities. The results obtained in this experiment are presented in the following table (Table 5.1).

		Output Power [W]		
		500	1000	1500
EQ [-]	0.6	20%	20%	20%
	0.8	15%	20%	20%
	1.0	20%	20%	20%
	1.2	20%	20-25%	20-25%
	1.5	20%	20%	20-25%
	1.7	20%	20%	20%
	2.0	20%	15%	20%

Table 5.1: Limits for amount of hydrogen to obtain a stable flame

The limits related to equivalence ratio and output power mainly depend on the maximum and minimum flow amount that flowmeters can measure correctly. So no experiments were done to find out the limit values.

5.2.3 Experimental setup

The experimental setup for this master thesis first experiment is represented in Figure 5.2. Metal pipes are used for ammonia due to the fact of corrosion. Three flowmeters control the amount of hydrogen, ammonia, and air. The burner has a cooling system to maintain the temperature at 20° Celsius degree. The distance between the heater and the burner will be 3 centimeters.

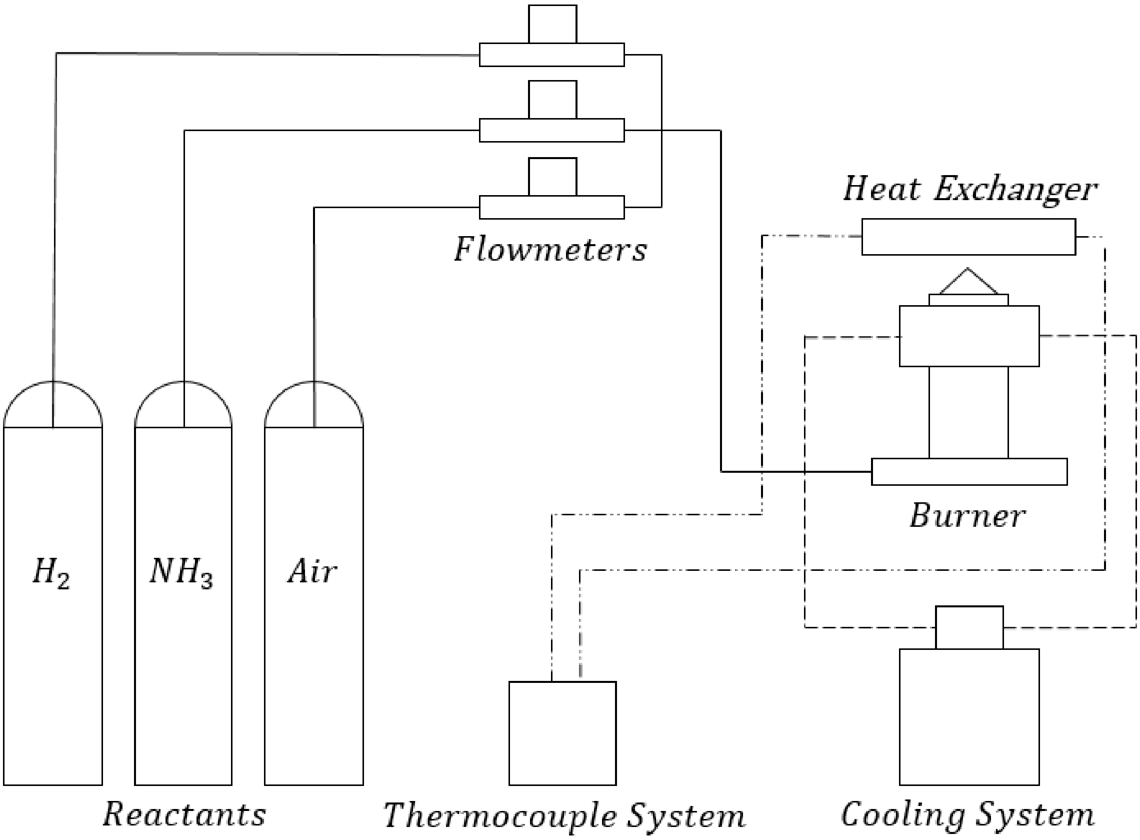


Figure 5.2: Thermal efficiency experiment setup sketch

In order to calculate burner thermal efficiency, it is used a heater with thermocouples type K at the entrance and at the exit of the water to the heater exchanger, measuring this temperate difference it is possible to calculate the heat provided from the combustion. Also, it is needed the mass flow of water.

$$\varDelta T = T_{out} - T_{in} \tag{5.12}$$

$$\dot{Q}_{out} = \dot{m}_{water} \cdot c \cdot \varDelta T \tag{5.13}$$

Specific Heat constant of water is represented by c; this constant is defined as the relation between heat energy that is added to a substance and the different temperature change. This relationship between heat energy and the temperature is different for every material. Finally, the thermal efficiency is calculated using the following equation (Equation 5.14), the $\dot{Q}_{in}$ in the energy that fuel liberate during the combustion process, and the $\dot{Q}_{out}$ is the energy that the water inside the heat exchanger is receiving. So at the end is available energy and useful energy.

$$\eta_{th} = \frac{\dot{Q}_{out}}{\dot{Q}_{in}} \tag{5.14}$$

$\dot{Q}_{in}$ is calculated using lower heating value LHV_{fuel} multiplying by fuel mass flow $\dot{m}_{fuel}$ (Equation 5.15).

$$\dot{Q}_{in} = LHV_{fuel} \cdot \dot{m}_{fuel} \tag{5.15}$$

In this kind of process (energy transformation), the thermal efficiency values are usually high, when the combustion case is optimized, it can reach 90% of thermal efficiency. It is important to not confused with the expression engines thermal efficiency when the expression is the following one: $\eta_{th} = 1 - \frac{\dot{Q}_{out}}{\dot{Q}_{in}}$. For engines the heat that is not transformed into mechanical work is making lower the efficiency.

5.3 Results

In this part of the chapter, it is presented the results obtained from the first experiment. The data obtained is displayed in multiple ways. It was also commented on the trends in the results.

In all the three different output power values cases (1500 W, 1000 W, and 500 W) there are high thermal efficiency values when the equivalence ratio (Φ) is higher, the efficiency grows when this parameter also grows.

If the three output power cases are compared the higher thermal efficiency values are situated in output case 500 W, the average of this values along equivalence ratio is approximately between 0.7 and 0.6 when the output cases 1000 W and 1500 W are between 0.55, and 0.5. These results are easily observable in Figure 5.9. In addition, Figure 5.6, Figure 5.7 and Figure 5.8 are thermal efficiency maps, and it is possible to observe that the higher efficiency values are in the area of higher equivalence ratios. The differences between the lowest and higher equivalence ratio efficiency values are approximately 0.2.

The thermal efficiency seems to be independent of percentage of hydrogen in the fuel mix. In each case, the results present only random differences without any clear trend. This is logical due to the fact that the fuel amount is calculated in each case to maintain the potential energy in the fuel; this output power is equal for every percentage of hydrogen. It is possible to observe this in Figure 5.3, Figure 5.4, and Figure 5.5, where all the different lines are relative closer from each other. Also, in Figure 5.9 show the same trend. In addition, due to Figure 5.6 Figure 5.7 and Figure 5.8, it is possible to see that in the efficiency map, there is almost no changes when the hydrogen percentage varies.

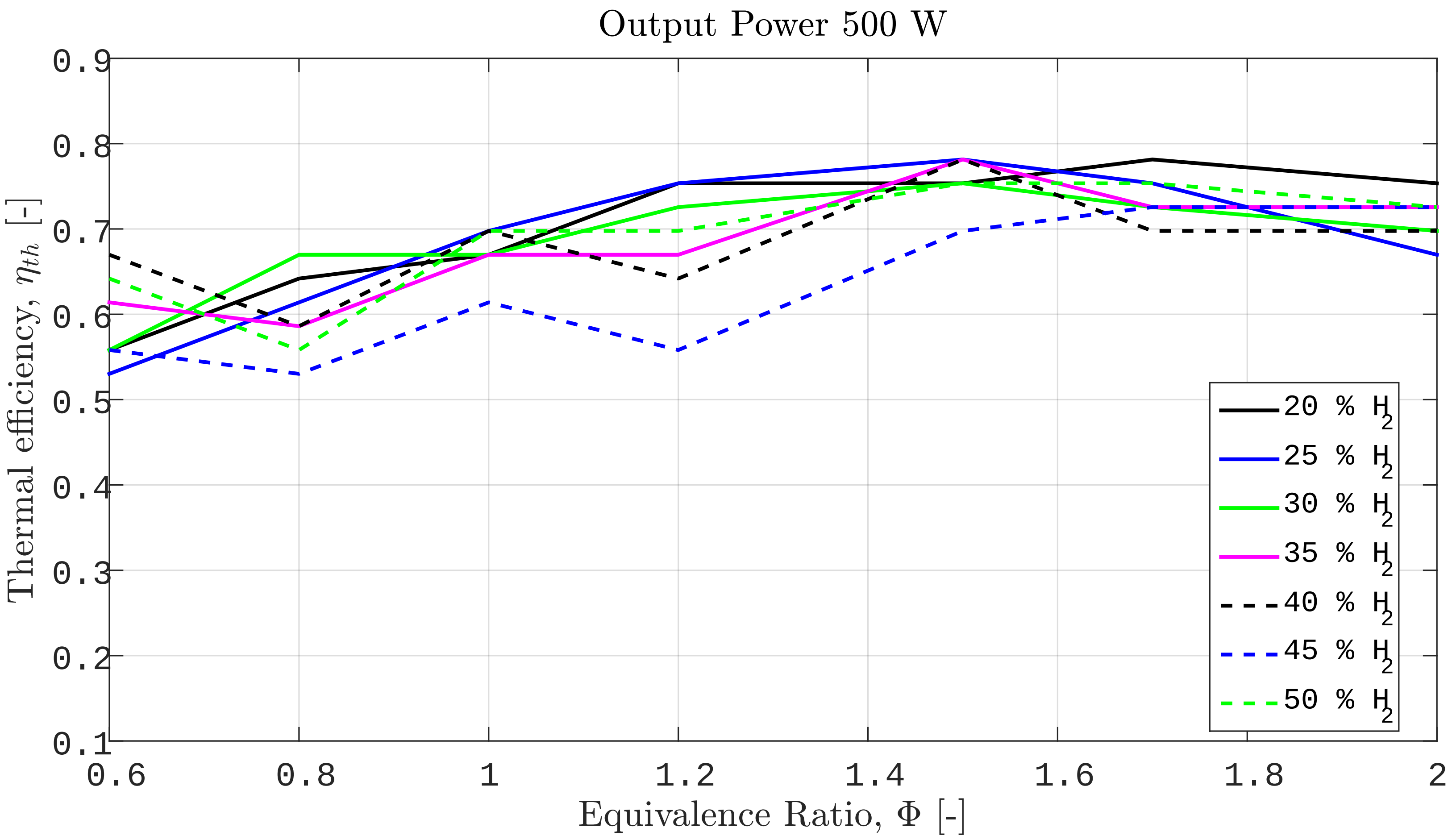


Figure 5.3: Flat flame burner thermal efficiency with 500 W Output Power

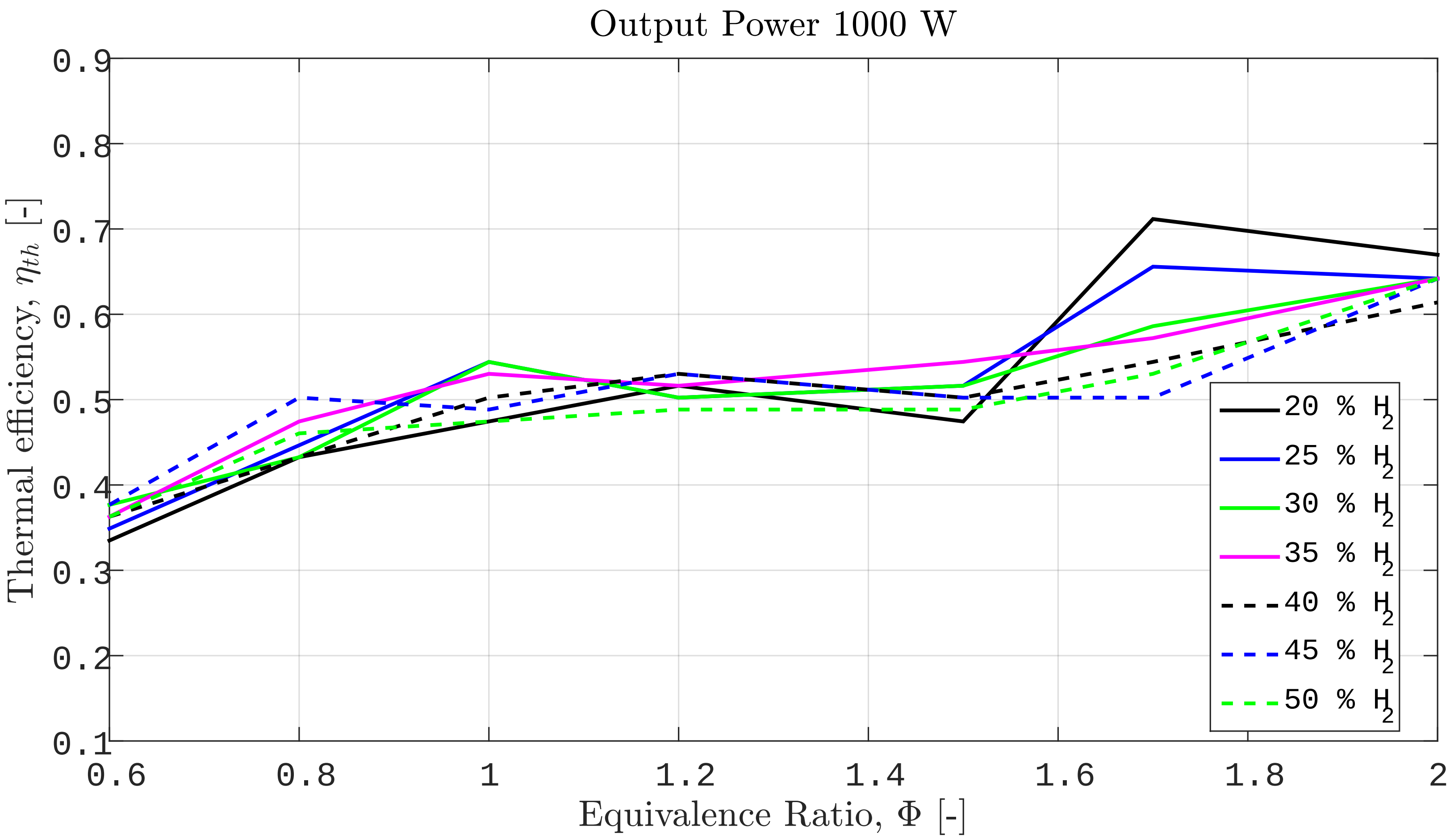


Figure 5.4: Flat flame burner thermal efficiency with 1000 W Output Power

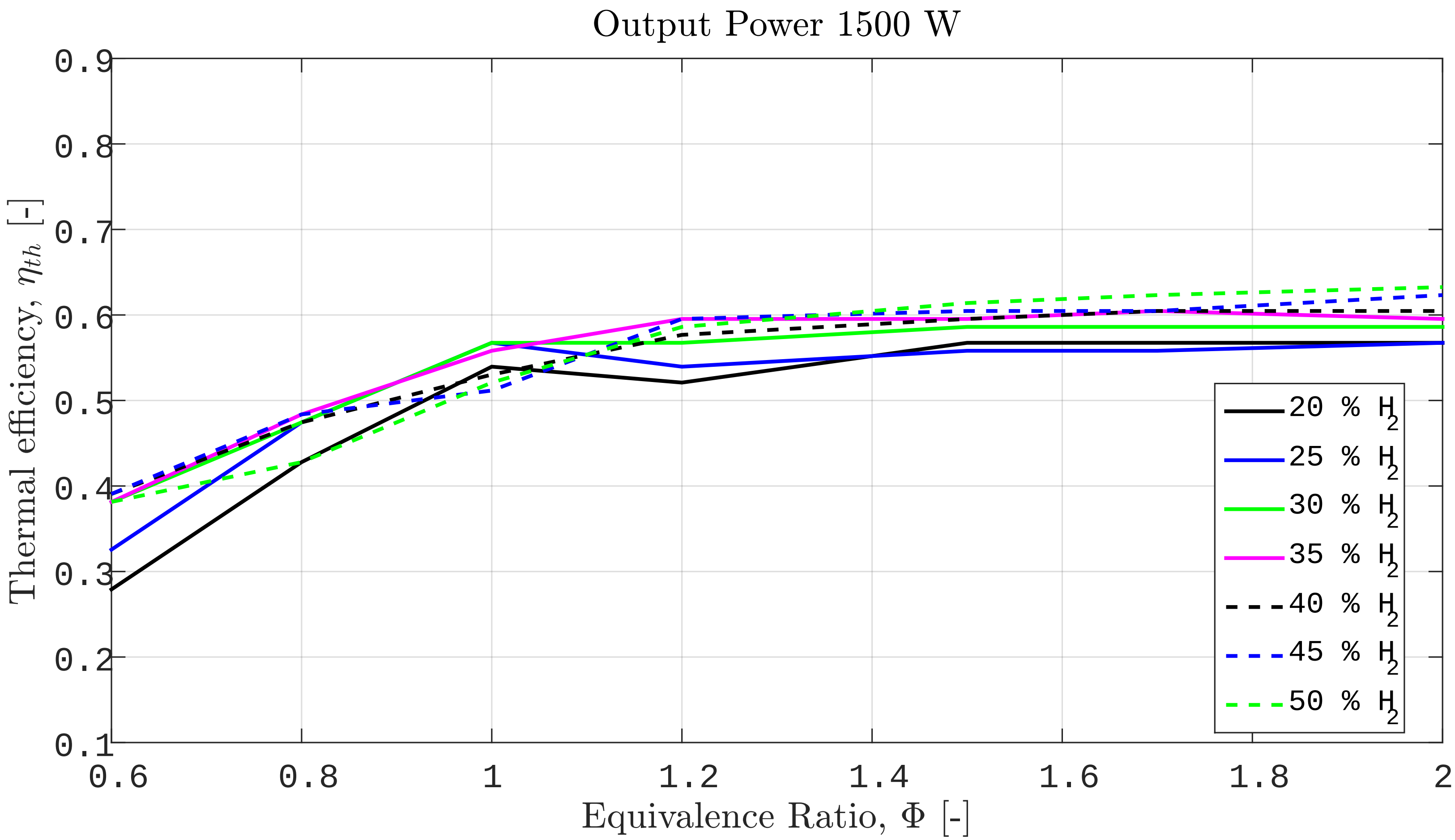


Figure 5.5: Flat flame burner thermal efficiency with 1500 W Output Power

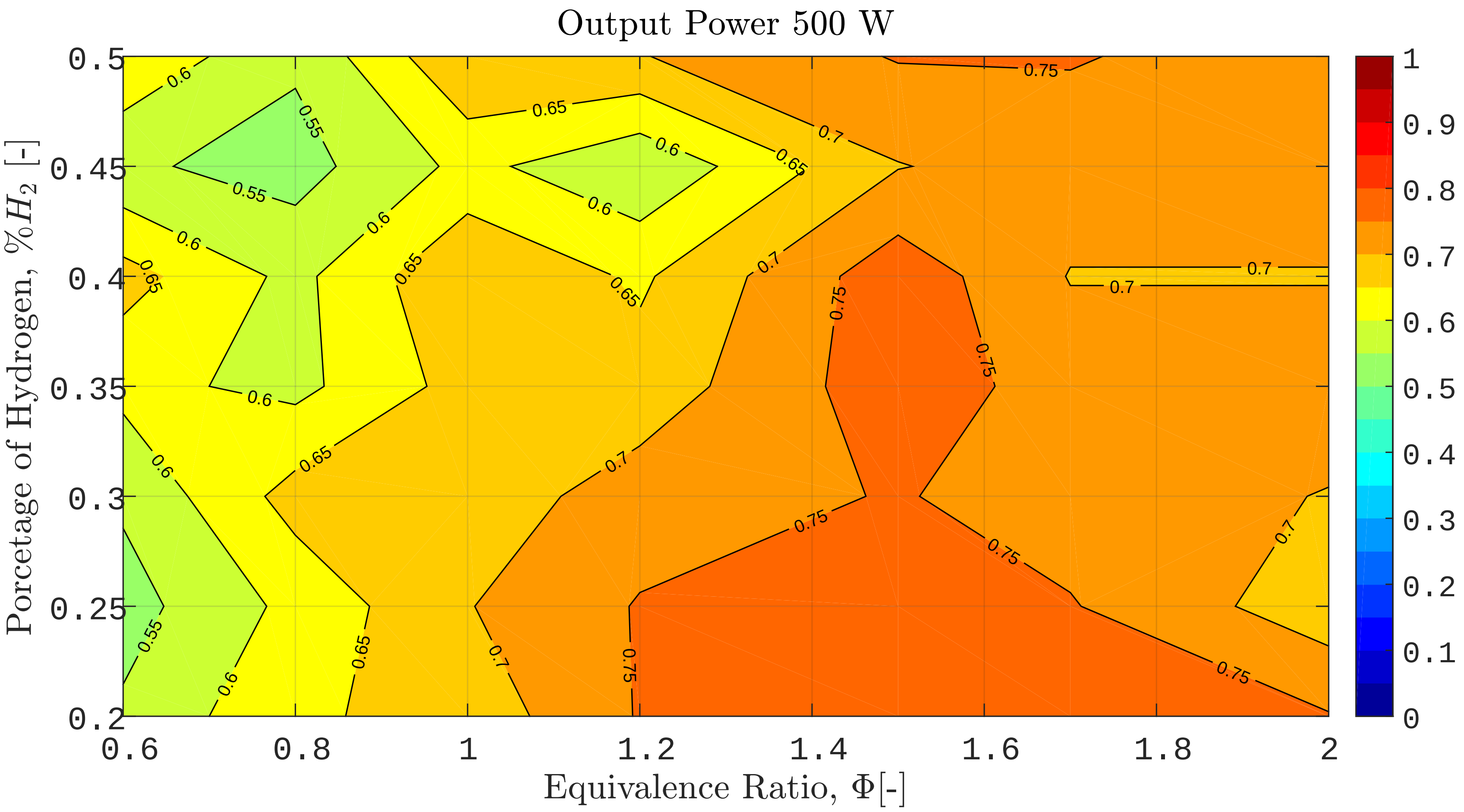


Figure 5.6: Flat flame burner thermal efficiency filled contour plot with 500 W Output Power

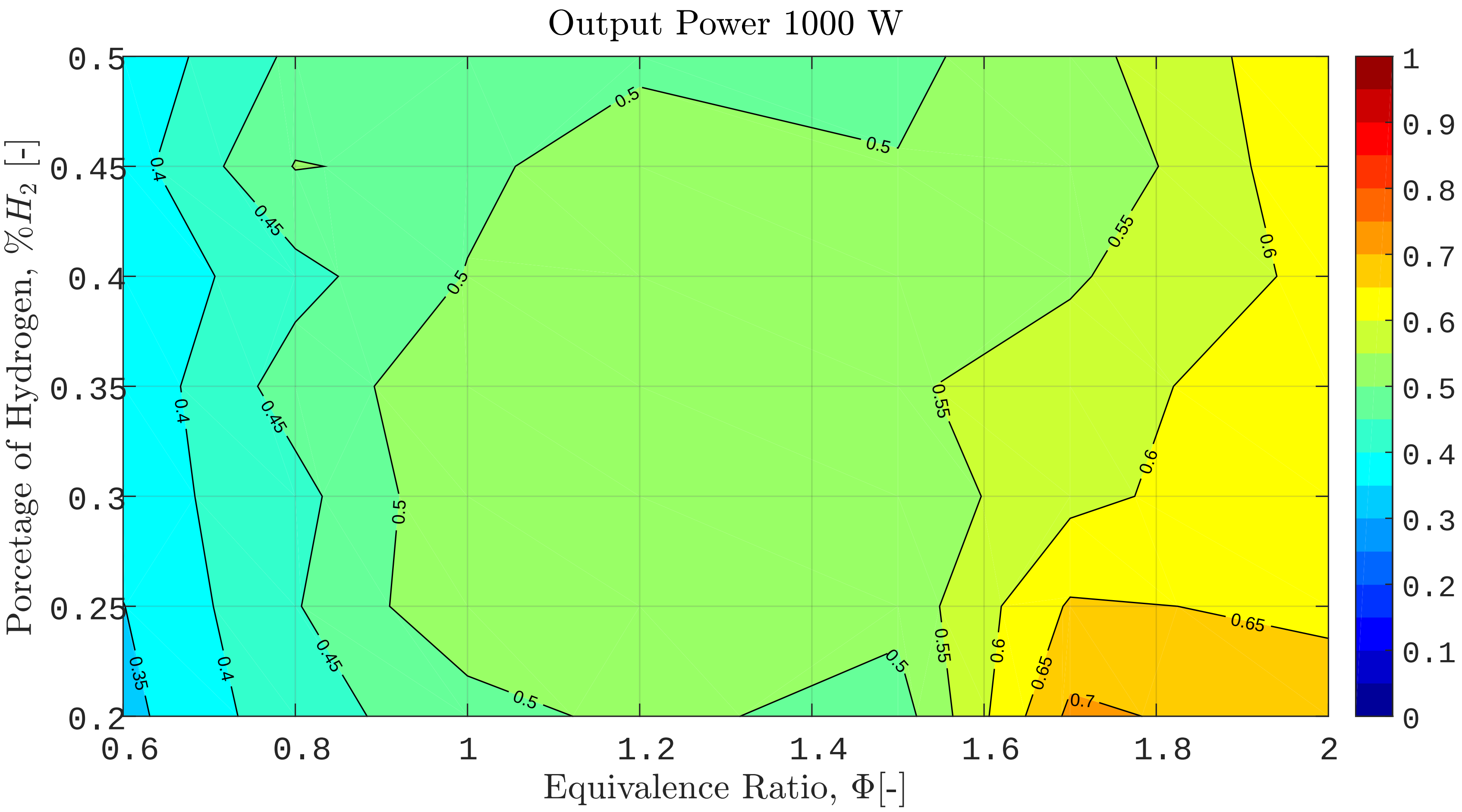


Figure 5.7: Flat flame burner thermal efficiency filled contour plot with 1000 W Output Power

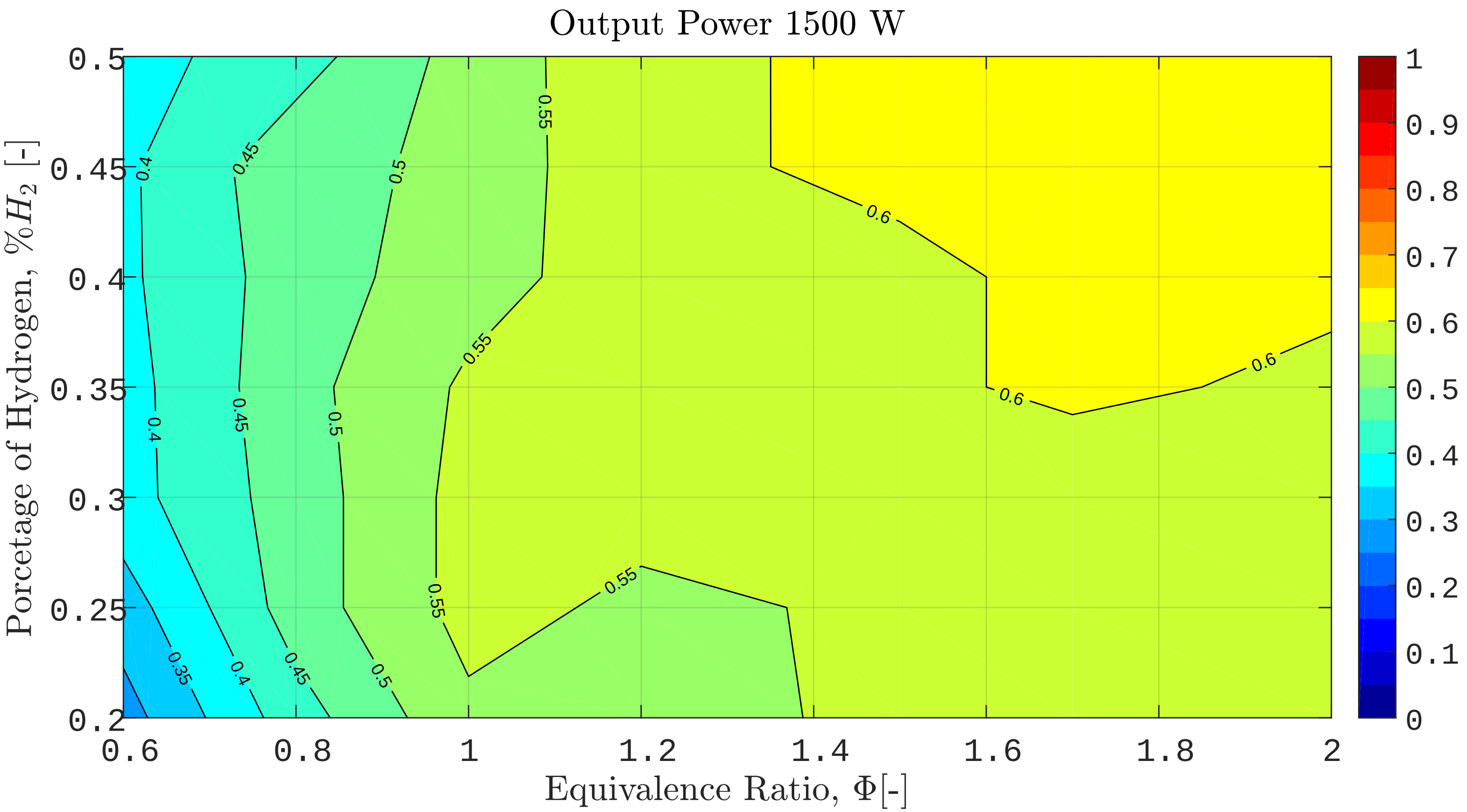


Figure 5.8: Flat flame burner thermal efficiency filled contour plot with 1500 W Output Power

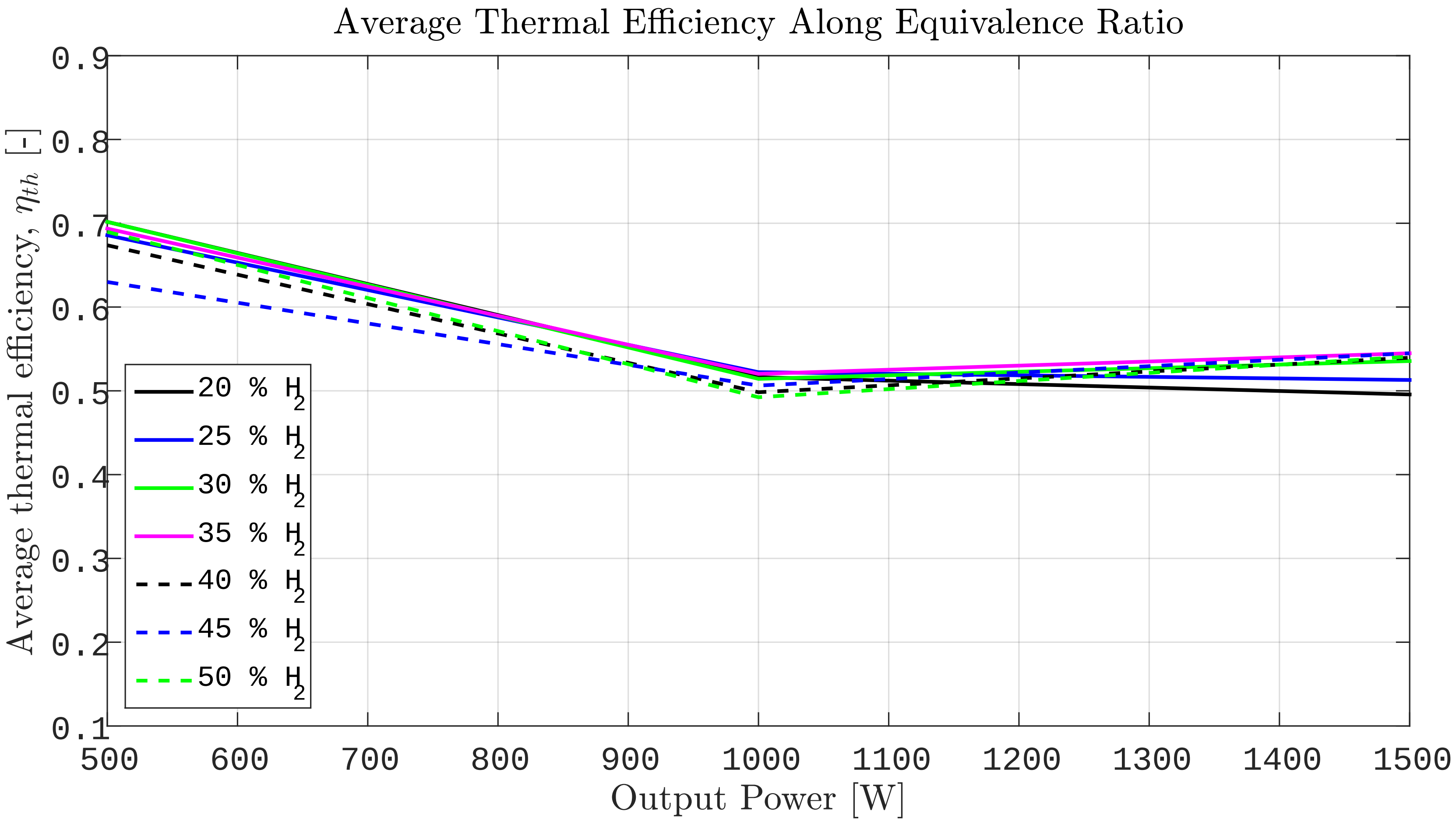


Figure 5.9: Average thermal efficiency values along equivalence ratio with difference values of hydrogen, this figure shows the differences between the three output power cases

Chapter 6

Experiment 2: Gas Analyzer

6.1 Introduction

In this chapter, the emissions are measured and discussed using the same setup from the first experiment, in other words using the same flat flame burner and the heater. For this, the same three output power cases that have already been tested for the thermal efficiency experiments are used but with fewer points density as it will be explained later in the chapter. In this way, it will be calculated exergy for the combustion in every point, thanks to knowing the real products created in the reaction.

In the next section, it will presented by the graphs of the data once processed with Matlab and the conclusions will be presented in the final chapter.

6.2 Explanation of the experiment

The points that were studied for this experiments are also covering the same range as the thermal efficiency experiment: equivalence ratio goes from 0.6 (poor fuel flame) to 2.0 (a very rich fuel flame), hydrogen percentage in the fuel mix is varied from 20% to 50% and the output power that will have three cases 500 W 1000 W and 1500 W.

These parameters will vary in order to be able to thoroughly represent all the possible operating states of the burner as in the first experiment. The gas analyzer will measure the NO, NO_2, and O_2 concentration.

The main difference between this experiment and the thermal efficiency experiment is the density in the experimental data. At the begging the points for both experiments were planned to be the same, however this changed due to the fact gas analyzer was only available for using one day. Reducing the number of points that were studied in this second experiment. Finally end up with these values which are shown below:

- **Equivalence ratio, Φ:** 0.6, 1.0, 1.5 and 2.0
- **Amount of hydrogen, $\%H_2$:** 20%, 30%, 40% and 50%
- **Output Power:** 500 W, 1000 W and 1500 W

The number of points for each output power case is 16, the sum of all cases for this experiments reach 48 points.

6.3 Designing process and experimental setup

The designing process for this experiment was simple. Once the first was designed, points for this one were tried to be the same for this second experiment. Owing to the impossibility of being able to use analyzer gas as much as possible, it was possible only to use one day, it was needed to reduce the number of points for these experiments to have time to do it in that amount of time.

The experimental setup for the gas analyzer experiment is represented in Figure 6.1. This setup is almost equal to the first experiment: metal pipes are used for ammonia due to the fact of corrosion, three flowmeters, etc. There is only one difference between both setups, for this experiment is also including gas analyzer collecting the products coming from the combustion as it is represented in the figure below.

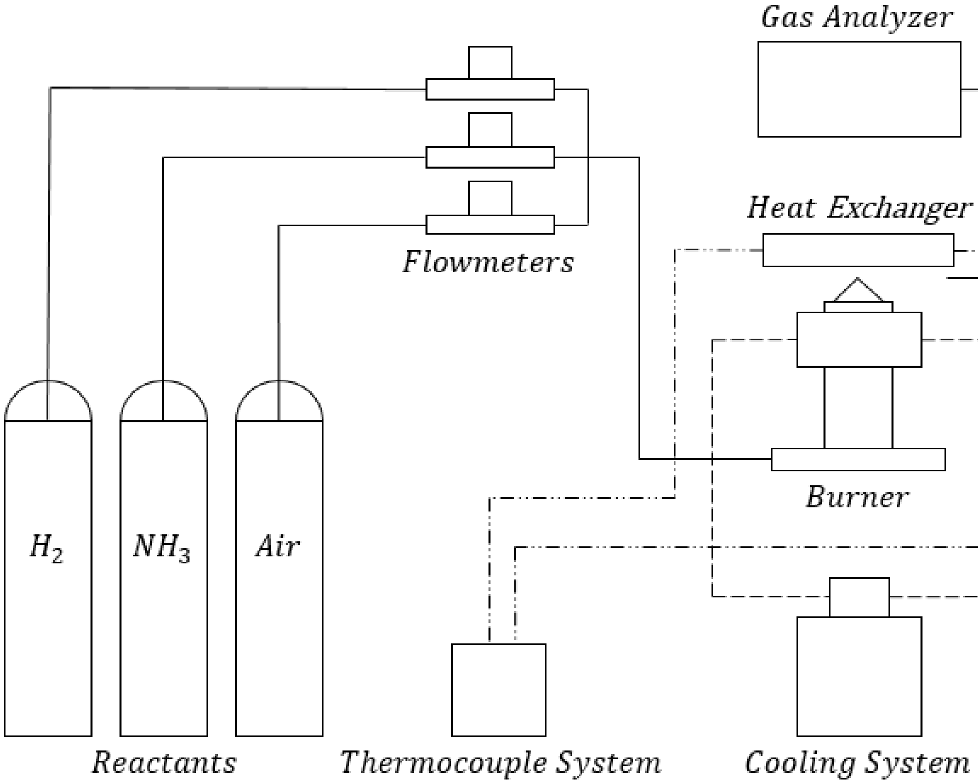


Figure 6.1: Gas analyzer experiment setup sketch

It is important for the comparison between different cases establishing emission indexes. For burning ammonia with hydrogen due to the impossibility to detect the unburned fuel it was not used EI (Emission Index) defined as the weight of pollutants released per kilogram of fuel consumed. Instead of this Index, it is used NO_x concentration in ppm emissions at referenced with the amount of O_2 detected.[9]

$$NOx_{Adjusted} = NOx_{Measured} \cdot \frac{20.9 - O2_{Ref}}{20.9 - O2_{Measured}} \tag{6.1}$$

Where 20.9 is the O_2 percentage in air, $O2_{Ref}$ will be the reference oxygen percentage in this case 3 %, $NOx_{Measured}$ and $O2_{Measured}$ are the data collected from gas analyzer.

6.4 Results

NO concentration is represented in three graphs, one graph for each output power case. In these graphs, there are 4 lines for each equivalence ratio value (0.6, 1.0, 1.5 and 2.0), the percentage of hydrogen in the fuel is represented on the x-axis and the concentration in ppm of NO on the y-axis.

For equivalence ratio higher than $EQ = 1$ (stoichiometric case), $EQ = 1.5$ and $EQ = 2.0$, the NO concentrations remain stable, approximately around 1500 ppm for 1000 W and 1500 W output cases, and a little bit higher for 500 W, around 1700 ppm, in this case also the stoichiometric cases remains stable (Figure 6.2). In the $EQ = 1.0$ (for 1500 W and 1000 W) and $EQ = 0.6$ (for all the cases), NO concentration grows when the percentage of H_2 on the fuel gets higher (Figure 6.4 and Figure 6.6). NO concentration in the stoichiometric case is higher than in $EQ = 0.6$, reaching 50 % of H_2 10000 ppm in 1500 W and 8000 ppm in 1000 W.

NO_2 graphs show same trends as NO plots (Figure 6.3, Figure 6.5 and Figure 6.7), concentration for this chemical is lower than for NO, $EQ = 1.5$ and $EQ = 2.0$ stays below 50 ppm NO_2 concentration stable values, the stoichiometric case reaches the maximum value, around 200 ppm NO_2 concentration, for 50 % H_2.

NO_x comparison with thermal efficiency graphs (Figure 6.8 and Figure 6.9) shows that there is not a direct relation between these parameters. It can be detected there is more thermal efficiency in 500 W and decrease when is higher the output power (1000 W and 1500 W). NO_x emissions are more concentrated in 500 W around 1000 ppm in NO. NO_2 values are below 200 ppm for each output power case only some 500 W are above this value.

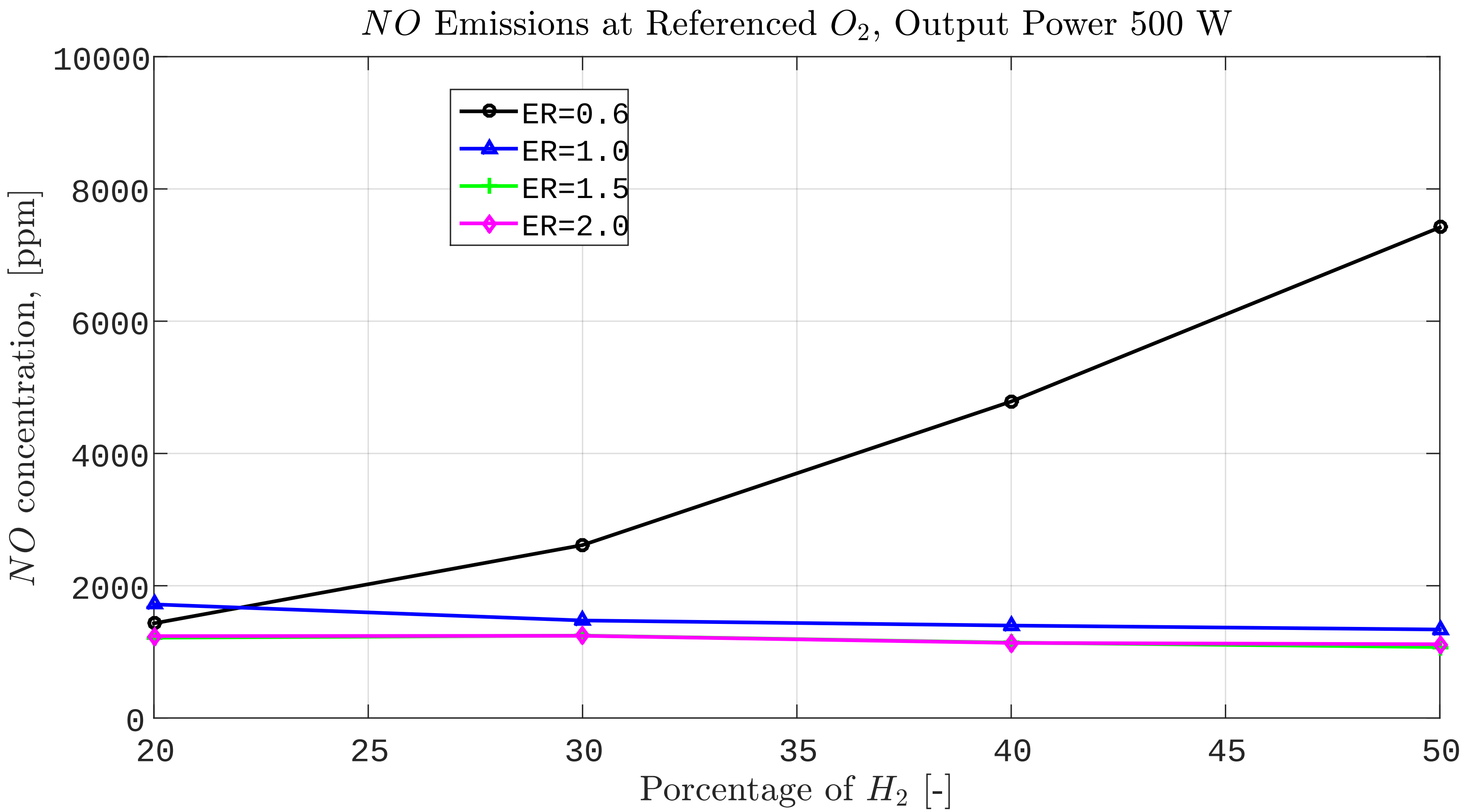


Figure 6.2: NO concentration in ppm emissions at referenced with the amount of O_2 detected, with different percentage of hydrogen in the fuel mix and different equivalence ratio with 500 W output power

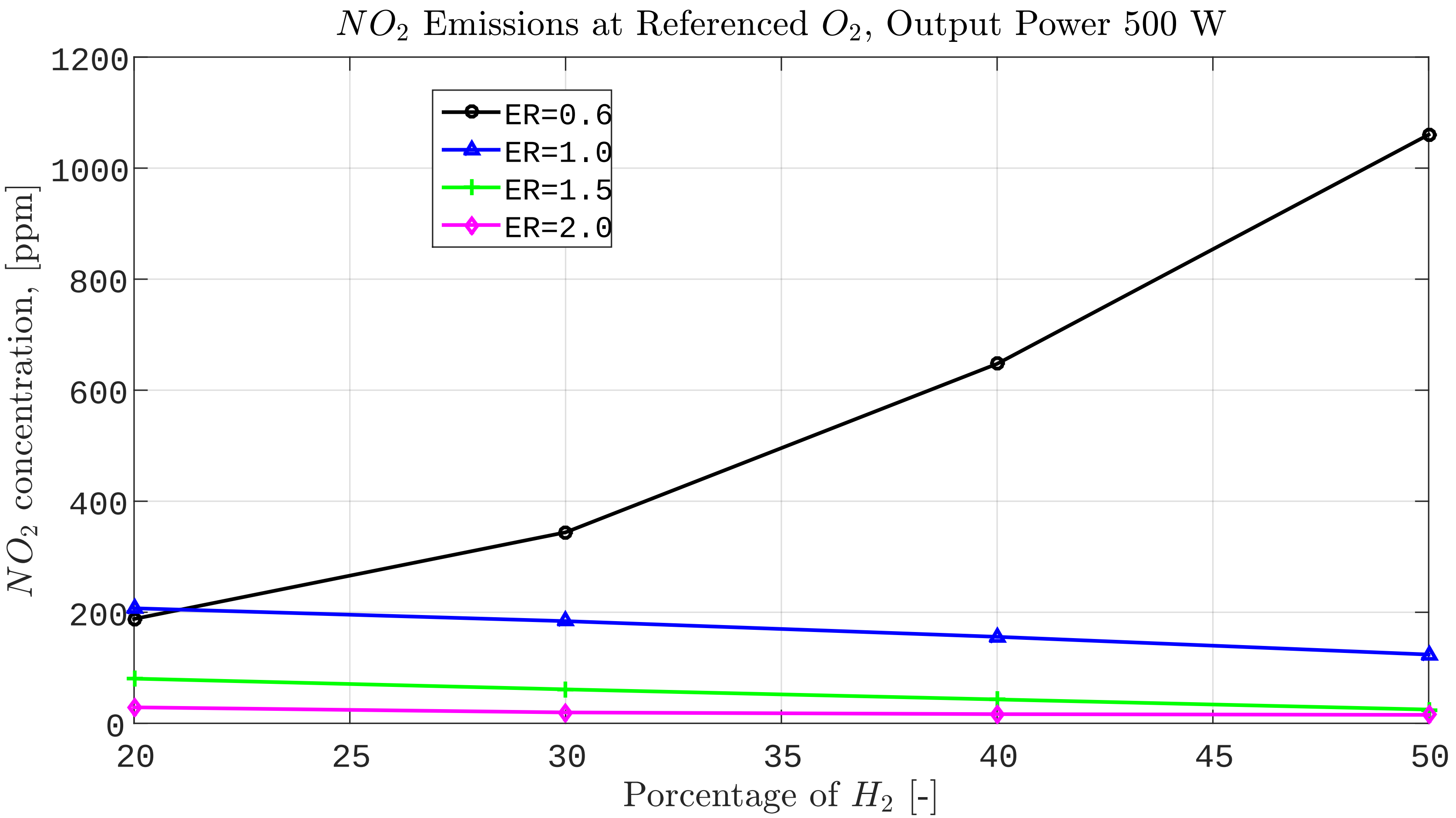


Figure 6.3: NO_2 concentration in ppm emissions at referenced with the amount of O_2 detected, with different percentage of hydrogen in the fuel mix and different equivalence ratio with 500 W output power

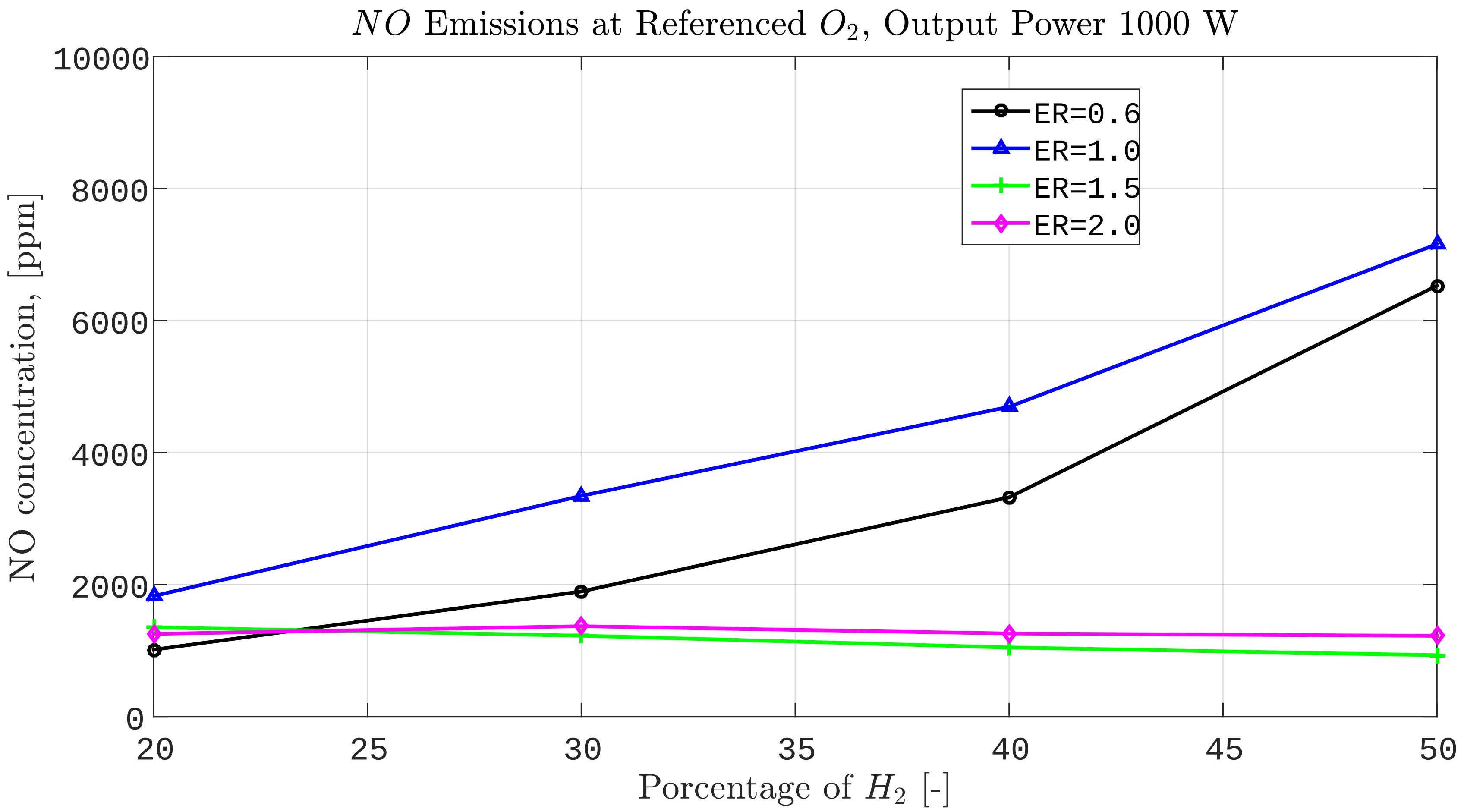


Figure 6.4: NO concentration in ppm emissions at referenced with the amount of O_2 detected, with different percentage of hydrogen in the fuel mix and different equivalence ratio with 1000 W output power

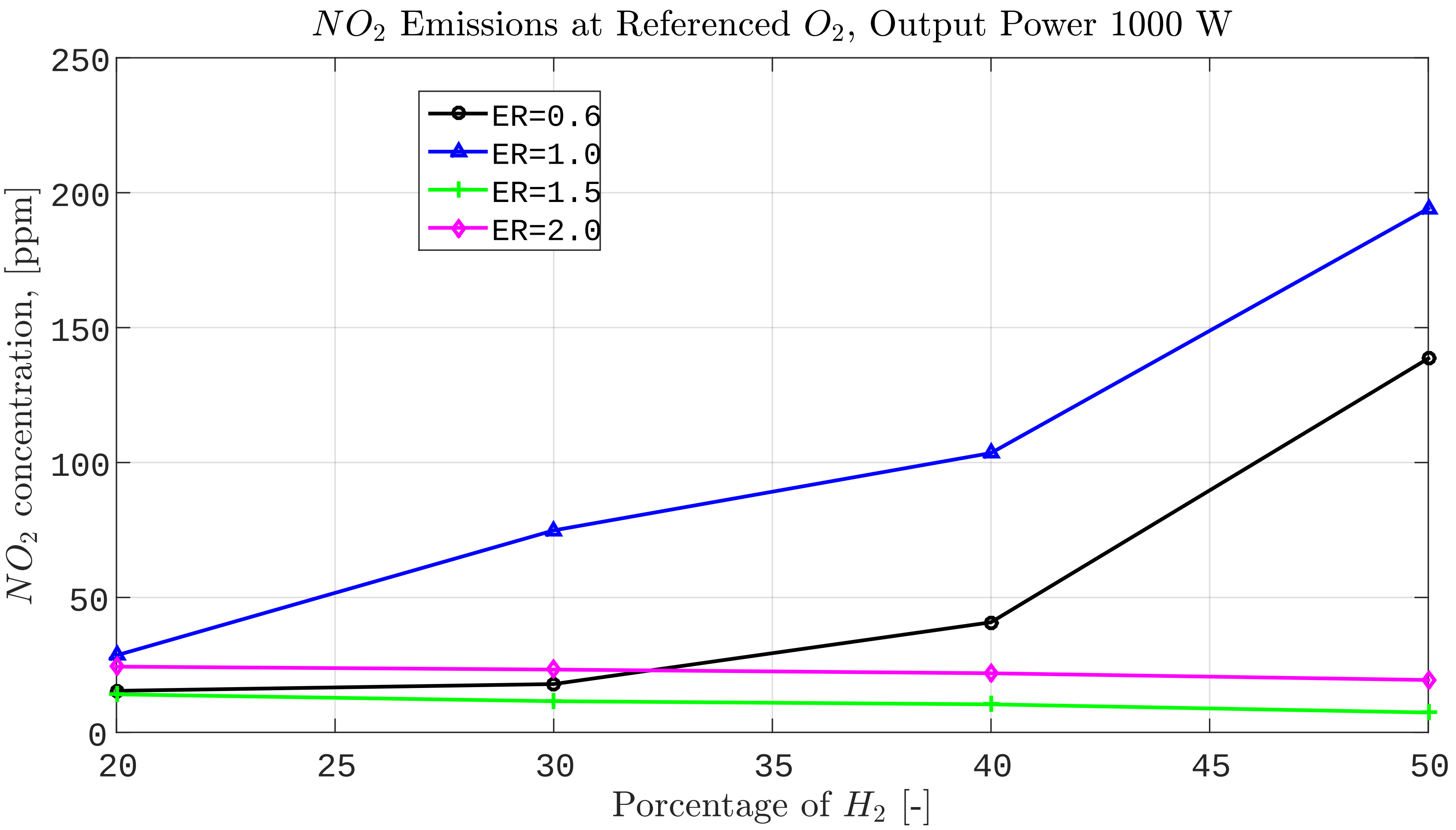


Figure 6.5: NO_2 concentration in ppm emissions at referenced with the amount of O_2 detected, with different percentage of hydrogen in the fuel mix and different equivalence ratio with 1000 W output power

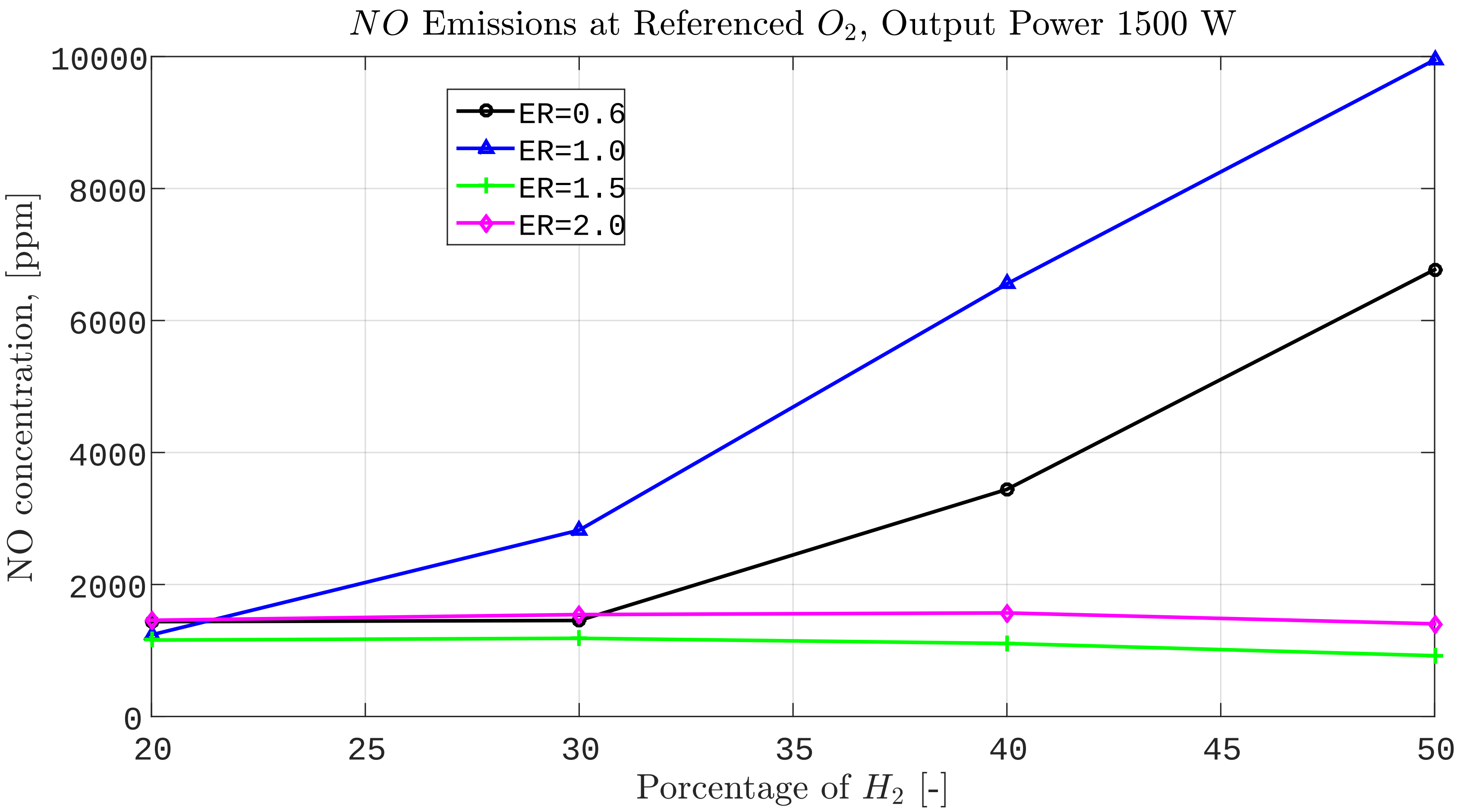


Figure 6.6: NO concentration in ppm emissions at referenced with the amount of O_2 detected, with different percentage of hydrogen in the fuel mix and different equivalence ratio with 1500 W output power

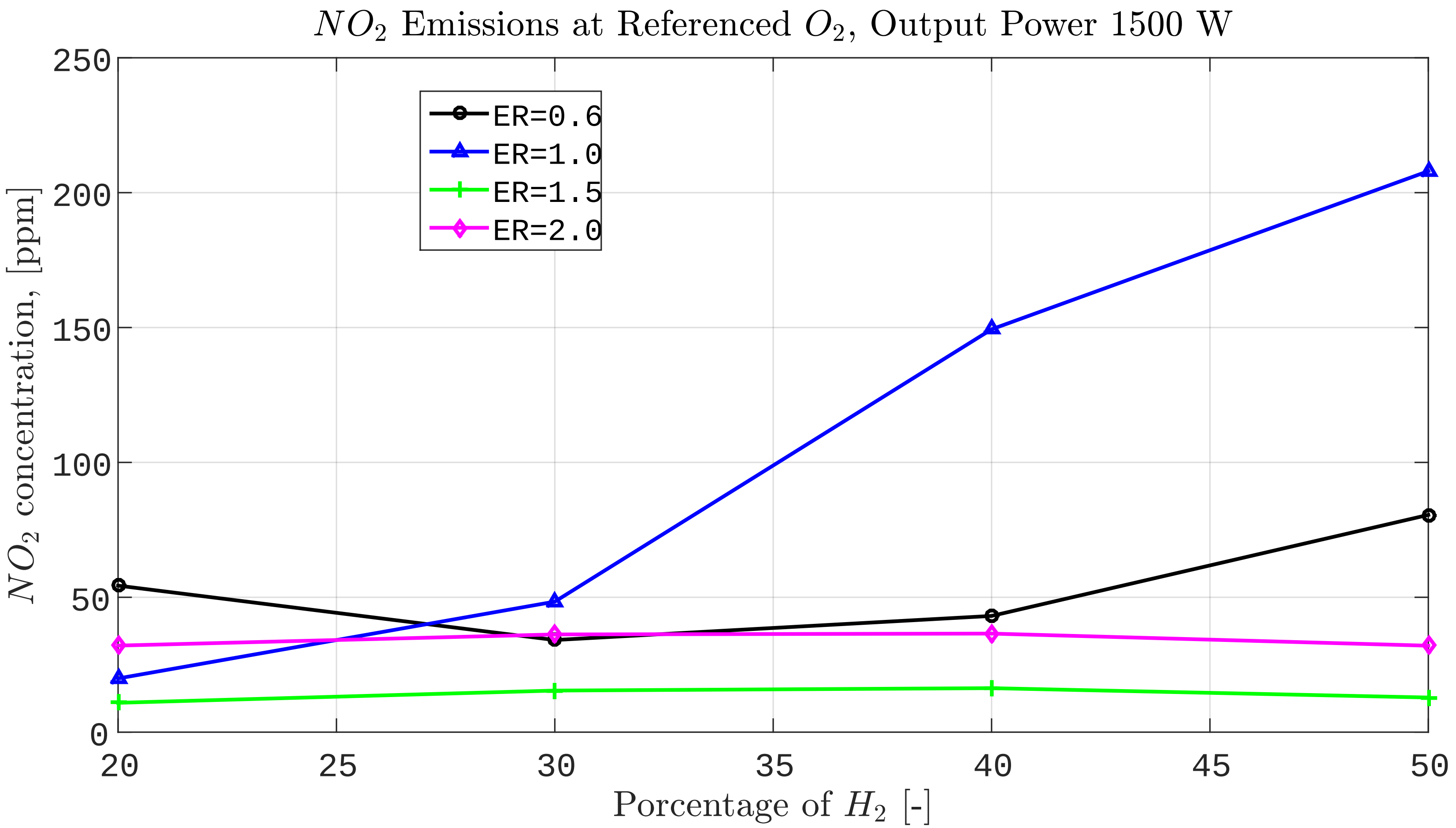


Figure 6.7: NO_2 concentration in ppm emissions at referenced with the amount of O_2 detected, with different percentage of hydrogen in the fuel mix and different equivalence ratio with 1500 W output power

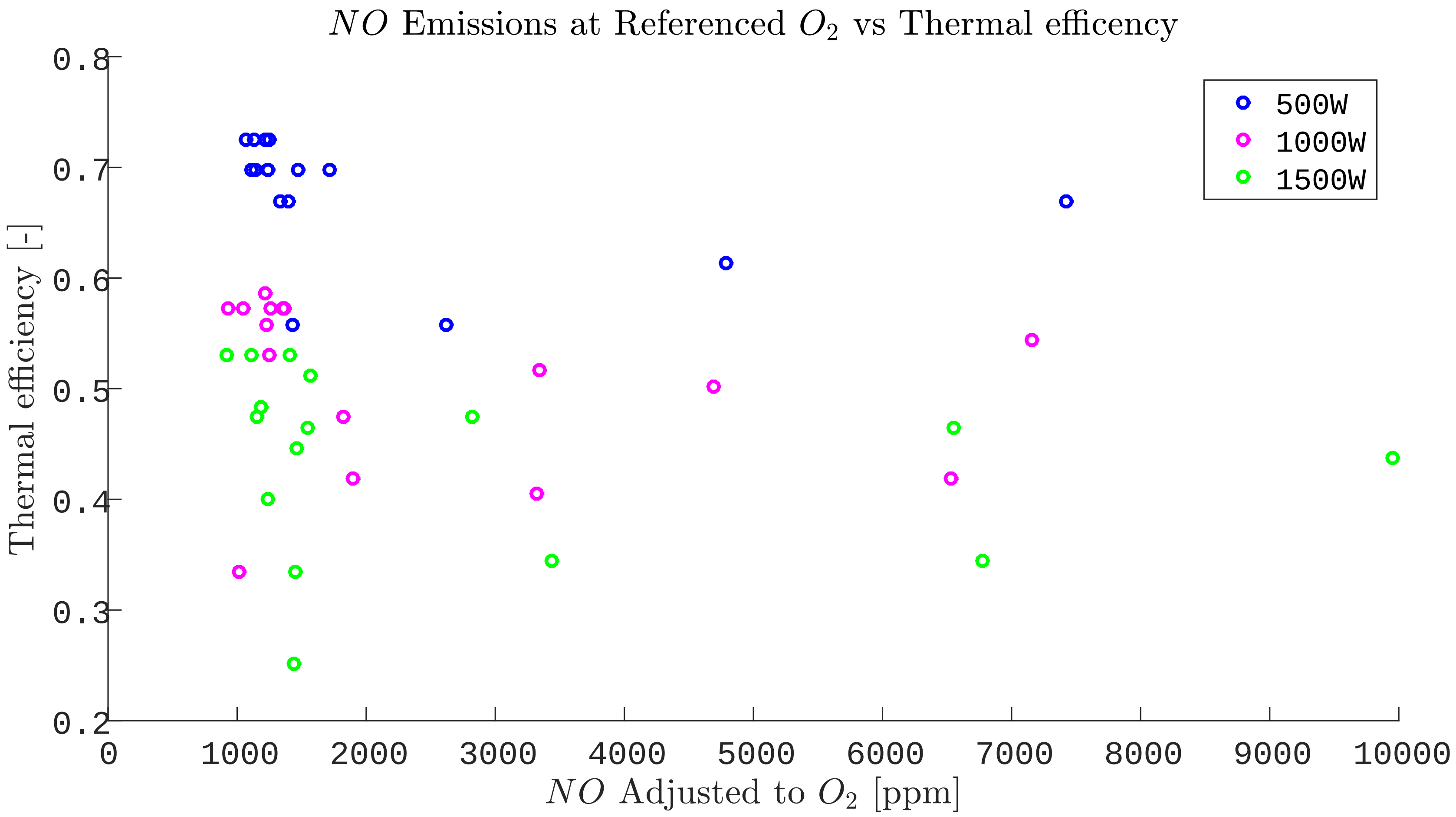


Figure 6.8: NO concentration in ppm emissions at referenced with the amount of O_2 detected represented with thermal efficiency

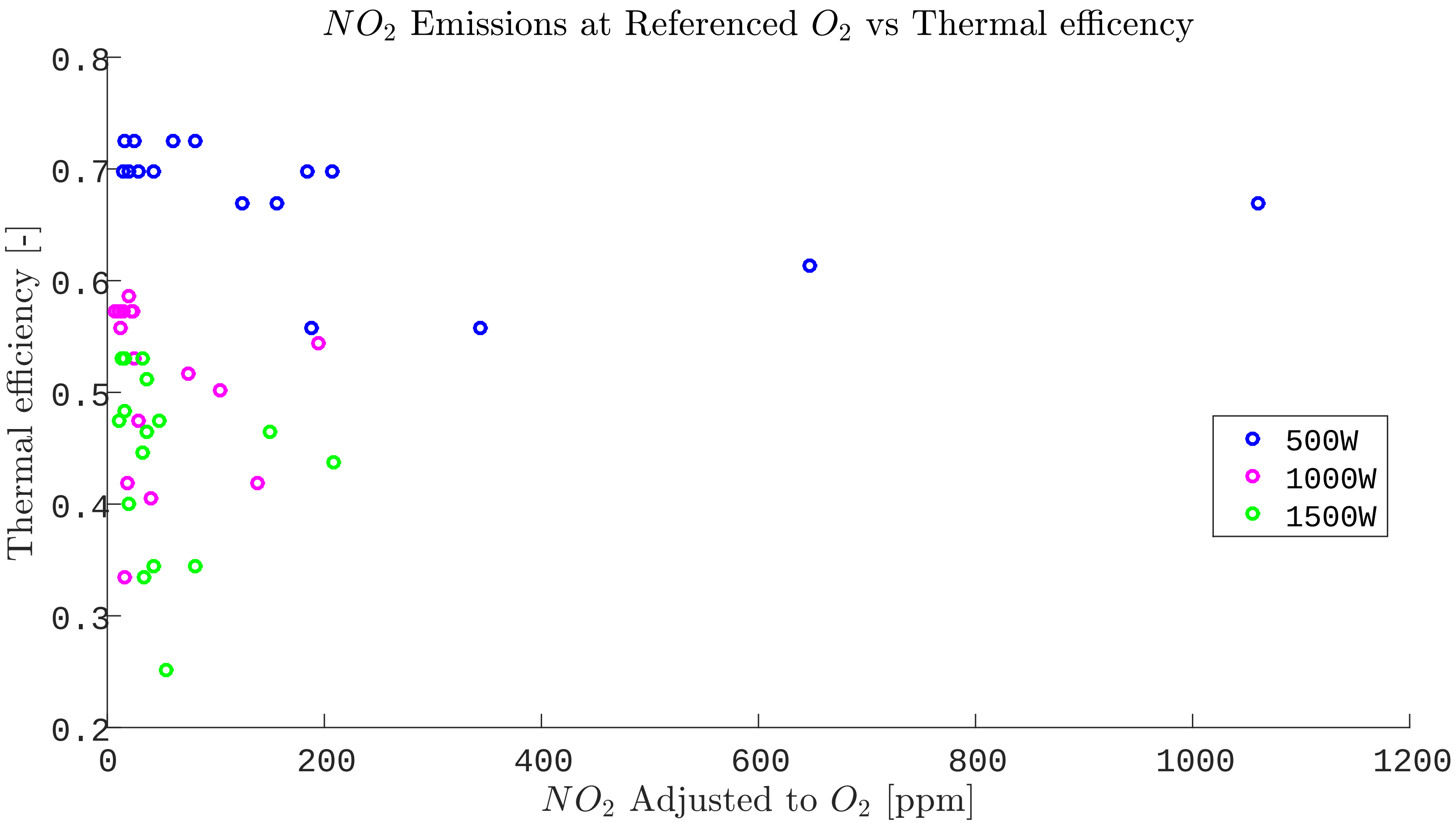
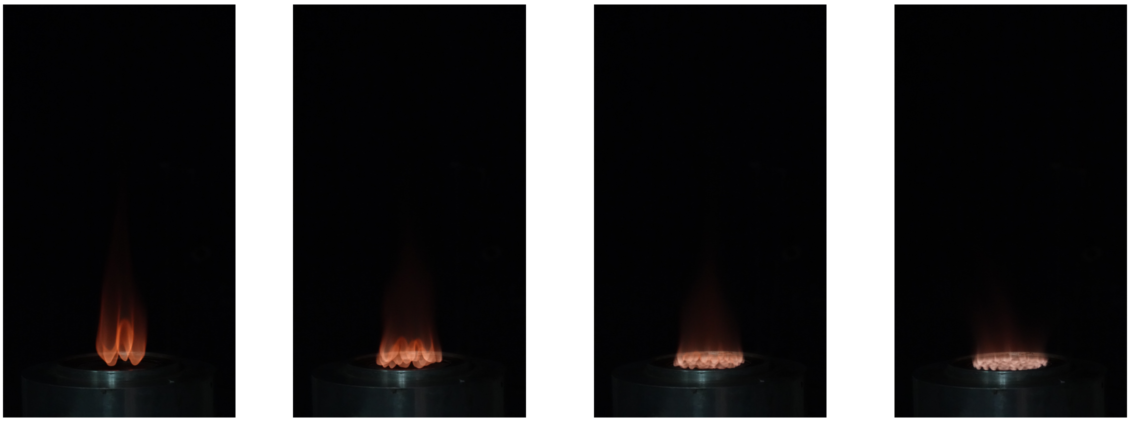


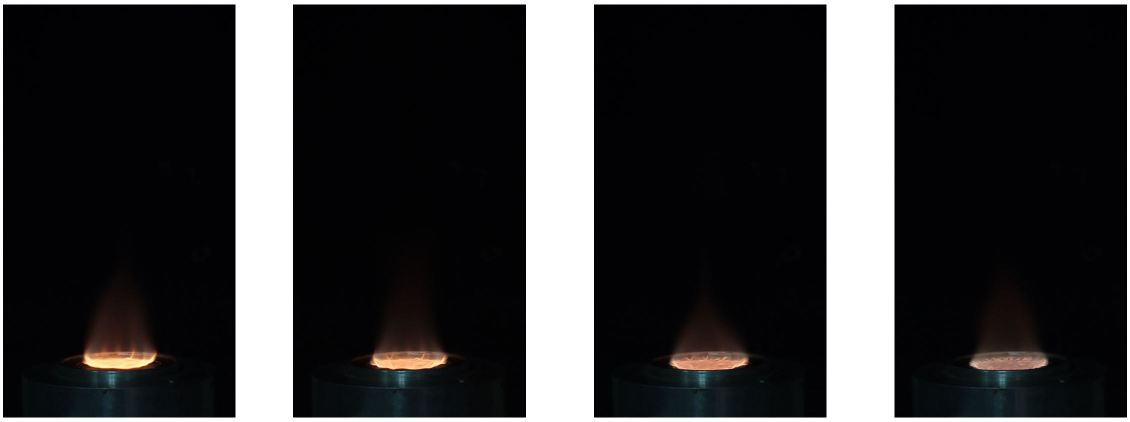
Figure 6.9: NO_2 concentration in ppm emissions at referenced with the amount of O_2 detected represented with thermal efficiency

6.5 Flame appearance



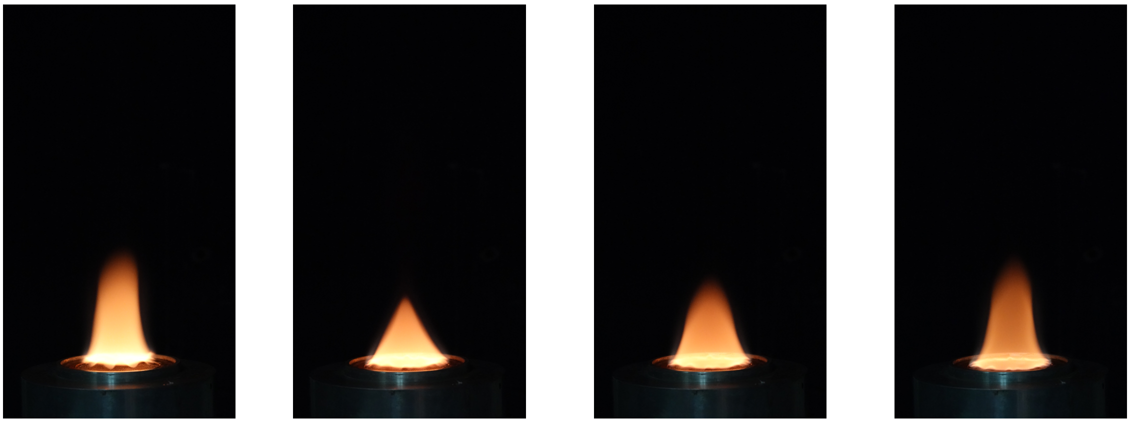
(a) 20 % H_2 (b) 30 % H_2 (c) 40 % H_2 (d) 50 % H_2

Figure 6.10: Cases with equivalence ratio of 0.6 and output power 500 W



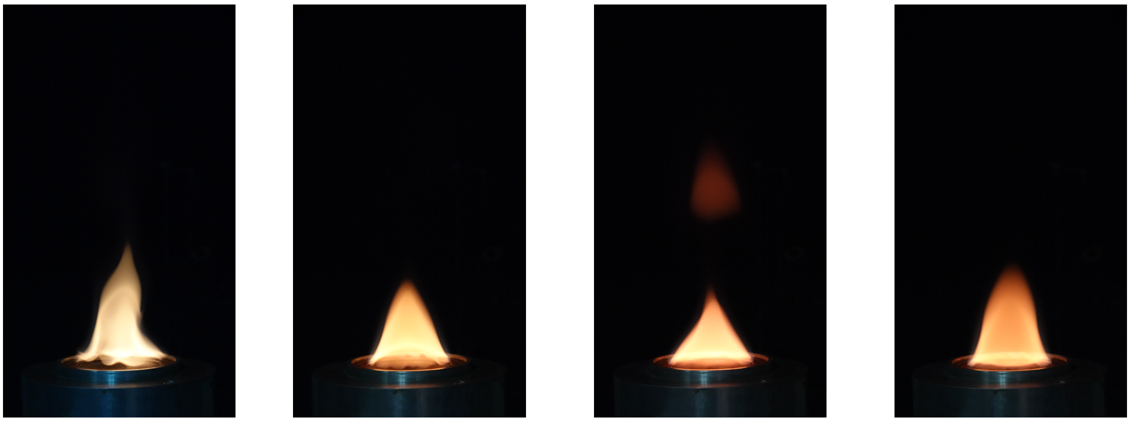
(a) 20 % H_2 (b) 30 % H_2 (c) 40 % H_2 (d) 50 % H_2

Figure 6.11: Cases with equivalence ratio of 1.0 and output power 500 W



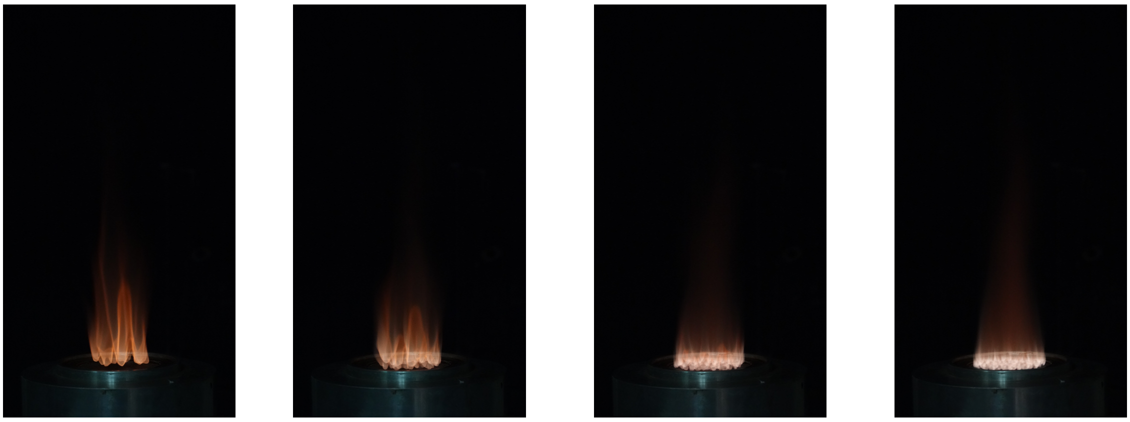
(a) 20 % H_2 (b) 30 % H_2 (c) 40 % H_2 (d) 50 % H_2

Figure 6.12: Cases with equivalence ratio of 1.5 and output power 500 W



(a) 20 % H_2 (b) 30 % H_2 (c) 40 % H_2 (d) 50 % H_2

Figure 6.13: Cases with equivalence ratio of 2.0 and output power 500 W



(a) 20 % H_2 (b) 30 % H_2 (c) 40 % H_2 (d) 50 % H_2

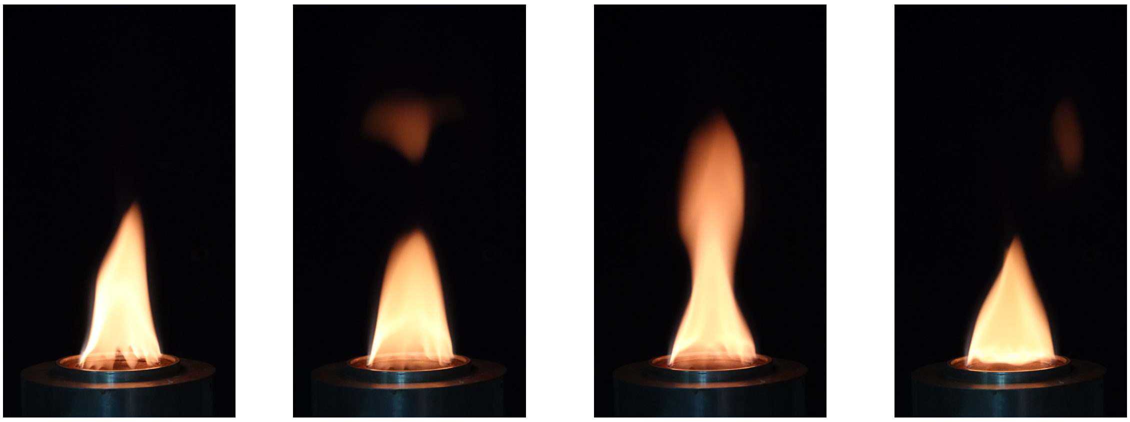
Figure 6.14: Cases with equivalence ratio of 0.6 and output power 1000 W

(a) 20 % H_2 (b) 30 % H_2 (c) 40 % H_2 (d) 50 % H_2

Figure 6.15: Cases with equivalence ratio of 1.0 and output power 1000 W

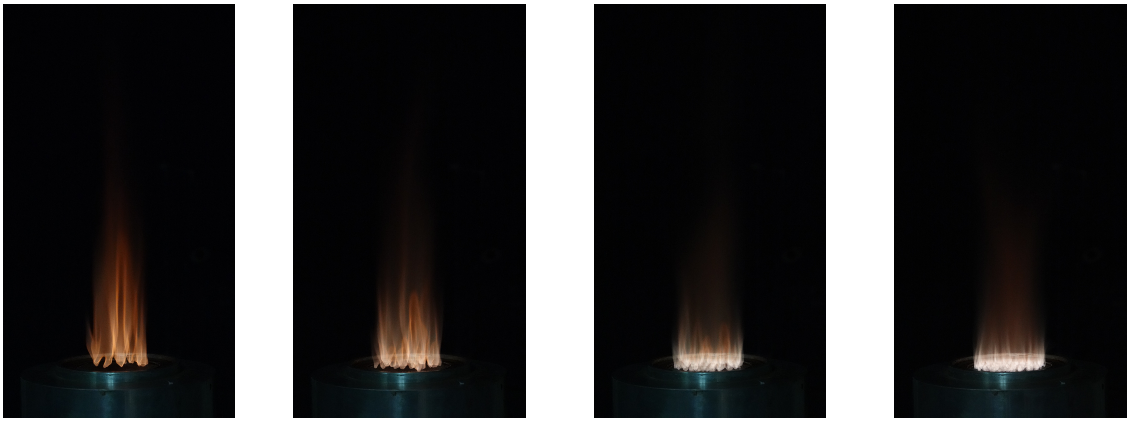
(a) 20 % H_2 (b) 30 % H_2 (c) 40 % H_2 (d) 50 % H_2

Figure 6.16: Cases with equivalence ratio of 1.5 and output power 1000 W



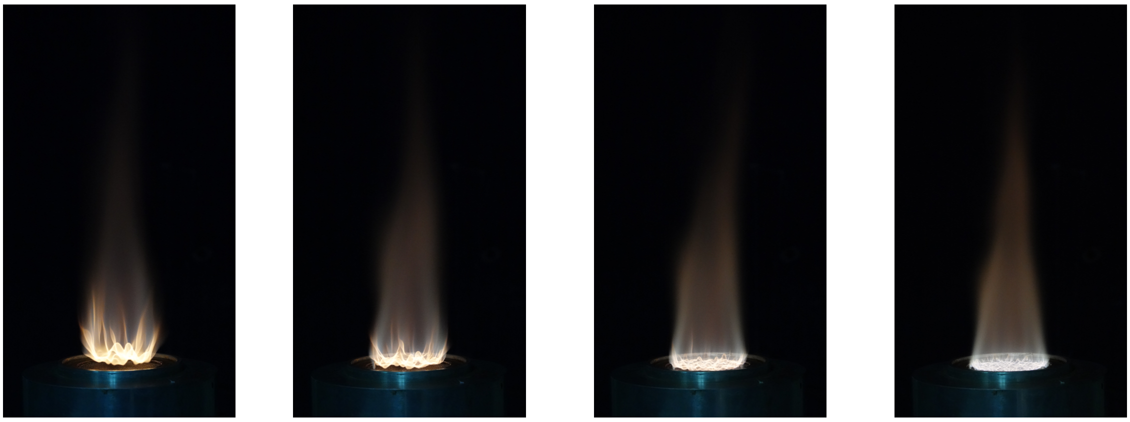
(a) 20 % H_2 (b) 30 % H_2 (c) 40 % H_2 (d) 50 % H_2

Figure 6.17: Cases with equivalence ratio of 2.0 and output power 1000 W



(a) 20 % H_2 (b) 30 % H_2 (c) 40 % H_2 (d) 50 % H_2

Figure 6.18: Cases with equivalence ratio of 0.6 and output power 1500 W



(a) 20 % H_2 (b) 30 % H_2 (c) 40 % H_2 (d) 50 % H_2

Figure 6.19: Cases with equivalence ratio of 1.0 and output power 1500 W

(a) 20 % H_2 (b) 30 % H_2 (c) 40 % H_2 (d) 50 % H_2

Figure 6.20: Cases with equivalence ratio of 1.5 and output power 1500 W

(a) 20 % H_2 (b) 30 % H_2 (c) 40 % H_2 (d) 50 % H_2

Figure 6.21: Cases with equivalence ratio of 2.0 and output power 1500 W

Flame appearance is an important factor to detect if the flame is laminar or turbulent. For all the cases in this master thesis, laminar status was found as it is showed in the pictures. The three parameters selected for this experiments affect the flame appearance. Increasing hydrogen percentage in the fuel mixture, reduce the orange color of the ammonia flames. Increasing equivalence ratio make brighter the flame. Increasing of the output power make the flame bigger.

Chapter 7

Conclusions and Future Work

7.1 Summary

Ammonia has been produced industrially for approximately 100 years as part of certain fertilizers. The cycle to produce it has been well known, there is a transport network for this chemical, and it may be the future energy vector for hydrogen storage, NH_3 present really interesting properties which could be used for different purposes. However, the main aim of this master thesis was to study the feasibility of ammonia as a fuel for domestic stoves applications. It was used as a flat flame burner to burn the premixed flames of NH_3 and H_2; this last one was added to sustain ammonia flame due to the low flammability of this chemical. This master thesis continue the aim of finding a highly efficient and clean gaseous fuel stove that also was the goal on previous researches, for instance the experimental study of porous metal burners for domestic stove applications by Chih-Yung Wu. This chapter includes a discussion of results in a broader context considering other works and research to explain the results obtained during the experiments.

The first experiment was based on obtaining thermal efficiency along with different fuel configuration, equivalence ratio, and output power. It was knowing the points in which better efficiency could make this technology closer to be a solution in the decarbonization process.

The second experiment was to focus on emissions. One of the main drawbacks of ammonia is the NO_x formation due to the nitrogen in ammonia. Therefore gas analyzer was used to detect these pollutants in the combustion products. NO_x emissions are the main drawback for this technology to be implemented, especially for domestic applications.

7.2 Conclusions

In this section, it will be presented the main conclusions about the master thesis, explaining why are the obtained results like they are. Experiments were designed trying to answer the question, is it feasible using ammonia as a fuel for a flame flat burner?

Two big topics are discussed below these lines, first discovering it is efficient, and second, is it secure for human health? NO_x emissions are the main restriction for diesel engines, many European governments are legislating against these engines because of that, could this happen to this technology?

7.2.1 Thermal efficiency experiment

Thermal efficiency results show areas in the operating range of this burner with high efficiency. The highest efficiencies are located in 500 W output power with high equivalent ratios (flames rich in fuel).

The percentage of hydrogen on the fuel mix is not affecting thermal efficiency. This is explained because the amount of the different fuels used for each case was calculated, maintaining the Lower Heating Value of the mix at the same value during each output power value.

Another conclusion that can be drawn from the experiments is the fact that when the output power increases, the performance drops, as it has already said the maximum performance at 500 W and the lowest at 1500 W.

7.2.2 Gas analyzer experiment

Due to fuel-bound nitrogen, ammonia combustion can lead to high NO_x emissions if it is not burned in a controlled environment. In this second experiment, it will be found out which operating points, for this kind of burner using ammonia and hydrogen as a fuel, are more likely for NO_x to be produced. To measure emissions, a gas analyzer was used.

In some of the cases was detected an increment of NO_x when amount of hydrogen increase in fuel mix. This could be explained probably due to the generation of OH and O radicals, as it is said by other researcher reports [4].

Higher equivalence ratios than stoichiometric reduce the amount of NO_x found in the combustion products. These results are also observable on Duynslaegher et al. research [7]. The effect of the equivalence ratio on NO_x formation is an important clue, which means that this parameter has to be taken on consideration in order or controlling the formation of these emissions.

Finally, output Power and also thermal efficiency does not show any defining trend in NO_x emission.

Summarizing, the optimal performance for this burner under these operating conditions occurs when hydrogen percentage is low and equivalence ratio is higher than stoichiometric, this lead in low NO_x emissions and high thermal efficiency. Further research on this topic will be needed to be completely secure on the feasibility of this technology. Anyway the results obtained during the experiments for this master thesis are optimistic.

7.3 Problems

There were some difficulties during this master thesis, some of these problems are written in the following lines:

Ammonia is a corrosive substance it can produce damage on skin, eyes, and lungs. Some protection has been taken to avoid this during the experiments. As was said in chapter 4 it needed to wear a mask and protection glasses, especially when there were gas leaks or at operating points where there was much unburned fuel.

Not only is it dangerous, but also its odor could be unpleasant. The smell of ammonia makes uncomfortable the experience during experiments. This disadvantage, the smell of ammonia, is an good sign to detect leaks of this gas.

Burning hydrogen is dangerous. Hydrogen rating on the NFPA 704 flammability scale is 4 [20], the maximum value, because ignition can occur at a volumetric ratio of hydrogen to air as low as 4% [8] due to the oxygen in the air and the simplicity and chemical properties of the reaction. However, hydrogen has no associated problems for natural hazards for reactivity or toxicity.

Limitation in laboratory equipment, some tools, and systems were missing, including a gas analyzer. To have the possibility to use it, it was needed to borrow from other laboratory however it was only possible to used it one day.

Besides, this gas analyzer has no sensors to detect the unburned hydrogen and ammonia used in the experiments making impossible exergy calculations.

Some help was needed it due to the fact that the author of this master thesis at the begging of the project had no experience in managing the laboratory. A learning process on how to setup experiments, how to clean and how to burn was needed it.

7.4 Project management

This section is covering the tasks as a part of work plan and progress as well as how time and resources are managed. For this purpose, Gantt chart is used due to the fact that in this kind of chart it is possible to express how the project was developed in an easy visual way (Figure 7.1).

Also, to control the progress and give advise and guidance, there were weekly meetings to present for all laboratory members progress related with experiments, to share new information found and to ask for help with equipment or in applying theoretical concepts.

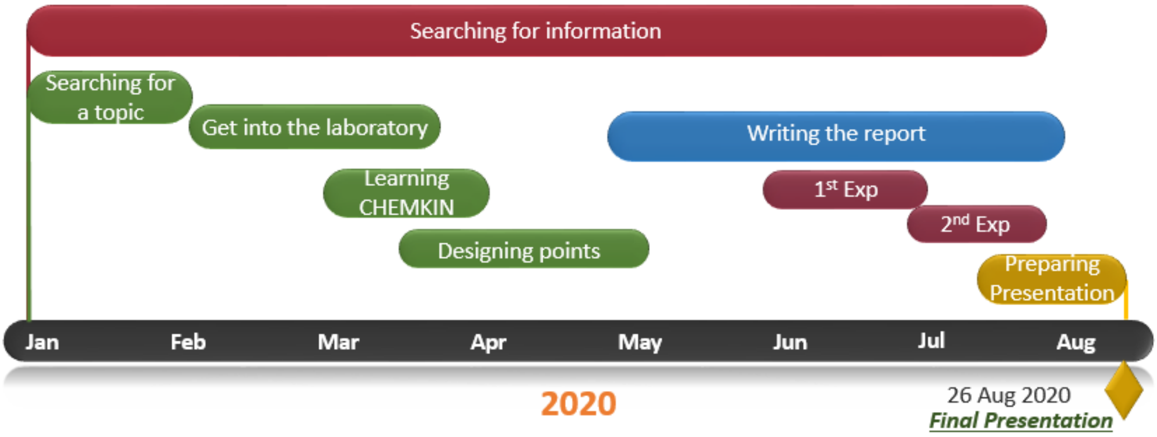


Figure 7.1: Gantt chart for this master thesis

7.5 Objectives

The main objective for this master thesis is to prove the feasibility of using ammonia as a fuel in a flat flame burner, to help ammonia in the oxidation problem it is used hydrogen. Distribution of this chemical is complex and the price of this technology will be increased due to this fact.

Also one of the aims of this research was to find a clean and highly efficient burner for domestic stove applications. The problems related with carbon dioxide emissions and CO

emissions are solved, however NO_x emissions still a big issue for certain operating points.

After obtaining the conclusions from the experiments in this master thesis, it is possible to affirm that this technology is not still viable. Further improvements will be needed. In the future work, the following section, there are some related projects with this one, that could enhance this technology and sole some of the problems related.

7.6 Future work

The ammonia challenges for fuel applications are mainly divided into the following topics: Low combustion intensity, high NO_x emissions and low radiation intensity. For this master thesis, it was tried to solve low flammability problem by mixing ammonia with hydrogen. However another fuel mix could be proposed and studied.

The points studied during the experiments were selected to cover as much as possible the operating range of the burner using ammonia and hydrogen as a fuel. It could be interesting studying a narrower operating area but with more point density and in a more profound way, for instance, related to equivalence ratio point close to stoichiometric.

Providing more details of NO_x emissions, studying the chemical kinetics, and the radicals, which are important for NO_x to be produced using this kind of burner. Also, comparing emissions with different types of burners could be an important issue in order to find the optimal way to use ammonia as a fuel.

To detect radicals, more precise instruments is needed. Knowing better combustion products could make possible an exergy study for the operating range.

Designing new catalyst components o process for NO_x removal in ammonia combustion. Especially finding out which one is optimal and more efficient.

Bibliography

[1] Agency, H. P. Ammonia: health effects, incident management and toxicology., 2014.

[2] Agency, U. S. E. P. Global greenhouse gas emissions data, 2015.

[3] Company, C.-P. I. Chemical compatibility database, ammonia, anhydrous.

[4] da Rocha, R. C., Costa, M., and Bai, X.-S. Chemical kinetic modelling of ammonia/hydrogen/air ignition, premixed flame propagation and no emission. *Fuel 246* (2019), 24 – 33.

[5] Dean, A. M. *Gas-Phase Combustion Chemistry-Combustion Chemistry of Nitrogen.* Springer, 2000.

[6] Desonie, D. *CLIMATE: Causes and effects of Climate Change.* Chelsea House, 2008.

[7] Duynslaegher, C., Jeanmart, H., and Vandooren, J. Flame structure studies of premixed ammonia/hydrogen/oxygen/argon flames: Experimental and numerical investigation. *Proceedings of the Combustion Institute 32*, 1 (2009), 1277 – 1284.

[8] Gregory, F. D. Safety standard for hydrogen and hydrogen systems, 1997.

[9] Hudson, S. Nox emissions at referenced o2, 2015.

[10] Hussein, N. A., Valera-Medina, A., and Alsaegh, A. S. Ammonia- hydrogen combustion in a swirl burner with reduction of nox emissions. *Energy Procedia 158* (2019), 2305 – 2310. Innovative Solutions for Energy Transitions.

[11] J. Warnatz, U. M., and Dibble, R. *Combustion: Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation.* Springer, 2006.

[12] Klippenstein, S. J., Harding, L. B., Glarborg, P., and Miller, J. A. The role of nnh in no formation and control. *Combustion and Flame 158*, 4 (2011), 774 – 789. Special Issue on Kinetics.

[13] Kobayashi, H., Hayakawa, A., Somarathne, K., and Okafor, E. Science and technology of ammonia combustion. *Proceedings of the Combustion Institute 37*, 1 (2019), 109 – 133.

[14] Kumar, P. An experimental and numerical study of nox formation mechanisms in nh3-h2-air flames, 2012.

[15] Malte, P. C. The importance of the nitrous oxide pathway to nox in lean-premixed combustion.

[16] Miller, J. A. *Kinetic Modelling of the Oxidation of Ammonia in Flames.* Gordon and Breach Science Publisher, 1983.

[17] NASA. Global climate change: Vital signs of the planet, 2014.

[18] NH3 Fuel Association; Karabeyoglu A, B. E. Fuel conditioning system for ammonia fired power plants, 2012.

[19] NH3 Fuel Association; Smith G, Mott J, G. T. A hazard assessment of ammonia as a fuel: understanding the hazards and managing the risks threats of ammonia as a fuel, 2013.

[20] of Hydrogen As an Energy Carrier, H. S. Deliverable d113 initial guidance for using hydrogen in confined spaces - results from inshyde, 2009.

[21] Turns, S. R. *An Introduction to Combustion Concepts and Applications.* McGraw-Hill, 2012.

[22] Unit, W. G. I. T. S. *Climate Change 2014 Mitigation of Climate Change, Working Group III Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change.* Cambridge University Pres, 2014.

[23] Valera-Medina, A., Xiao, H., Owen-Jones, M., David, W., and Bowen, P. Ammonia for power. *Progress in Energy and Combustion Science 69* (2018), 63 – 102.

[24] Winterbone, D. E., and Turan, A. Chapter 15 - combustion and flames. In *Advanced Thermodynamics for Engineers (Second Edition)*, D. E. Winterbone and A. Turan, Eds., second edition ed. Butterworth-Heinemann, Boston, 2015, pp. 323 – 344.

[25] Wu, C.-Y., Chen, K.-H., and Yang, S. Y. Experimental study of porous metal burners for domestic stove applications. *Energy Conversion and Management 77* (2014), 380 – 388.